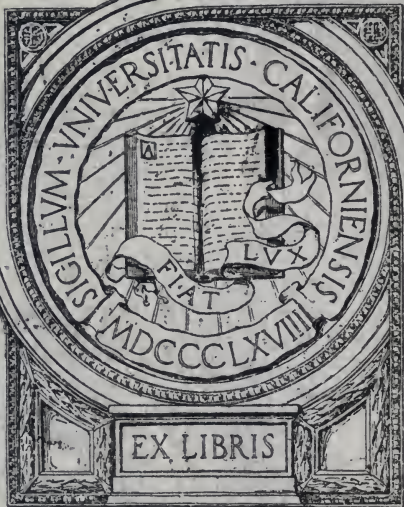


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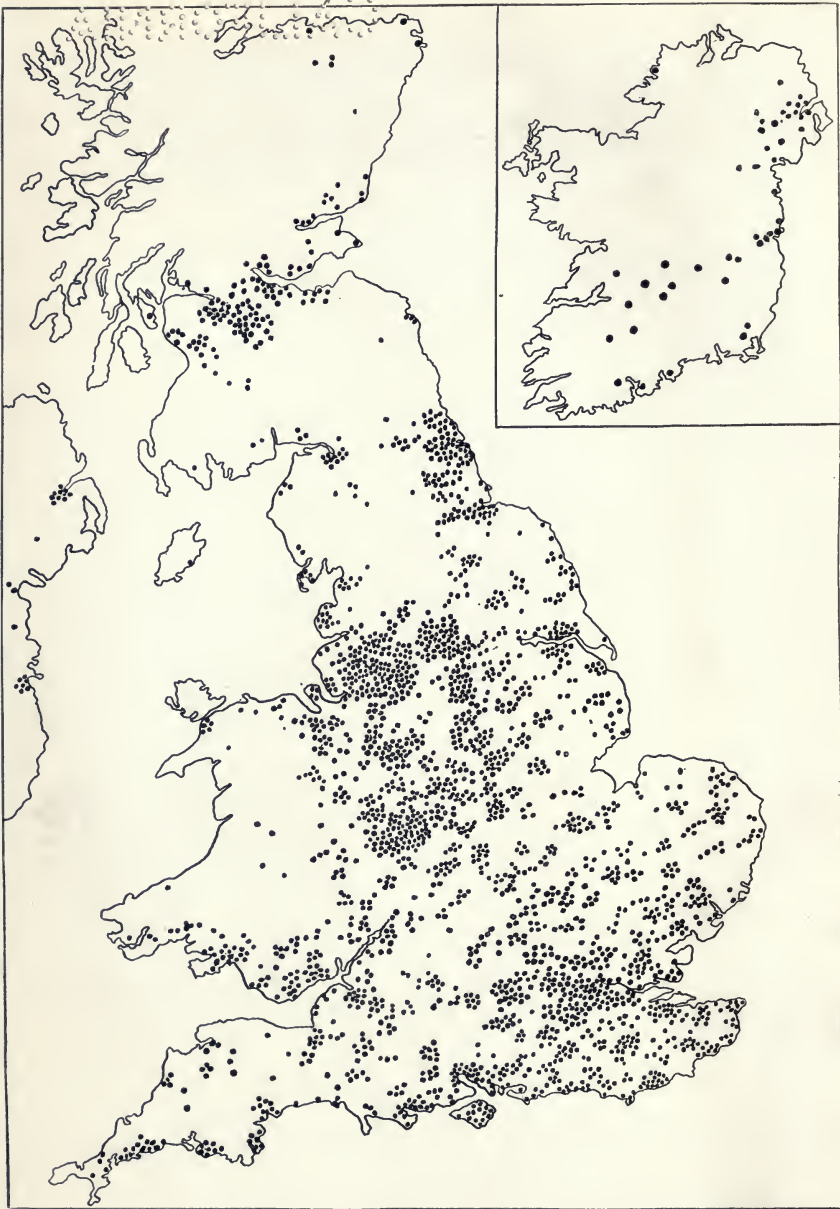
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The Chief Clayworks in Great Britain.

[Frontispiece.]

AN INTRODUCTION
TO
BRITISH CLAYS, SHALES,
AND SANDS.

BY

ALFRED B. SEARLE,
CONSULTING EXPERT ON CLAYS AND CLAY PRODUCTS;
LECTURER ON BRICKMAKING UNDER THE CANTOR BEQUEST:
AUTHOR OF "THE CLAYWORKER'S HANDBOOK," ETC.

With 10 Plates and 53 Figures in the Text.



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TO THE
MEMBERS OF THE

PREFACE.

SOME thirteen years ago the editor of one of the leading trade journals stated that, "if asked in what direction reforms were most needed in the clayworking industries, he should have no hesitation in suggesting 'a classification of the clays in the British Isles, which are not only numerous, but vary, both as regards constitution and properties, in the widest possible manner. Not one confined to their geological occurrence alone or to their chemical composition or physical properties, but a classification embracing all three, together with complete and reliable data as to locality, cost, and the particular work for which they are best adapted.'"

To fulfil these conditions would require a work of such great magnitude that it could not be left to individual enterprise; yet, notwithstanding the large number of people interested in the subject, the great and important industries dependent upon it, and the amount of information in existence, no book has yet been published in which British clays receive their proper share of attention. Usually these substances occupy a subsidiary position in works on geology or on brick or pottery manufacture, and their importance is, consequently, overlooked.

This is, in part, due to the inherent difficulty of the subject and to its extent, for though clays are found in almost every part of the British Isles, their true constitution is, even now, not known with certainty, and the characteristics of many of them require much more investigation than they have hitherto received.

The ordinary reader, searching for detailed information on clays, in geological and chemical books and papers, experiences considerable difficulty. This is partly due to the inaccessibility of many of the most important documents, the widely divergent

views of writers of great reputation, and the curious manner in which a statement has been copied and re-copied by successive writers without any attempt to verify its accuracy.

Another serious difficulty is due to the difference between the view-points of the reader and the writers of such works. For example, the majority of geologists devote their attention almost exclusively to the fossils in a deposit, and to a great extent disregard its economic value. Thus, one eminent stratigrapher observes that the Triassic system in the Midlands is "lithologically, uninteresting, the greater part consisting of red marls and shales without fossils." Yet the clay deposits thus briefly dismissed are amongst the most important industrial rocks of the extensive area in which they are situated. There is also a strong tendency among geologists and others to consider a bed as of uniform composition because it contains the same fossils throughout, whereas from the clayworker's point of view it may consist of several materials, some of which may be quite useless or even harmful. Thus, a Coal Measure clay or shale may be valuable if sufficiently free from iron, lime, soda or potash compounds, and it may be almost worthless if as little as 6 per cent. of these substances are present. Yet the majority of writers on the Coal Measures not only fail to indicate the purity or otherwise of the clays in the beds they describe, but also class together valuable clays with useless sandstones, or they entirely overlook beds of clay which are, commercially, of great importance.

Quite apart from its value to the practical potter, brickmaker, or cement manufacturer, the scientific investigation of the occurrence and nature of clays has an intrinsic importance because of the light it throws on some obscure and difficult problems in geology and in the chemistry and physics of the alumino-silicates and their corresponding acids. The study of colloidal substances, for example, has opened up new and wide fields of research of great theoretical and practical importance, and the difficulties afforded in it only add to the interest of attempting their solution.

During the last twenty years so much work has been done and such great advances have been made in those branches of geology and chemistry which have a direct bearing on the occurrence, composition, and properties of clays and the associated rocks, that a general statement of the results in a handy form has become imperative to certain branches of science and industry. Moreover, the increasing attention paid to the testing of materials by engineers and others has created a demand for a handbook in which the essential characteristics of clays are described in a convenient form.

The chief purpose of the present volume is to state briefly the most important characteristics of the clays, shales, and sands occurring in the British Isles, together with some information as to the localities where they are accessible in commercially valuable quantities, and some indication as to their sources. No attempt has been made to describe the limits of individual clay-beds with the minuteness of a detailed geological survey, but as far as is possible within the compass of a single volume the areas within which may be found all beds of present or prospective commercial value have been indicated. Some beds of great palæontological interest, but otherwise unimportant, have been purposely omitted.

In selecting information from the large amount available, the author has placed the most importance on facts which have come within his own personal experience as a consulting technologist, but he has also availed himself largely of documents and books by a number of writers in various fields of science and industry. No one recognizes better than he how difficult it is to deal with all the problems which arise in connection with the widely differing professional and industrial requirements of civil engineers, chemists, geologists, architects, builders, manufacturers of pottery, cement, bricks, tiles, terra-cotta, paint, paper, ultramarine and other chemicals, fullers, oil refiners, colliery proprietors and employees, and a large number of other persons whose employment is not usually regarded as being associated with clays and clay products. Consequently, the author's chief efforts have been expended in endeavouring to state as clearly as he is able the most important characteristics of the commercially valuable clays, with a general outline of their distribution and of the problems connected with their utilization.

With so vast a subject—even under the limitations just mentioned—and the lengthy period during which he has been engaged in its study, the author finds it impossible to acknowledge every writer, client, or friend to whom he is indebted for information, much as he would like to do so. He is, however, particularly grateful to his late friend Mr G. F. Harris for much information and some illustrations on “Brick Earths,” some of which appeared in the *British Clayworker*; to the firm of Dr Seger & E. Cramer, the proprietors of the *Brick and Pottery Trades Journal*, Messrs Duke & Ockenden, W. H. Patchel, G. Bishop, and J. T. Turner for illustrations; to Mr G. E. Tucker for reading part of the manuscript, and to Mr J. W. Merchant and other members of his staff for reading the proofs and compiling the index.

The invaluable Maps and Memoirs of the Geological Survey are indispensable to the student of clays; the information in

them has been utilized as occasion required, and, as far as possible, acknowledged.

Credit is given to other investigators as far as their names have been ascertained, though the special circumstances under which some of the author's notes were made preclude acknowledgment in every case.

ALFRED B. SEARLE.

THE WHITE BUILDING,
SHEFFIELD, *November 1911.*

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BRITISH CLAYS, SHALES, AND SANDS.

CHAPTER I.

IGNEOUS ROCKS FROM WHICH CLAYS ARE DERIVED.

IN spite of the numerous efforts of many investigators, man's total knowledge of the structure of the earth on which he lives is, after all, very small. The surface has been explored with thoroughness, and here and there careful examinations of materials which have been ten miles below the surface have been made, but these form a smaller proportion of the whole earth than the skin of an apple does to the fruit itself. Yet for a complete study of the origin and formation of clays, shales, and sands, it is essential to know what has occurred nearer to the centre of the earth in past geological ages.

Much progress in this direction has been made during recent years, and the patient investigation of the large amount of indirect evidence available has furnished sufficient information to enable the simpler facts as to the source of the materials under consideration to be answered satisfactorily, though innumerable others are still receiving attention.

As a whole, the earth weighs five and a half times as much as a globe of water of equal size; but as the common rocks and other materials on its surface are only two and a half to three times as heavy as water, it is clear that, whatever be the constitution of the whole earth, the lighter materials are on the surface and the heavier materials are in the interior. This much denser interior is attributed to the enormous pressure to which it is subjected; but as this is so great as to be entirely beyond human experience, it is impossible to state accurately what are the properties of matter under such conditions as there occur.

The measurement of the temperature of the earth at different depths indicates a rise of 88° F. per mile, or a heat sufficiently intense to melt the most refractory substances at a distance of only forty miles below the surface. This evidence of an intensely hot interior is also confirmed by the materials expelled by geysers and volcanoes.

There is, however, strong evidence showing that the earth is an entirely rigid body—that it is more rigid than steel; so that it is difficult to conceive the physical condition of its interior.

The volcanoes most commonly recognized as such are only a very small proportion of the total number which have existed, and scarcely any part of the earth is free from traces of volcanoes which existed in past ages. Britain abounds with their remains, though they are not easily recognized, because even the latest of them have been extinct so long that their cones have been exposed so much as to be almost entirely destroyed.

Modern geologists are now agreed that all rocks¹ have originally been in a molten condition, though it is improbable that any portion of the original surface of the earth now remains in its primitive condition, owing to the action of the weather and to the movements in the earth itself.

Rocks, the nature of which shows that they have passed through and solidified from a molten state are known as “igneous rocks,” and they form the primary material from which all clays, shales, and sands are produced. After being exposed to the weather, and to various chemical and mechanical agencies, they are converted into “secondary” or sedimentary rocks in a manner which is described, in greater detail, later.

In addition to this, so much of the earth’s surface has been disturbed by earthquakes and other movements, that the igneous rocks are distributed quite irregularly and in no determinate manner.

The primary igneous rocks appear to have been thrown out from the interior of the earth by violent volcanic action. In the absence of any outlet for the steam and other gases in the interior of the earth, they accumulated until a sufficient pressure was generated near the surface to form an opening, or vent, in a sudden and violent manner; explosion has followed explosion in rapid succession, and huge masses of solid rock have been hurled through the opening, and have finally fallen on the surface of

¹ Geikie has defined a rock as “any naturally formed mass of mineral matter.” Hence it may be hard or soft, compact or loose, and uniform or heterogeneous in structure. Blown sand, mud, clay, gravel, and peat are “rocks” just as much as granite, sandstone or limestone.

the earth. At the same time, earthquakes may cause an alteration in the positions of other rocks in the neighbourhood. The masses of rock, dust, and lava shot out in this manner eventually form a conical mountain or volcano.

In many cases the cone has suffered so much by the action of the weather and other forces that its volcanic origin is only realized with difficulty, and subsequent displacements have often been so extensive that igneous rocks must usually be recognized by their physical nature and chemical composition rather than by their situation.

In some cases the igneous rocks have not been shot out of a volcano as lava, but have been injected (by pressure from below) into cracks and fissures in the earth's crust, and in solidifying have formed *dykes* and *veins*.

Although all igneous rocks are originally the result of internal pressure which exhibits itself in the manner just mentioned, and so are, in a broad sense, due to volcanic action, it is customary to divide them into three groups, the term "volcanic" being limited to materials which have been thrown on to the surface of the earth in geologically recent times. In this way igneous rocks may be classified as—(i.) Granitic Rocks, (ii.) Trappean Rocks, (iii.) Recent Volcanic Rocks.

There are five chief magmas, which may be conveniently represented in the following table:—

Origin . . .	Plutonic.	Intrusive.	Volcanic.	Volcanic.	Chief Constituents.
Nature . . .	Holo-crystalline.	Hemi-crystalline.	Semi-glassy.	Glassy.	
1. Acid . . .	Granite.	Quartz Felsite, Elvans.	Rhyolite.	Obsidian.	Quartz, Felspar (Orthoclase), Mica (Muscovite, Biotite).
2. Sub-acid . .	Syenite.	Minettes.	Trachytes.	Pitchstone.	Alkali-Felspars, Hornblende.
3. Sub-basic . .	Diorite.	Kersantite.	Andesite.	..	Plagioclase - Felspars, Hornblende.
4. Basic . . .	Gabbro.	Dolerite.	Basalt.	Tachylite.	Plagioclase - Felspars, Olivine, Augite.
5. Ultra-basic	Peridotite.	Picrite.	Limburgite.	..	Olivine and Augite or Hornblende.

This table shows that *granite* is a holocrystalline rock, and was formed at a great depth, where it was subjected to a high pressure and cooled slowly. Granite usually contains more felspar than quartz, and more quartz than mica, but the proportions of these constituents vary too greatly for any reliable

average to be stated. The *elvans* and quartz *felsites* solidified under much less pressure, and may have been intruded as a dyke in a thin vertical sheet. *Rhyolite* is a compact, earthy rock, often with a well-defined banded glassy structure, due to micro-lites. It has been formed on the surface of a lava-flow. *Obsidian* is formed on the surface, has been cooled quickly, and is black, smooth, and shining like glass. In *syenite* the mica is replaced by hornblende.

Similar remarks will apply to any other horizontal row. The rocks in the vertical rows vary from acid to ultra-basic as the percentage of silica decreases. They are primarily different, due to the magmas being of different natures. As a rule, an igneous rock cannot be accurately named or classified without a microscopic examination of the various constituent crystals. This is even more important than a chemical analysis.

GRANITIC ROCKS.

The granite rocks are widely distributed, and form the principal mass of the chief mountain ranges, especially those in West Northumberland, Cumberland, Westmorland, Devon, and Cornwall in England, the Grampians in Scotland, and in Antrim and Wicklow, Ireland. One of the largest granitic areas in Devonshire is Dartmoor; but those around Bodmin, St Austell, St Stephen's, etc., in Cornwall, are of special importance on account of their content of china clay.

They are mixtures of various siliceous minerals,¹ cemented together into a hard and compact mass, the chief being felspar, quartz, and mica, though leucite, nepheline, free silica in various forms and small quantities of various other silicates, may also, be present.

The following granites—Dalbeattie, Kemnay, Shap, Penzance, Dartmoor, and Mount Sorrel—all contain quartz, orthoclase felspar, plagioclase felspar, and biotite; and, in addition, Kemnay and Dartmoor contain muscovite, and Shap and Mount Sorrel contain hornblende. The principal constituent of all granites is quartz, which often surrounds and encloses less stable and less durable minerals, thus acting as a protective agent. For this reason, in a typical granite the silica percentage is high, always above 66, and may be 80. The specific gravity is about 2.65.

The true granitic rocks are all highly crystalline and granular, and show every evidence of having been cooled very slowly from

¹ For trade purposes some limestones and conglomerates are termed granites, but this misuse of the word should be avoided,

a molten state in the interior of the earth before they reached its surface in a semi-solid condition.¹ This explains the presence of large and small crystals in the same mass.

Being the oldest of the rocks, they are usually found beneath the others, but in many instances they have been thrown upwards by earth movements or have been uncovered by weathering, so that they also form prominent mountains and hills. Granitic rocks also form dykes and veins in sedimentary rocks of much later formation, or even in other granitic rocks. The material forming these veins and dykes is often somewhat different mineralogically from the main granitic mass from which it is apparently derived, and it often contains minerals not found in the latter, such as beryl, garnet, and other precious stones. Granite rocks may, in fact, occur in any formation or may be produced at any time.

To the clayworker, the minerals of chief interest which are found in granitic rocks are the felspars, micas, and quartz, the other silicates occurring with them only being of importance as introducing undesirable constituents into the clay. These accessory minerals give to the various granites their distinctive colours. Thus, granite from Devonshire and Cornwall is chiefly grey in colour, with a well-compacted grain, in which hornblende is very noticeable. Nearer Land's End yellow porphyritic granite is found containing large characteristic crystals of felspar known as "horse's teeth." In Leicestershire the igneous rock is chiefly syenite, consisting mainly of mica and hornblende and often green in colour; whilst the Shap granite of Westmorland contains large, red felspar crystals, and takes a beautiful polish.

Scotch granites are usually bluish-grey, as is much of that in Ireland, though red granite is found in Galway and Donegal.

There is a general impression that granite is one of the most weather-resisting building materials known; but this is only true of certain varieties. Some granites crumble readily after a few years' exposure, and these are the most important in a study of the origin of clays. As Sir Archibald Geikie has said: "There is no necessary relation between the hardness or softness of a stone and its durability under the attacks of the weather. Granite, basalt, limestone, and many other materials are much harder than soapstone, slate and chloritic schist, yet they decay much more rapidly." The polishing of granite, by depriving moisture of a lodgment, vastly adds to the durability of the stone.

As granites are really heterogeneous mixtures of certain

¹ Schwarz states that Cornish granites have been intruded in a state of solution under pressure and not as a molten mass (see p. 20).

minerals, they have no definite chemical composition, and in the same hill half a dozen varieties may often be found, the differences being due to variations in the compositions and the proportions of the various feldspars and mica present in addition to the quartz and accessory minerals. Those richest in feldspar are the chief source of clay, the granites of Devon and Cornwall being specially noted as the rocks from which china clay is derived.

According to Flett, three distinct changes are produced in granite by pneumatolytic action, viz. :—

(a) Tourmalinization, or the conversion into tourmaline and quartz of the original mica and feldspar. This action produces schorl rock (see below).

(b) Greisening, or the conversion of feldspar into white mica and quartz, fluor spar also making its appearance.

(c) Kaolinization, or the conversion of the feldspar into china clay, mica, and quartz (p. 34).

These modifications of the granite are not sharply distinguished from each other, as schorl rocks often contain mica, greisens are usually rich in tourmaline, and much tourmaline occurs in china clay rock in the form of "schorl."

Pegmatite is a kind of granite, generally occurring in veins, in which the feldspar and quartz have intergrown with one another by simultaneous crystallization. It is sometimes termed Cornish stone by potters, though the latter is really one of its (partial) decomposition products.

Schorl is granite in which the mica (biotite) has been completely converted into brown or black tourmaline and the feldspar into blue tourmaline and quartz. It is important on account of its close association with china clay, and is variously known as *weed*, *caple*, *stent*, and *shell*. This strongly coloured material must be carefully removed from the china clay, preferably before washing.

Black Ram is a term applied to most black or dark-brown rocks occurring with china clay, but of no value. They are chiefly granite, schorl, and tourmaline.

Petuntse is a term introduced from China, and is sometimes used to indicate a partially decomposed granite, which must not be confused with other granites from which china clay is also derived. Amongst British potters it is generally considered to be equivalent to English Cornish stone or china stone, and is valued as a flux. It is prepared by the Chinese by a simple process of crushing and levigation, the coarser particles being again crushed and washed.

The variation in samples from a single district are, however,

so great, that any comparison of Petuntse with other British rocks is at best imperfect, and the most that can be said is that in general characters it resembles Cornish stone and pegmatite. It usually contains some fluorides, which increase its fusibility.

Being resistant to weather, it is not readily decomposed, but if its alkalies are completely removed in this way it apparently forms a mixture of china clay and quartz.

China Stone or **Cornish Stone** is, strictly speaking, a partially kaolinized felsitic granite, and has numerous local names, such as *elvan*, *growan stone*, and *St Stephen's stone*, which are often applied, somewhat carelessly, to other granites. Its value lies in the fact that it contains in a natural aggregate the materials essential for porcelain body, and in this respect corresponds to the Chinese Petuntse and the French and German pegmatite. It is chiefly quarried at Restowrick Downs, Treviscoe, Tregargus, north of St Stephen's, between there and Kermick, at Goanvean, and at Bloomdale and Gounamaris.

The harder and less decomposed varieties (pegmatite) are much used for building purposes; that used by potters is generally of a softer nature. Its discovery in Cornwall (the only place where it is found in quantity in Great Britain) is due to William Cookworthy, the discoverer of Cornish china clay, who first found it at Tregonning Hill (1745), and later at St Stephen's.

It is composed essentially of felspar crystals lying in a quartz matrix—the latter, naturally, predominating,—with white mica, schorl, and small quantities of other minerals, some of which cause curiously coloured spots or stains. It is often associated with fluorspar, which materially increases its fusibility. On complete decomposition it loses alkali (from the contained felspar) and forms a heterogeneous mass of which china clay is the most interesting ingredient, though it appears probable that most of the china clay in Cornwall has been derived from a somewhat different variety of granite of less weather-resisting power.

Those engaged in quarrying Cornish stone in different districts recognize several qualities, and even in the same place two sorts are not uncommon, as at Tregonning Hill, where one variety has a fine grain and a peculiar snow-like appearance, and another is very coarse-grained and yellowish-buff in colour, while both these are easily distinguishable from the china stones quarried in the neighbourhood of St Stephen's.

According to W. Jackson, the most important difference between these varieties is in their alkaline contents, which may vary from about 7 per cent. in the "blue" to 3 per cent. in the "yellow" stone.

Commercially, the chief varieties recognized are:—

Hard Purple.—A hard china stone consisting of quartz, partially kaolinized felspar, pale and greenish-silvery mica (gilbertite and lepidolite), and fluorspar (which gives it its colour). It is considered to be the most valuable variety, though costly to grind.

Mild Purple.—Similar to hard purple, excepting that the felspar is more decomposed into kaolin and pale mica.

White Stone.—Resembles hard or mild purple, but contains very little fluorspar and is much softer.

Buff Stone.—Similar to the white stone, but the decomposed felspar is stained to a buff colour.

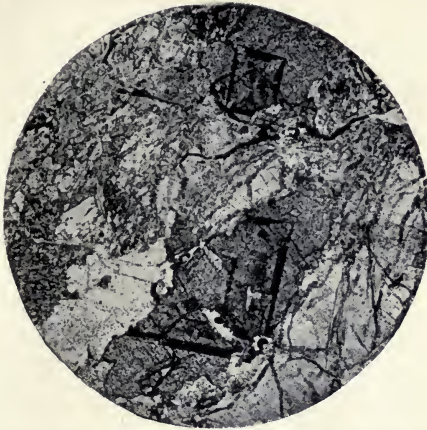
A fifth variety, known as *Shell*, is useless as a flux and consequently is rejected. It must not be confused with schorl (p. 6).

Jersey stone is very fusible, but detracts from the whiteness of the ware. It is frequently used in admixture with "white stone."

Cornish stone is usually found at a depth of 6 to 20 feet from the surface; the overburden consisting of a little loose earth and much gravel and small stones. The china stone itself is from 12 to 16 feet thick, underlaid with a harder purple variety of china stone or with a granite. In quarrying it, those parts in which it becomes intermixed with schorl or black tourmaline should be avoided.

China stone, when heated sufficiently, fuses to a white opaque mass, the temperature required being between 1200° and 1500° C., according to the proportions of orthoclase, oligoclase, and fluorspar present.

It is much used by potters as a cheap substitute for felspar, though it is far less fusible and does not behave in quite the same manner as a mixture of felspar, china clay and quartz of the same chemical composition. This difference in behaviour has been attributed by Ashby to lack of sufficiently accurate comparison, as he has found no difference observable in wares made from natural china stone and an artificial mixture of felspar, china clay and quartz, providing that the proportions are accurately maintained and the materials are equally finely ground. When mixed with clays and fired, it cements the less fusible particles together into a compact, hard, and durable mass, which "rings" when struck. For potter's use, china stone should contain no minerals which might impart a tint to the fused material, and the softer rock is frequently preferred, as it is more readily ground, though the hard purple variety is regarded as more valuable.



Photomicrograph of mild purple CHINA STONE from
Tregargas, St Stephens ($\times 15$ diam.).
The cube outlines are blue fluorspar.



Photomicrograph of purple CHINA STONE from St Dennis,
between crossed nicols ($\times 27$ diam.).

This photograph shows the abundance of well-shaped albite crystals in some china stones. There is also orthoclase and quartz. The felspar contains many fluid cavities and small plates of white mica.

(From "Memoir of the Geological Survey, No. 347.")

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The composition of china stone varies considerably, but an average composition of the qualities used by potters contains:—

Silica	72	per cent.
Alumina	18	„
Lime and magnesia	1	„
Potash and soda	6	„
Fluorine	$\frac{1}{2}$ to 1	„
Iron, etc., about	2	„

Occasionally the fluorine may be as high as 2 per cent., but it is usually about 0.75 per cent.

China stone which contains dark tourmaline and much iron is unfit for commercial purposes.

Langenbeck has investigated this subject by means of numerous “rational analyses,” and finds—as would be expected from its geological nature—that “Cornish stone is by no means as uniform in character and composition as potters generally believe. The portion insoluble in sulphuric acid and sodium carbonate solution is in many cases markedly richer in alumina than in that of which the analysis has been given, and not infrequently the silica is either largely soluble in the sodium carbonate solution, or is more readily made so by the action of the sulphuric acid than quartz.”

The fact is that chemical and “rational” analyses alike fail to show the different varieties of felspar and other minerals occurring in china stone, and it is to these, as well as to the proportion of each, that attention must be given when an explanation of the otherwise curious behaviour of this material is required. For these reasons it is impossible to calculate the quantities of felspar, quartz, and mica which may be satisfactorily used as a substitute for Cornish stone, unless the particular varieties of the different minerals (*e.g.*, orthoclase or microcline felspar, or one or more of the numerous plagioclases) and the proportion of each in the stone are known. That the result of a calculation of this sort, based on the assumption that all the felspar is orthoclase, is often sufficiently accurate for commercial purposes, may be little more than a fortunate coincidence which, at times, obscures the real facts.

All the best china stones appear to have suffered alteration by pneumatolytic action, resulting in the introduction of fluorspar and the removal of part of the silica in solution in some way. Much of the felspar in these rocks is very fresh, and as complete as in the greisens. In the softer china stone there has been a

certain degree of kaolinization. The felspar becomes very white, soft, and friable, so that it can be broken down with the fingers. There is always plenty of fresh felspar; the china clay appears as fine scales which lie in the interior of the felspar crystals or are deposited along cracks and cleavages.

Many of the best china stones contain much fluorspar spread along the cleavages of the muscovite or enclosing small plates of mica.

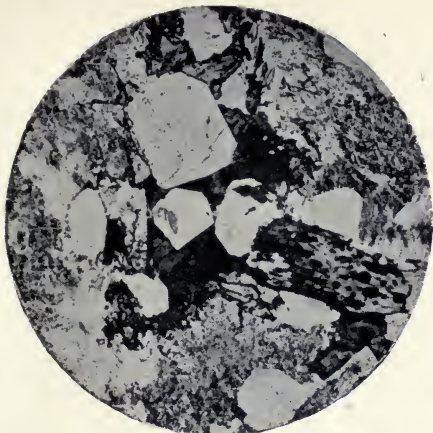
The production of china stone appears to be due to the action of fluorine and other gases in the presence of water on the felspars, lithium being introduced at the same time. It is thought by some investigators that china stone is formed by the process of kaolinization (p. 34), similar to that which occurs in the formation of china-clay rock. MacAlister suggests that the fluorspar present was formed by the interaction of fluoride vapours and the lime in the felspar. This fluorspar frequently has a purple colour from which two varieties of china stone derive their name.

China-clay Rock (carclazite) is a soft granite easily broken up by the weather and sufficiently decomposed to be treated for the removal of its contained china clay. The nature of this decomposition is described later (p. 35).

China-clay rock is found in the granite hills of Cornwall, its presence being indicated by a depression at the surface, locally known as a "slade." It never occurs at the surface, but is covered with a thick overburden of peat earth, disintegrated granite, and occasionally with firm granite.

The china-clay rock is not stratified, but occurs irregularly distributed in the granitic mass, the softer portions of which are treated with water, which removes the clay along with fine particles of mica, etc. The slurry or cream so formed is pumped up to a convenient level, and is then subjected to a process of fractional sedimentation, whereby the china clay is separated in a state of commercial purity. Large quantities of material have to be treated, as ordinary china-clay rock only contains about 20 per cent. of clay, the remainder being 15 to 20 per cent. mica and about 50 per cent. sandy quartz. Occasionally portions containing as much as 50 per cent. of china clay are found, particularly from the greatest depths. It is a curious fact that, broadly speaking, the greater the depth the richer is the material in china clay.

The term "china-clay rock" is used indifferently for the granite itself and for the whole of the materials produced by its decomposition, consisting of granite, china clay, felspar, mica, quartz and other minerals. It is generally supposed to be identical with the original "kaolin" of the Chinese, but the term "kaolin"



Photomicrograph of TOURMALINE GRANITE from
Carbear's Quarry, Luxulian ($\times 15$ diam.).

In the centre of the view there is a mass of brown tourmaline enveloping idiomorphic crystals of quartz. Above and below, it terminates in spongy growths ramifying through felspar. On the right there is a chloritised biotite with dark pleochroic halos; it is partly enveloped in tourmaline. The rest of the field consists of turbid felspar and transparent grains of quartz.



Photomicrograph of CHINA-CLAY ROCK from
Treviscoe, St Stephens, between crossed nicols ($\times 12$ diam.).

The photograph shows a little quartz and larger felspar crystals through which dense aggregates of fine kaolin are spreading along cleavage cracks and other fissures.

(From "Memoir of the Geological Survey, No. 347.")

is now used in Europe in a different sense, as applying to the china clay itself and not to the rock from which it is derived.

There has been, and still is, much confusion of thought as regards china stone (petuntse or pegmatite) and china-clay rock, and it is essential to remember that, though both are granitic rocks yielding china clay and quartz on weathering, yet the granites themselves are by no means identical. There are, indeed, as Collins states, some phenomena connected with the occurrence of the former in various places, such as St Stephen's, St Dennis, St Austell, and others in the Hensbarrow granite district of Cornwall, which seem to indicate some specific difference between them. In the above districts the china stone occurs in irregular patches, bands, and dykes in the granite, and, unlike the *carclazite*, or china-clay rock, it does not appear to be necessarily connected with veins of schorl and other materials which are more or less characteristic of the latter; and as regards decomposition, it appears to occupy an intermediate position between it, on the one hand, and the hard, unaltered granite on the other, while *carclazite* also occasionally passes into *petuntzite* in depth, and more frequently in horizontal extension, and Collins states his belief that the latter is never unconnected with the former. Yet there are instances where, as, for example, at Little Treviscoe, in the parish of St Stephen's, the china stone is found *above* an underlying mass of *carclazite*; and were there not some specific difference in the composition of their constituent feldspars, it is difficult to understand how the latter could have been decomposed while the former remained unaltered or decomposed—providing that both have been subjected to the same decomposing agencies, which naturally and generally decompose the overlying masses first. Again, sometimes crystalline masses are found enclosed in the china stone, having the appearance and composition of yellow mica, and yet the figures of these masses are those of a triclinic feldspar, not found associated with the *carclazite*. Occasionally, too, crystals of undecomposed or partially decomposed feldspars of different species occur in the "stone." It thus appears probable that the occurrence of china stone and china clay in one district is simply a coincidence, the two materials having no real relationship to each other.

Moorstone is a Cornish name for any granite cropping out on the surface of the moors.

Growan or **growanstone** is a term used by W. Cookworthy (1768) and others to indicate a yellowish-brown disintegrated or rotten granite (*arkose*) which overlies china-clay rock. It is quite valueless, and is thrown away. It must not be confused

with growan clay, which is identical with crude china clay. (See *China Stone*.)

In some districts "growan clay" is a term used for a clay containing many stones (*e.g.*, glacial drift).

Protogene granite, which contains talc, is readily disintegrated by the weather, and is a prominent source of china clay, being one of several varieties of granite which are conveniently grouped under the term "china-clay rock" (*q.v.*).

Notwithstanding the statements of early writers, that it is this granite which forms the source of china clay, it is not found in Britain in notable quantities, but is well known in France.

OTHER PLUTONIC IGNEOUS ROCKS.

Amongst numerous other rocks of a granitic nature, the following are important as possible sources of clay. They do not contain quartz in more than an insignificant proportion, and their composition varies considerably.

True **Syenite** consists of a pinkish orthoclase with some plagioclase and hornblende, but, as a class, the syenites form a group of rocks of varying composition and bearing different names, according to the ferro-magnesian minerals and the felspar present.

The term "syenite" is, however, applied to a number of rocks of similar petrological nature, the prevailing minerals being the felspars, feldspathoids, and hornblende.

Gabbros are essentially soda-lime felspars with a granitic structure, usually containing augite, hornblende, iron compounds, and apatite, with some accessory quartz. They are readily affected by weathering, but the felspars in them cannot always be shown to form clays. (*See p. 17*).

TRAP-ROCKS.

The term "trap" (meaning a terrace or stair) includes many igneous rocks less prominently crystalline than the granite and more compact and less cellular than the recent volcanic rocks.

The most important trap-rocks are *basalts*, *clinkstones*, *wacke*, *greenstones* (*whinstones*), *felstones* (*claystones*), *trachytes* or *grey-stones*, *pitchstones*, *tuffs*, and *agglomerates*. Of these the first three are close-grained subcrystalline rocks composed of felspar, augite, and hornblende, whilst the others are softer and more amorphous.

They are widely distributed, forming large portions of the Cheviot, Northumberland, Cumberland, Welsh, and Derbyshire hills, and occur less extensively in Leicestershire, South Devon-

shire, and Cornwall, the Pentland and Lammermuir ranges in Scotland, and the bulk of the Irish hills; in short, the chief districts occupied by the "Old Red Sandstone" and the "Coal Measures."

They are often columnar in form (*cf.* Giants' Causeway), and are undoubtedly of igneous origin; but some having been formed at great depths, some under the pressure of water, and others having been re-fused and passed through more than one eruption, their texture and character are naturally extremely varied, especially as some of them have been cooled more rapidly than others.

Trap-rocks may be named, according to the predominating mineral, as augitic, felspathic, hornblendic, or porphyritic, when they are composed of isolated crystals set in a crystalline magma. They are termed "tuffs" when soft and porous. Some soft, earthy varieties are termed "wacke" (pp. 39 and 49).

The principal minerals in trap-rocks are dark in colour (hornblende being a black or dark green, and augite black or dark brown), and their decomposition products are usually dark in colour, and are very different from the white or almost white clays obtained from the Cornwall and Devon granites. The colour is due to the presence of ferrous oxide, which partially replaces magnesia in the hornblende and augite, and contaminates the products formed by their disintegration.

Dolerites or **Greenstones** are composed of augite and felspar; *diorites* of hornblende and felspar. Greenstones (the whinstones of Scotland) are composed of crystals of hornblende, augite, hypersthene, etc.

Basalts are essentially augitic, with some olivine and iron. They occur as solidified lava in all geological periods, and may be either crystalline or glassy. Usually they resist weathering strongly.

Clinkstones (phonolites) are similar in composition, but are softer.

Agglomerates are masses of small stones which have been thrown out by volcanic action. When rounded by water transport they become **conglomerates**. These terms refer to the shape of the materials and not to their composition.

Trachytes are chiefly composed of fine-grained orthoclase, together with scattered crystals of hornblende, biotite, or augite.

Porphyry is the term given to a large number of rocks consisting chiefly of a crystalline mass, in which larger individual crystals are clearly visible, as granite containing porphyritic crystals of felspar, or a felspar containing similar crystals of another felspar. Porphyries are formed when a fused mass containing more of one mineral than is required to form a eutectic

is cooled. The substance in excess forms the larger crystals, the magma being the eutectic. The term "porphyry" is not by any means confined to felspathic minerals, though most porphyries are felspathic, but may be applied to many igneous rocks which have cooled rapidly. Originally confined to a definite red felspar found in Upper Egypt, it is now used to indicate so many minerals that it is better to consider it as indicating a definite physical arrangement rather than as representing a single mineral. Like other felspathic rocks the elvans and porphyries undergo kaolinization (p. 34). The term refers to the structure of the rock rather than to its composition; thus there are:—

Quartz-porphyries or elvans, consisting of a fine-grained crystalline or felsitic mass composed of quartz and felspar with larger crystals of these and other minerals embedded therein.

They exist chiefly as intrusions or dykes in the overlying beds, but the term is also used in Cornwall for fine-grained granites.

Felstone or **Claystone** is composed essentially of amorphous felspar, but becomes felstone-porphyry when crystalline masses of felspar are found in it.

The **Pitchstones** are closely related, but have vitreous lustre resembling pitch when broken.

Felsite or quartz-porphyry is a mass of very small crystals of orthoclase and quartz, in which are larger isolated crystals of quartz or felspar, or both.

To the clayworker the most important trap-rocks are those richest in felspar, as these form the raw material of a considerable number of clays, though usually of less value than clays derived from granitic rocks. The hardness and durability of most trap-rocks renders their decomposition extremely slow and difficult to study, but it is generally considered that they play a similar part to the granites in the formation of clays and sands.

Geologically the felstones and porphyries are thought to belong to the Old Red Sandstone period, the greenstones (diorites), trap-tuffs, and trap-agglomerates to the Carboniferous period, and the basalts and pitchstones to the Upper Secondary formation, though these classifications are by no means settled.

RECENT VOLCANIC ROCKS.

The more recent products of volcanic action are **lavas**, which, when cooled, form various trachytes, basalts, and tuffs of all kinds, from glassy obsidian to a soft earthy material, and in pieces of all sizes from large masses to the finest dust. This dust when moist often forms a kind of hydraulic cement, which binds scoriæ, small

stones, and sand into conglomerates, breccias, etc. Alone it forms *puozzolana* and *trass* (a kind of natural Portland cement).

As no active volcanoes have existed in Britain within recent geological times, the products of volcanic action during them need not be considered in relation to British clays, sands, and shales.

THE CONSTITUENTS OF IGNEOUS ROCKS.

The constituents of igneous rocks are, as already mentioned, feldspars, micas, and quartz, together with minerals derived from them and innumerable other minerals occurring in relatively small proportions, though often in sufficiently large quantities to exercise considerable influence.

The quartz, muscovite, and biotite may be regarded as having existed in the original granite, but the tourmaline and some of the less important minerals are probably of secondary origin. Muscovite is also present as a secondary constituent in some granites.

FELSPARS.

Igneous rock minerals may be divided into two groups—the *feldspars*, in which the silica and alumina combine with lime and alkalis, and the *hornblendes*, in which they are combined with iron and magnesia.

There are many interesting varieties of feldspar, orthoclase or potash feldspar being the most important, though microcline, albite, oligoclase, labradorite, andesite, anorthite, and sodalite also occur in considerable quantities. These varieties are divided into two groups according to the cleavage planes of the crystals, namely: (1) orthoclase (=straight cleavage), and (2) plagioclase (=oblique cleavage), the former group including the so-called potash feldspars—that is, those which contain silica, alumina, potash, and soda in varying proportions; whilst the second group includes the soda or lime feldspars, according as soda or lime predominates in their composition.

It has been calculated that the various feldspars and the products of their decomposition constitute about two-thirds of the entire rock crust of the earth, and they are undoubtedly the raw material from which most clay is produced.

They occur in a relatively pure state in isolated masses and dykes in granitic rocks, in which they constitute the larger and softer crystals, but most frequently with quartz, mica, etc., in granites and porphyries. In a less crystalline form they occur in trap and other rocks.

Felspars have the general formula $ROAl_2O_3 \cdot 6SiO_2$, the base RO being potash, soda, lime, magnesia, or any combination of these in any proportions, so long as the total bases are equivalent to the alumina and silica in the formula.

The colour of felspars varies from white or pale grey to drab and light red; the pale pink varieties being in much demand.

Felspars crystallize in two main forms: (a) monoclinic, as orthoclase, and (b) triclinic, as microcline and the plagioclase group containing albite, oligoclase, andesine, labradorite, anorthite, and anorthoclase. Orthoclase is generally characteristic of granitic, trachytic, and syenitic rocks, whilst the triclinic felspars are chiefly associated with gabbros, diorites, andesite, etc.

On exposure to the weather, felspars slowly decompose, the alkalis being washed away together with some of the silica, and kaolin or clay being sometimes formed (see *Kaolinization*, p. 34.)

Orthoclase is a felspar consisting essentially of potassium aluminium silicate ($K_2OAl_2O_3 \cdot 6SiO_2$), but usually contains 2 to 8 per cent. of lime and soda in place of some of the potash. According to Zirkel, magnesia and iron cannot replace the base in true felspars, so that when present they indicate the existence of other minerals as impurities in the felspars. When perfect, its crystals are rhombic, oblique prisms (monoclinic system), twin-crystals being common.

Its colour is white, or, if sufficient iron is present, reddish. Its hardness is 6 on Mohs' scale, or just sufficiently soft to be scratched by a good penknife. When heated to 1300° C. (or with some finely ground specimens to only 1000° C.) it melts to a white enamel-like mass, and at a higher temperature it fuses to a fairly clear glass. When finely powdered and soaked in water, the latter becomes distinctly alkaline.

Day and Allen have found that pure orthoclase has a much higher melting-point than the commercial article. This is due to the fact that mixtures of different felspars are more fusible than any one of them taken separately.

There are several varieties of orthoclase, such as adular (moon-stone), pegmatolite, sanidine (vitreous felspar), and eisspar (rhyakolite), but they all have the same chemical composition. Varying quantities of impurities occur, but the average composition of orthoclase is:—

Silica	65 per cent.
Alumina	18 „
Potash	16 „
Other matter	1 „

The triclinic feldspars are of two kinds: (1) microcline, which is chemically identical with orthoclase, but has a different crystalline structure, and (2) the plagioclases, which vary in composition, from pure sodium aluminium silicate (albite) to calcium aluminium silicate (anorthite), with several minerals of intermediate composition, and vary in colour from white to green or blue. They usually contain a higher percentage of alumina than does orthoclase.

According to Tschermak, only *albite* and *anorthite* are really distinct minerals, the other triclinic feldspars being produced when mixtures of these two in various proportions crystallize, their specific gravity varying with the proportions of albite (light) and of anorthite (heavy) from 2.6 to 2.75.

Albite is readily decomposed by hot hydrochloric acid, but anorthite is not appreciably attacked. It is seldom found pure in Great Britain.

So far as the part they play in clays, shales, and sands is concerned, it is sufficient for most practical purposes to class all triclinic feldspars together as a single mineral, with a composition and characteristics intermediate between albite and anorthite, *i.e.* a soda-lime feldspar in which the proportion of soda and lime vary relatively to each other, but in which the total bases always bear a constant molecular ratio to the alumina and silica present.

Oligoclase is a feldspar of this character, which may be taken as typical. In it the soda is the predominant alkali, but lime is nearly always present and potash frequently so. Its composition may be stated as equivalent to a mixture of anorthite with two to six times its weight of albite, thus:—

	Albite.	Oligoclase.	Anorthite.
Silica, SiO ₂	69	60 to 65	43
Alumina, Al ₂ O ₃	19	22 to 25	37
Lime, CaO	3 to 6	20
Soda, Na ₂ O	12	7 to 10	...

Oligoclase is found in most British granites, gneisses, diorites, and porphyries; but labradorite, albite, anorthite, and andesite are seldom met with in this country, unless in a form too highly decomposed to admit of definite identification.

Gabbros consist of plagioclase feldspars and pyroxene (augite and hornblende) rich in iron, and often with accessory quartz.

The **feldspathoids** approximate in composition to the feldspars,

but are more basic and crystallize differently. Thus, nepheline, a hexagonal sodium-aluminium silicate, contains 45 per cent. silica, 34 per cent. alumina, 15 per cent. soda, and 5 per cent. potash, with small quantities of lime and other bases; but its composition is not accurately known, the commonly accepted formula, $\text{Na}_2\text{Al}_2\text{SiO}_4$, not fully agreeing with some of the properties of nepheline. It is easily decomposed by hydrochloric acid, silica being thrown out, and common salt crystallizing out on evaporation. Powdered nepheline (like felspar) yields an alkaline reaction to water.

Leucite is a potassium-aluminium silicate crystallizing cubically and resembling albite deprived of about 16 per cent. of its silica, but many specimens of leucite also contain soda. It is completely decomposed by hydrochloric acid. Powdered leucite, when soaked in water, makes the latter alkaline, as does felspar.

MICAS AND OTHER SILICATES.

The large variety of silicate minerals occurring in igneous rocks, in addition to the felspars, may be represented by augite (pyroxene), hornblende (amphibole), olivine, and mica.

With the exception of muscovite, they are all characterized by containing magnesia, and may be regarded as iron-lime-magnesia-alumina silicates of varying composition. Augite, hornblende, and olivine are chiefly found in trappean rocks, but the micas occur chiefly in granites.

Augite and hornblende are dark brown, black, or greenish-black in colour. Olivine is green, and, if present in clays in a decomposed state, usually imparts a dark shade to the latter.

Hornblende—a calcium-magnesium-iron silicate of variable composition and the chief of the amphibole group of minerals—is a common constituent of many syenites and of some granites, as well as of other igneous rocks. It is usually brown or green in colour.

According to Tschermak hornblende is a polymer of augite.

Augite—a calcium-magnesium silicate—is the most important of the pyroxene minerals; is difficult to distinguish *in situ* from dark hornblende, as it is dark brown or black in colour, but is more easily recognized in thin sections. Like hornblende, it varies in composition.

Augite in some rocks is converted into hornblende.

Olivine—a magnesium-iron silicate in which the proportion of magnesium varies greatly—appears in the form of greenish grains in gabbros, basalts, and other trap-rocks, sometimes turned brown by decomposition.

These minerals are of much importance in a study of the formation of clays, but for a detailed description of their characteristics a treatise on mineralogy should be consulted.

The **Micas** occurring in granite and other rocks which take part in the formation of clays, shales, and sands are too numerous for a complete descriptive list to be given here.

The name is derived from their glistening appearance. They are all characterized by their fissility into infinitely thin plates, and consist of the oxides potash, soda, lithia, magnesia, ferrous oxide, ferric oxide, and alumina, combined with silica. They seldom contain lime.

Micas are found primarily in granitic rocks (in which they may readily be distinguished as dark, shining scales), and in other secondary minerals as a derivative of decomposed granite. They only occur in brick-clays in unimportant proportions, but crude china clay (before washing) contains much mica.

When present in clays, they darken the latter on heating, and produce yellow and brown spots. Hence they must be removed from clays intended to burn white.

The most important micas are biotite, muscovite, lepidolite, and gilbertite, the last named being specially characteristic of some Cornish granites.

Biotite is a ferro-magnesium silicate, and occurs as hexagonal plates or irregular scales of a brownish-black colour; but it is so easily decomposed by weathering that it is not observable in low-grade clays, though it forms one source of the iron they contain. The term is frequently used to include a number of other micas.

Muscovite (pale or white mica) or potash mica is a potash-aluminium silicate, silvery white or pale brown in colour. It resists the weather more than biotite, and may often be recognised in clays in the form of minute glistening specks.

When mixed with china clay, muscovite causes a marked lowering of the fusing point of the former.

Tourmaline, though not a mica, is a characteristic product formed by the breaking down of biotite and other dark micas occurring in some granites. It occurs freely in some clays as a secondary product, as, according to Butler, there are two generations of tourmaline, the first belonging to a period previous to, and the second to a period contemporaneous with, or subsequent to, the development of china clay. Original tourmaline is stated to have suffered corrosion by alkalis derived from felspars during their decomposition by solutions containing carbon dioxide. The second generation of tourmaline is the acicular variety derived from

free alumina or china clay, and the alkalis (derived from the breakdown of felspar) not carried away in solution.

The presence of this secondary tourmaline is commercially an advantage, as the iron derived from the first breakdown of the biotite would have existed as an oxide, staining the clay to a buff, pink or brown colour. By recombining to form tourmaline, the iron is locked up in a form in which it is readily separated by the ordinary dressing processes applied to the purification of china clay. Tourmaline is by no means so common in brick-earths and other secondary clays.

Tourmaline is widely distributed in the Cornish granites from which china clay is obtained. It occurs in several forms: (*a*) as microscopic radiating crystals penetrating the quartz or felspar, (*b*) as a mass of microscopic crystals or fragments of crystals scattered throughout the china-clay rock, and (*c*) in compact black masses many tons in weight, forming tourmaline schists.

According to J. M. Coon, in the East of Hensbarrow granite boss the tourmaline, in black crystals or fragments, forms a primary constituent of the rock. It is very commonly found as an enclosure, frequently in zonal arrangement, in the orthoclase crystals, which latter are markedly porphyritic and whiter than those of most other parts.

In the central and western parts of Cornwall it is dispersed through the granite and clay rock in a much more fragmental manner, and, as massive schorl rock, fills innumerable veins—sometimes so fine as to appear mere lines, at other times many feet in thickness. Much of this tourmaline is of secondary nature in relation to its present position, and owes its origin to recrystallization from rock material dissolved in the intertelluric water.

The study of the different varieties of tourmaline is valuable as an indication of the origin of granite, particularly in a comparison of the ordinary theory of an intruded molten mass with that of E. H. L. Schwarz, who maintains that Cornish granite has been formed as the result of a concentrated aqueous solution, at high temperature (180° C.) and under great pressure, being suddenly released, the crystals forming, as the viscous fluid cooled, in proportion to the reduction in pressure.

CHAPTER II.

FORMATION OF CLAYS, ETC., FROM IGNEOUS ROCKS.

Two important groups of actions constantly affected the composition and arrangement of all the primary rocks, and, if these were suitable, produced all kinds of clays and other "secondary" rocks and mineral deposits. These actions are conveniently termed:—

(a) *Hypogenic* actions, which are the result of heat or chemical activity, and are closely connected with earthquakes and volcanoes. Where they exist, minerals become consolidated, or even crystalline, and form new minerals. These changes are sometimes known as metamorphoses. When air or other gases and superheated steam, or other forms of water-vapour, take part in these changes, they are known as *pneumohydrogenic*; or if air or other gases without water form the chief chemical agent, the action is said to be of a *pneumatolytic* nature. The chemical and other changes involved are so numerous and so complex that no single term for the whole of them can be completely satisfactory, though Sir Charles Lyell's term "hypogenic" (meaning "formed under the surface") is convenient, as distinguishing all those changes which are of an internal and not of a superficial nature.

(b) *Epigenic* or surface actions are produced by the circulation of air and water, and to some extent by the alternation of heat and cold. Epigenic actions may conveniently be summarized under the term "weathering."

Thus the hypogenic actions are largely constructive—forming new compounds, such as those in the metamorphic rocks (*q.v.*); but epigenic actions are chiefly destructive, though this distinction is not invariably true. Hypogenic action appears to play the chief part in forming Cornish china clay, but epigenic actions are by far the most important so far as the formation of some kaolins and most plastic clays and sands is concerned.

The formation of clays may be stated, briefly, as consisting chiefly of the decomposition of certain portions of primary rocks

by epigenic action (weathering), though certain hypogenic actions are undoubtedly responsible for the formation of some clays. The primary clays and other minerals so formed are sorted out by various natural agencies and form beds or deposits. When these beds are subjected to further weathering, secondary clays are produced from the primary ones; but if the beds are subjected to hypogenic action, minerals other than clay are produced, and if these new minerals are of the nature of felspar or similar minerals they form a fresh source of primary clays. There is, therefore, a continuous cycle of changes, the primary clays being formed partly into secondary ones and partly (in conjunction with other minerals) into metamorphic rocks; though the present formation of the latter is now unimportant. The processes by which clays are formed are, however, so slow and complex, that the foregoing statement must be taken as broadly representing the views of modern geologists, but with the understanding that these views may be altered as further facts are discovered.

Hypogenic actions have occurred chiefly during the cooling of the igneous rocks after their discharge from the interior of the earth. Within the earth itself the materials cool so slowly that large crystals of felspar and other minerals can form, and probably float about in a pasty liquid made up of fused minerals. When, however, a mass of this pasty material is discharged by extrusion or volcanic action, the liquid portion cools relatively quickly, with the result that crystalline matrixes are formed, or in many cases a natural glass will be produced. The coarser portion is known as the "plutonic" or slowly cooled phase, and the much finer crystalline or glassy magma is the "volcanic" or rapidly cooled phase of the same material. In this way the physical condition of the minerals at the time of their discharge determines, to a large extent, whether they form granitic or trappean or volcanic rocks. The first-named appear, to a large extent, to have intruded into the overlying rocks in a pasty or almost solid condition. The traps, on the contrary, appear to have been poured out in a semi-liquid form as lava, and to have cooled more quickly, whilst the lava from more recent volcanic action is still, in some cases, undergoing the rearrangement of its constituents which is termed hypogenic action.

The ever-changing internal pressure of various parts of the earth's crust brings about important modifications in the nature and characteristics of the rocks affected by it. Sudden upheavals or depressions of the ground may occur, and may result in serious changes in the physical character of the neighbouring rocks. Volcanic action may cover a rocky mass with lava, and the heat

from this may cause a further change in the character of the rock itself, and the effect of the enormous pressure (caused by large masses of other rocks being piled up on a particular bed of material) is usually to consolidate a material so much as to convert it into a dense rock or, if sufficient heat be present, to change it from a bulky amorphous material into a mass of compact crystals. In this way many rocks have changed their character completely, as is described in the section on metamorphic rocks (later).

The chemical action of various vapours and of substances in solution is also responsible for many changes in the composition of rocks, and, in so far as it relates to the formation of clay, is considered later. The most important chemical and hydrolytic actions are treated under the heading *Kaolinization* (p. 34).

This group of actions consists chiefly in the formation of various definite chemical compounds from others, in accordance with well-known laws of chemical equilibrium and mass action; but, so far as the formation of clays is concerned, they are of minor importance except in connection with china clay and with the later action of the weather. The chemical reactions taking place as the result of weathering are, however, more properly considered as epigenic actions.

Epigenic actions comprise all those changes in the composition and distribution of minerals which are brought about by the action of air, water, and ice in conjunction with climatic conditions, and known as "weathering." They include the chief geological changes.

Epigenic actions are of four main kinds:—

1. The influence of air and water vapour.
2. The action of water in the form of rain, rivers, hail, lakes and ocean.
3. The action of snow and ice, as in glaciers, etc.
4. The part taken by plants and animals in their growth and decay.

These all unite their mechanical and chemical influences, and operate in a highly complex manner.

Air acts partly in a mechanical and partly in a chemical manner. When dry it has little chemical influence, unless the rocky material is rather moist, when oxidation often occurs, as in the conversion of greenish or black ferrous compounds into red ferric ones.

Carbon dioxide is contained in air in very small proportion, but the total quantity present is very great. This gas dissolves readily in water, forming carbonic acid, which combines with free

bases, or very weak salts, in the rocks, to form carbonates and bicarbonates. As a solvent of various minerals, its action is best considered under another section.

Other gases, such as fluorine, act chemically. (*See* p. 36 and p. 40.)

The heat of the sun, transmitted through the atmosphere to the rocks, causes those near the surface to expand, particularly in tropical countries, and the contraction which takes place at night (when the temperature may fall over 50° C.) is frequently a powerful factor in the breaking up of such rocks. The daily variations only affect the ground to a small depth, but the seasonal changes have a much greater influence. If water enters into crevices between pieces of rock and freezes, it will expand and so will tend to break up the rocks by its pressure; whilst if the rock is at all porous, the disintegration by freezing water will be still more complete. This action is more noticeable on higher ground, where soil does not gather, and in mountain ranges the cracking of the rocks in winter may frequently be heard. When large masses of rocks become detached, an avalanche or landslip is the result, and this mechanically causes a further breaking up of rocks by the force it exerts in its passage to a lower level.

Rapidly moving air (wind) will often exercise a serious abrasive action on rocks by blowing sand on to them. In the form of a gale or hurricane, air moving at a high speed will often carry large pieces of rock for considerable distances, and may cause the disintegration of others by the hammering action of the pieces it carries. Wind also forms accumulations of material, such as the sand-dunes near Blackpool.

Water acts (*a*) mechanically and (*b*) as a solvent. By mechanical action it loosens crystals from a softer matrix, washes small or light particles away from the heavier masses, and by throwing one piece of rock against another it rounds them into almost globular pebbles. Most rocks contain some water held within their pores by capillary attraction: this water expands on freezing, and so tends to break up the rocks containing it.

If water can enter beneath a piece of rock it may, in time, loosen it and cause a landslip. Thus in 1839 a mass of chalk on the Dorset coast slipped over a bed of clay into the sea, leaving a rent $\frac{3}{4}$ -mile long, 150 feet deep and 240 feet wide.

Rain beating down on a rock dislodges loose particles, and, gathering itself into streamlets, carries them away; but its chief action is that of a solvent, whereby it removes some of the rock constituents in solution, and thus permits of the easier

removal of the remainder by wind and by the mechanical action of water.

If a surface of granite rock which has been exposed for a long time be examined, it will be found that the quartz crystals stand out clearly, whilst the felspars have been corroded owing to the rain dissolving out some of their alkali and thus loosening them, so that in many cases they have been washed away from the quartz. In due course the quartz crystals will also fall away as their cementing medium or matrix is washed out.

The difference between the purely mechanical and purely solvent action of rain may be clearly seen by comparing its influence on granite and on soft sandstone. The granite is decomposed by the removal of the alkalis in the felspar, which weakens the whole structure of the material and so permits its rapid disintegration. The soft sandstone, on the contrary, can resist the solvent action of water indefinitely; but, being porous, it readily absorbs the rain falling on its surface, and this, as it freezes, brings about its destruction in a purely mechanical manner.

Rivers and Streams act partly as solvents, but also have a great power of transporting pieces of rock. The amount of material carried depends on the volume and velocity of the stream, and on the size, shape and density of the rocky material.

D. Stephenson has ascertained that the *bottom* of a stream of water moving at the following rates will move the materials mentioned in the third column:—

Inches per second.	Miles per hour.	Material moved.
3	·17	Fine clay.
6	·34	Fine sand.
8	·45	Sand as coarse as linseed.
12	·68	Fine gravel.
24	1·36	Pebbles 1 inch diameter.
36	2·05	Stones the size of hen's eggs.

Stones which are immersed in water lose about half their weight, and in this way large masses may be carried along by a stream which would not move them if they were not immersed. For this reason, also, the power of a stream is greatly increased during a time of flood, when both the volume and speed of the water are much greater.

The rocky material enters the rivers and streams in several

ways. It may fall in as the result of miniature landslips, or consequent on its being blown away from its site by a gale; it may be washed in by the accumulation of many rain-drops, each carrying its own grain of material; or it may enter as the result of the stream itself undermining its banks, the tops of which then fall into the water.

On entering a stream most fragments of rock are angular and irregular in shape, but during their passage they hit and rub against one another and against the floor and banks of the stream, and so become rounded (unless of unusual hardness) and are gradually worn down. The particles thus removed form clay, sand, and gravel, which are carried forward more rapidly than the stones, and are deposited at any points where the speed of the water is sufficiently reduced, or are carried onward until they enter the sea. The distances through which the finest particles may be transported are exceedingly great.

The amount of material transported by rivers is enormous, the Danube delivering some seventy million tons annually into the Black Sea.

Owing to this continual grinding of the bottoms of streams and the undermining of the banks by the abrasive action of the stones and sand and the solvent action of the water, the land through which such a current of water travels is gradually cut away and forms gorges, chimes, and valleys.

A sudden drop in the ground forming the bottom of a river may form a cataract or waterfall, at the bottom of which the erosive force of the water will be still greater; the battering of the stones in the water gradually breaking down the weir and causing it to wear slowly away. Rivers thus tend, on the one hand, to cut fissures and valleys in the land over which they pass, and, on the other, cause a levelling of the land over which they flow.

When flowing through more level stretches of country—particularly if its course is winding—a river often alters its direction somewhat rapidly. This is due to the frequent bends reducing the speed of the water and so permitting some of the sand, stones, etc., to be deposited.

At every change in the direction of the flow the water with its burden of minerals impinges on the bank and gradually cuts it away on the outer edge in the bend of the stream; and as the speed of the water is reduced at the inner edge of the bend, some deposition of material takes place. If the river cuts through the outer edge of the bend more rapidly than the matter displaced is deposited on the inner one, a short-cut channel is formed and a

large portion of the original course, sometimes amounting to several thousand acres, is left dry. This is clearly shown in fig. 1.

Whilst all British rivers, directly or indirectly, flow into the sea—which thereby becomes the great receptacle for the mineral matters carried by them,—there is an enormous proportion of clay, sand, and gravel which never reaches the sea, but is stopped at various points along the banks of the rivers, as just explained, and when the course of the water has been changed, these deposited materials form beds which are often of great value for the clay and sand they contain.

In past geological ages, rivers of frozen water (ice) played an important part in the formation and distribution of clays and

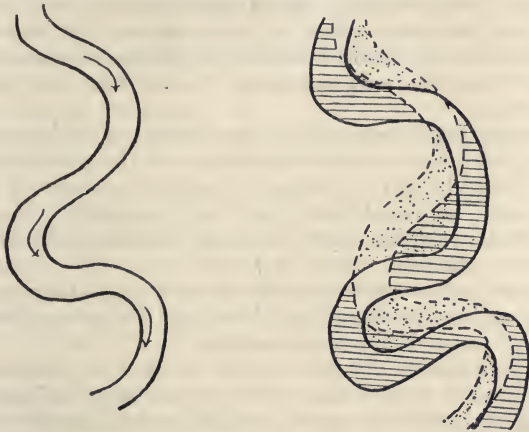


FIG. 1.—Diagram showing River Action. (After G. Hickling.)

sands. Some of these frozen rivers still exist in mountainous regions. Their action is described later in the section on *Glaciers* (*q.v.*).

Springs have an important epigenic action in many places, particularly near the coast, where it is usual to think of the erosion as the work of the sea. In reality springs may do a large share of the work by loosening the soil and facilitating the later action of the sea water. This is particularly noticeable on the coast at Filey (Yorkshire), in one part of which at every few hundred yards springs of water may be seen issuing out of the boulder clay, causing fissures in the soil and preparing it to be washed away at the next high tide.

The sea produces a similar effect to rivers and streams; but as

below the surface its relative movement is less, a much greater amount of deposition of mineral matter takes place.

The force of the sea as a grinding agent is far too great to be easily appreciated. Huge blocks of rock are churned and ground as in a monstrous mill, and are reduced to pebbles and finally to sand and clay.

The tides cause an almost incessant battering and washing away of material from the shore, and this is carried towards the more slowly moving parts of the ocean and there deposited.

The action of the tides is most effective in the crevices between the rocks, into which the water enters with almost explosive violence, at a pressure of two tons or more per square foot.

Caves are hollowed out by direct mechanical action of the water and of the boulders which it hurls against the shore during storms, and the enormous quantities of pebbles and sand around the coast form eloquent testimony to the force and power of marine action.

The result of the action of the sea through countless ages has been the destruction of whole continents and the re-distribution of their rock-masses into new forms of material, which can scarcely be recognized, so greatly have they been changed. The marine deposited clays are amongst the most valuable for brickmaking and similar industries. (*See Chap. V.*)

Tidal and other ocean-currents are also important agents in breaking up and transporting rocks and in sorting them into particles of varying sizes and densities.

The *solvent* action of water is of the greatest importance in the disintegration of many rocks. There is scarcely a mineral which is not slightly soluble in water, and many substances are dissolved readily, so that the contact of water with rocks is certain, in time, to remove some of their constituents. If the water contains any acid (as carbonic acid derived from the air) or other chemically active material, its action is greatly increased. Thus, chalk and its related rocks are scarcely affected by pure water, but are readily dissolved by water containing carbonic acid. Under some conditions, rain-water containing carbonic acid can decompose certain silicates and render them soluble (see footnote on p. 37).

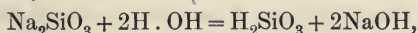
Many spring- and well-waters are rich in dissolved salts of various kinds, such as the medicinal waters of Harrogate, Bath, etc., the various chalybeate (iron-containing) waters, and the "hard" waters which are heavily charged with calcium bicarbonate and sulphate formed by the action of dissolved carbon dioxide on limestone or chalk and by the solvent action of water on gypsum. Sea-water owes its saltiness to the materials which have been dis-

solved out of various rocks and have been delivered to the sea by streams and rivers. As the various seas have no outlet except by evaporation of the water (in which case the dissolved salts are not removed), sea-water must continue to increase in saltness as time goes on.

Frequently, water dissolves out certain constituents of a rock without altering the crystalline form of the mineral, whilst completely changing its composition. In such minerals (termed *pseudomorphs*) clay may take the place and form of rock-salt, silica that of wood, and many other equally striking examples might be mentioned.

The chemical action of water on mineral substances (*hydrolysis*) has been studied much during recent years. It is now recognized that water contains free hydrogen-ions (H) and free hydroxyl-ions (OH) under certain conditions, and that its dissociation into these two kinds of ions is sufficiently powerful to decompose certain minerals, such as mica, felspar, etc., and thus to produce alkaline solutions.

The action of the water may be represented in the case of a simple silicate by



a weakly dissociated silicic acid being formed, together with caustic soda. The latter gives the alkaline reaction.

Through the formation of undissociated silicic acid, a loss of hydrogen-ions ensues, and to restore equilibrium this must be made good by the dissociation of more water.

The alkaline silicates are most strongly affected, then the calcium silicates, but those of magnesia scarcely at all.

Hydro-alumino-silicate (clay) offers a peculiarly strong resistance to dissociation, and, consequently, clay remains as a decomposition product of granites, felspars, and other complex minerals.

The solvent action of *hot water* on silicates is relatively great, and hot springs frequently contain a large proportion of silica in solution, but the few warm springs in England are not of importance in the formation of clays and sands.

Water falling on to a rock removes, by solution, rock ingredients, and often leaves a crust of a soft and friable nature on the rock. This crust may be washed away by a later rain and carried by the resulting stream for such a distance and deposited in such a manner that the various minerals removed may become quite separated from each other and may be recovered each in a relatively pure state. Thus the larger pieces will be near their source, the sand will be graded into several degrees of fineness, and the

clay and fine silt will be carried right away from the rest of the material.

In this manner water first acts as a solvent in "corroding" the rock, and afterwards by mechanically removing the decomposed material. Were this not the case, rocks would become covered with a crust of partly decomposed material, which would form a protective covering for the general mass of rock. The rain, however, keeps the surface of the rock comparatively clean by washing away much of the "corroded" material, and thereby facilitates continued action.

Where such "corroded" rock material is deposited close to its original rock, having been transported only a short distance, it is known as *arkose*. It consists of practically the same minerals as the original rock, though some of the finer grains (as of china clay) and some of the soluble substances may have been removed.

The action of rain and other water in decomposing some rocks is not nearly so slow as many people imagine, and in some cases it is quite rapid. The rate of action varies greatly, however, and, though constantly occurring, it is very irregular.

It frequently happens that a material dissolved out of one rock by water may have a direct chemical action on other rocks with which the water comes into contact. Thus water may dissolve potash and soda out of felspar, and these chemicals will react with further minerals such as certain silicates, rendering them soluble.

The action of rain on felspar and feldspathic minerals is, perhaps, the most interesting to clayworkers, as under some conditions the felspar yields up its alkalies, forming clay and free silica. If the felspar is very free from impurities a valuable china clay may be formed.¹ Each little rain-drop gathers its own charge of alkali, joins another rain-drop and then others, until a small stream is formed which gradually wends its way to a river or sea. As felspars are decomposed by this rain-water they lose alkalies and absorb water which becomes chemically combined with the clay.

If any oxidisable materials are present they will be oxidised by contact with rain-water, or, if the latter contains much humus, some oxides may be reduced. The loosened particles are then washed out mechanically by further supplies of water as previously stated.

The general result of the action of water (of whatever nature)

¹ China clay in Cornwall has, apparently, been chiefly formed by the action of water under pressure in the interior of the earth, and only to a small extent by weathering in the manner here indicated.

is to wear down the higher portions of the earth's surface, to grind down the large masses, and to transport the ground material to a lower level.

Some of this material is carried in solution (as salt in seawater), but by far the greater part of it is borne mechanically by the moving water. As soon as the velocity of the water is reduced, some of the heavier particles begin to sink, stones and gravel settling out first, then sands of varying coarseness or fineness, and finally clay, mud and silt-particles. The manner in which these are deposited is described in Chap. V.

As in most cases of chemical action, the influence of time is important. The solutions formed by the action of the water on the rocks are so dilute that the velocity of the reactions which occur is sometimes so slow as to be almost inappreciable, yet so long have they been acting in many cases, that incalculably large masses of material have been completely changed.

The action of **snow** and **icè** is purely mechanical, and is very similar to that of rivers. The snow on mountains forms large masses or "fields," and as the lower portion melts these masses slide downwards—often with great speed—and the resulting avalanche does serious damage to the rocks over which it passes. All the looser boulders in its path are carried downwards, and when the mass is arrested by a projecting rock its weight is so great that in many cases the stoppage is only temporary; the rock eventually gives way and falls with the snow into an adjacent valley.

Still more powerful in its total results is the snow which accumulates in the upper valleys as just described. As the depth increases, the lower layers are compressed into ice and the whole mass becomes a flowing river of ice and snow. Such a glacier behaves very similarly to a river in its action on the land, though its effect is more intense and its power of carrying huge boulders is much greater. As crevices or cracks form in the ice, huge masses of rock resting on the surface fall into them and slowly sink to the bottom. There they are crushed and ground and carried forward until the ice melts and most of its solid burden is left deposited, only the finest particles being carried forward by the water produced.

The banks of a glacier are not as rough and irregular as those of a river, but are smooth and more rounded, the harder stones having curious scratches on them which are characteristic of glacier-action. The smooth outlines of many British hills have been produced in this manner, and large tracts of country are covered with the fine material ("drift" or "till") deposited by

glaciers at the lower end of their course, the drifts in Lancashire and Yorkshire being particularly important to clayworkers.

The action of **plants** and **animals** in the formation and deformation of earth is important. Roots constantly penetrate into crevices, and if the ground is sufficiently soft, break it up into soil, and the decayed remains of plants and animals are constantly adding to the soil. Owing to the nature of clays and sands, the chemical influence of vegetable and animal matter upon them is unimportant, but many shales and not a few clays contain sufficient carbonaceous matter to render them difficult to use industrially. Oily shales are well known.

Micro-organisms are chiefly important as producing chalk (by foraminifera), flinty or siliceous earths (by polycystinæ and diatoms, etc.), and so form well-known deposits of chalk, sand, and (in connection with clay) certain marls. It is, however, their mineral remains rather than their own nature which are important, and the earths formed are chiefly of interest in so far as they form impurities in clays or valuable beds of sand.

WEATHERING.

The term "weathering" is convenient as including all those changes which occur as a result of the action of heat and cold, rain, hail, snow, wind, exposure to air, and other atmospheric processes in rocks and other substances.

The general tendency of weathering is to destroy the form of all materials and to so re-arrange their constituents as to form new substances. Thus most granites will, on sufficient exposure to weather, break down into a mixture of mica, quartz, and other minerals, together with some undecomposed felspar and clay. This destruction is brought about by the agencies already described, and may require an enormous period of time; it is largely a matter of fortuitous circumstances whether the products of the action of the weather remain together or are separated from each other, as when the clay and mica are washed out of the mass into separate hollows or pockets.

The extent to which weathering occurs depends on the nature and situation of the rocks; soft porous materials in exposed positions being most affected. Granites vary greatly in this respect. Rose has pointed out that many rocks which are quite unaffected by the most powerful acids in laboratory experiments, yet weather readily in nature under the apparently feeble influence of water, air, and carbonic acid. This is due to the influence of much larger quantities taking part in the reaction,



Cliffs of "Boulder Clay" at Filey, Yorkshire.

[*To face p. 33.*]

and is a typical example of "mass action." Dilute solutions—being more completely dissociated into ions—are, in fact, relatively more active than strong solutions.

As rain-water (usually charged with carbonic acid) penetrates into the rocks it slowly dissolves out any alkalies, and frequently some silica, and effects various changes in the constitution of some of the weaker minerals. Thus olivine and augite may be converted, by weathering, into serpentine or other magnesian silicate. The depth to which the water penetrates and the extent to which the rock is disintegrated will depend upon the severity of the climate, on the position of the rocks, and on their composition. The appearance of rock is often useless as a guide to the probable extent of weathering, as some granites and basalts form superficial crusts several feet in thickness, due to the removal of alkalies from the felspar in the former and lime as carbonate from the latter; when these crusts are washed off by the rain, or are detached by the action of wind and rain, they form deposits, often of great thickness, of a character entirely different from that of the original rock. In other cases the weather exerts a selective action so that some fossils and nodules can be more easily picked out of a weathered face than a fresh one. This is well shown in the cliffs of the East Yorkshire coast.

Most rocks weather in a characteristic manner which facilitates their identification even at a distance. This disintegrated matter may form "soil" on the site, or it may be removed to a different site by rain or other influences. Thus, at Filey on the Yorkshire coast, the cliffs of boulder clay are weathered to sharp pinnacles and ridges, in striking contrast to the rounded contours usually found with clay. (~~Plate VIII.~~) III

The individual substances produced by the action of the weather are often the result of a highly complex series of reactions, both direct and reversible. A more detailed study of these involves so deep a knowledge of the laws of dilute solutions, mass action, etc., as to be beyond the scope of the present volume, but the author proposes to deal with these in a future edition of his *Chemistry of Clayworking*.

From a commercial point of view the chief effect on rocks of the weather is the formation of clays and sands.

The greater facility with which clay which has been exposed to the weather can be worked into a plastic paste as compared with clay used fresh from the pit, makes "weathering" an important process in the manufacture of clay goods. At Ruabon, for example, exposure of the clay for a week at any season of the year greatly improves its quality. Clays in other districts

may require exposure to frost and rain as well as to air before goods from them will dry without twisting or cracking.

KAOLINIZATION.

The production of clays from igneous rocks is termed kaolinization, and is chiefly effected by the removal of alkalis from the felspars by the solvent action of water (with or without dissolved substances), but some other forces also appear to have been at work and to have made the rocks capable of being attacked in this manner.

It appears certain that the kaolinization of the deeper deposits in Cornwall must have occurred long after the formation of the granitic rocks, as otherwise it is difficult to account for the rapid variations in the composition of the material and its content of china clay. At the same time, this kaolinization cannot be chiefly due to "weathering," as it occurs most prominently at great depths from the surface. It is probably due to water containing other gases than air (p. 36).

The breaking up of the felspathic and other rocks which lose alkalis begins, naturally, on the outside; the crystals first lose their gloss and become dull, and the mass becomes whiter, with an outer skin resembling flour-paste. Regular lines of cleavage, hardness, and strength disappear as the alkali is dissolved out of the material, and the final product of the decomposition of pure orthoclase and similar felspars (p. 15) is a white, earthy hydro-alumino-silicate which is termed china clay or kaolin, though there are several objections to the use of the latter word.

On microscopical examination of a decomposing granite with polarised light the china clay may be seen to be forming in dense aggregates of very minute flakes, which permeate the felspar along its cleavages and other lines of weakness and gradually replace it entirely. At one stage of the process there are networks of kaolin enclosing residual patches of felspar which agree in their position of extinction and are evidently the remains of a single crystal. The large orthoclase crystals are usually hard and fresh, but on careful examination will be found to contain small nests of scaly white mica and china clay, showing that the decomposition in them has already begun.

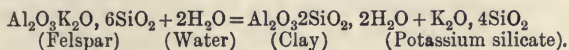
The various felspars vary greatly in the ease with which they form clay; thus, oligoclase (p. 17) kaolinizes more rapidly than orthoclase, and labradorite still more easily when the weather is the chief agent of destruction, but when fluorine vapours are present the orthoclase is most readily decomposed.

The reactions which occur are so complex as to be only imperfectly understood. Many eminent investigators have endeavoured to represent these reactions by a series of formulæ, but none are really satisfactory.

One of the least objectionable means of representing what occurs is the following:—

	SiO ₂ .	Al ₂ O ₃ .	K ₂ O.	H ₂ O.
100 parts of typical orthoclase consists of .	64·63	18·49	16·88	...
From this a soluble silicate is removed by water .	43·05	...	16·88	...
And water is simultaneously added	6·47
The resulting 46·5 parts of kaolin consists of	21·51	18·49	..	6·47

Expressed by formulæ, the decomposition may be represented according to Fiebelhorn as taking place after the following manner:—



Some chemists state that the simple silicate produced has the formula K₂O3SiO₂, the fourth equivalent of silica being found in the free state, so that it can either remain mixed with the clay, or, being in so finely divided a condition, it may be taken away by water at the same time as the soluble silicate.

This theory of the formation of pure clay by the decomposition of felspathic rocks is in unison with the decomposition of numerous rocks which is taking place at the present time, though it is extremely difficult to observe the direct formation of clay from felspar.

The variations in the composition of the rocks in which the felspar occurs, and special circumstances attending the decomposition, explain the formation of other hydro-alumino-silicates—halloysite, lenzenite, severite (with the same silica-alumina ratio as kaolinite, but yielding a different proportion of water on calcination), allophane (SiO₂, Al₂O₃, nH₂O), pyrophyllite (5SiO₂, Al₂O₃, H₂O), and a hydrous alumino-silicate corresponding to 4SiO₂, Al₂O₃, nH₂O, which is found in some calcareous marls.

The foregoing comparison and the use of an equation avoid all reference to the intermediate stages which the orthoclase undergoes during its kaolinization. What appears to take place is that the granites and porphyries first become porous by the

decomposition of the felspars in them, next they fall to powder, and finally produce a clay which is contaminated with undecomposed felspar and undecomposable material such as quartz and mica.

How far this decomposition is directly due to weathering, and how far to the action of water or to fluorine and boron vapours (or to free hydrofluoric and boric acids) emanating from the fissures or jointing in the granite in the dying phases of pneumatolytic action, is an open question. Fluorides are always found in china-clay rock, and a number of investigators consider that fluorine has played a far more important part than carbonic acid in the kaolinization of felspar. Von Busch and Daubrée, and, later, J. H. Collins, attribute the presence of lepidolite and tourmaline in Cornish china clays to the action of the hydrofluoric acid on the felspars and on the residual materials of the granite. According to MacAlister the fluorspar, of which the greater part occurs in cleavage planes in the mica and to a certain extent in the felspar, was probably formed by the interaction of fluoride vapours on lime abstracted from the decomposing felspar.

The decomposing agents are not necessarily confined to boron and fluorine vapours or to carbon dioxide, as these or other substances dissolved in the water which circulates through the material at considerable depths may also take part in the kaolinization, and there is good evidence that liquid water and not steam or other vapour is the chief agent, especially as the experiments of Bogojwlenki and Tammann have indicated that under sufficiently high pressures all acids and bases are equally active. Most investigators who have paid special attention to the Cornish clays are, however, agreed that the action has chiefly proceeded from below upwards—the amount of china clay produced by weathering being only a small portion of the whole. The greater richness of the material at great depths, the occurrence of fluorspar and the association of the kaolinized rock with lines of jointing and tin lodes, confirm this view.

J. M. Coon has pointed out that three series of jointing of the granite formation in the Hensbarrow district are well known (attributed to contraction on cooling, etc.).¹ One series approximately parallel to the surface contours is known as the bedding joints; the two others, inclined from the vertical and roughly at

¹ All masses of rocks are intersected by regular cracks termed *joints*, which usually traverse the rocks at right angles to each other. When these joints are very close together and are parallel the phenomenon is termed *cleavage* and the rock splits into slates, flagstones or shales. When the material splits into very thin leaves (as mica) it is said to be *laminated* or *foliated*.

right angles to each other, are known as heading joints. These joints or fissures occur in groups of close parallel fissures, and MacAlister has shown that the clay-pits now worked have a general linear distribution in the direction of the strike of the tin veins. J. M. Coon has shown that owing to these jointings the intertelluric water will be in constant alternation according as the seasons are wet or dry; and in flowing from one boss of granite to another much of the water will descend to great depths and will become heated and charged with such substances as are soluble under such conditions. This water rising upwards and again infiltrating through the granite mass decomposes it. As the dissolved substances do not enter into the composition of the china clay, the action is probably catalytic. J. M. Coon regards the underground hydrostatic level as the upper limit of formation of Cornish china clay, the lower limit being indeterminate so long as circulating waters bring the agents of decomposition into contact with the material, the kaolinization being most perfect at the greater depths.

More recent investigations on Cornish china clay by Ussher and others appear, however, to point to the probability that neither fluoric nor boric gases were the chief agencies of kaolinization, and to support Vogt's hypothesis that carbonic acid was the principal, though probably not the only gas involved.¹

Gagel has recently found that the granite at the mouth of the Giesshueblen spring at Carlsbad was sufficiently kaolinized to allow a considerable quantity of snow-white material to be collected. As the water in this spring is very pure but highly carbonated, Gagel concluded that it shows clearly that carbonic acid alone is capable of effecting the kaolinization of some granite at ordinary temperatures. Van Bemmelen has, however, pointed out that the kaolin may be much older, and may only recently have been brought to its present position.

The subject has also been investigated with a view to ascertaining how far kaolinization has been the result of humic acid and other organic substances, but without much result; and more recently Rohland has suggested that it is the result of the simple hydrolysis of felspar and similar rocks, with the simultaneous formation of colloidal silica and caustic alkali, the residual matter being clay, which is peculiarly resistant to hydrolytic action. This resistance is due, to some extent, to the complex constitution of kaolin, as the simpler minerals analogous to it, such as *collyrite*,

¹ Under the enormous pressures existing in deep-seated regions silica decomposes carbonates, but near the surface of the earth the reaction is reversed, carbonic acid decomposing silicates.

are also hydrolyzed, and when dilute hydrochloric acid is added form gelatinous silica.

The details of the manner in which kaolinization occurs are, however, so obscure that any statement further than one alleging that most British china clay appears to be derived from the decomposition of the felspars in certain granites by fluorine, boron, or carbonic acid and water, is little more than a speculation, and it is unwise to dogmatize as to the reactions which occur during kaolinization, especially as very small quantities of materials present in the clay may cause so many complicated secondary reactions as frequently to obscure the main one, though these secondary minerals sometimes assist in studying what has occurred.

The proportion of accessory ingredients in the clay is increased by the presence of concretions and veins of opal, chalcedony, quartz, etc.

It is generally understood that *all* clays must have been originally derived from the many kinds of igneous rocks containing felspars, but as the clays derived from comparatively pure felspars (china clays) have many properties different from others, there is much variation of opinion on this subject.

It appears most probable that material of the chemical composition of clay may be obtained from a variety of sources, and that the plasticity which is so distinguishing a feature of some clays depends upon the manner in which they have been formed, and is largely, if not quite, independent of the felspar or other original material. Thus, in the formation of some plastic clays organic substances appear to have played an important part.

Although the various felspars may be regarded as the chief primary source of clays, there are many other minerals and rocks which can become secondary producers of clay. Thus dolomite limestone usually contains iron and manganese carbonate and clay as impurities. If the weathering removes the true dolomite, a residue consisting of clay rich in iron and manganese (*Terra rossa*) remains.

The production of clay from *augite* and *hornblende* (the two chief constituents of trappean rocks) appears to be chiefly due to the action of water containing carbonic acid, which first acts in the removal of magnesia and some iron, and in the addition of water, so that hydro-alumino-silicate (clay) remains, but is usually rich in iron. Small quantities of a very pure china clay may, however, be obtained by carefully washing the white seams—rich in hornblende—occurring in some trappean rocks in the Isle of Man.

Kaolinization is very widespread in the *elvans* (quartz porphyry) in the district south of St Austell. The amount of china clay

produced is too small to be of commercial value, but theoretically the occurrence of this decomposition is interesting, as the china clay does not occur in the ground-mass. Flett considers that these elvans have been first greisened (p. 6) and the remaining felspar being afterwards converted into china clay, and he supports MacAlister's opinion that tourmalinization and kaolinization are closely connected (p. 6).

The decomposition of felspar and augite is specially pronounced in basalts and olivine. The rain-water (rich in carbonic acid) soaks into the basalt mass and converts the lime, magnesia, soda, potash, and ferrous silicates into acid carbonates. These carbonates are washed out of the rock, together with the silica set free during their formation. The residual hydro-alumino-silicate and iron oxides form the well-known **wacke clay** or **trap clay** on the surface of basalt formations.

The change of composition in basalt which is effected by weathering is shown in Table I.

TABLE I.

PERCENTAGE COMPOSITION OF ROCKS IN THEIR NATURAL STATE AND AFTER WEATHERING (PRESTWICH).

	1. Basalt (Bohemia).		2. Greenstone (Cornwall).	
	Unaltered.	Altered.	Unaltered.	Altered.
Silica	44·4	42·5	51·4	44·5
Alumina	12·2	17·9	15·8	22·1
Lime	11·3	2·5	5·7	1·4
Magnesia	9·1	3·3	2·8	2·7
Potash	0·8	} 0·2	1·6	1·2
Soda	2·7		3·9	1·7
Iron protoxide	12·1	...	12·9	...
Iron peroxide	3·5	11·5	2·5	17·6
Manganese oxide	0·5	...
Titanic acid	trace	1·2	0·7	1·0
Water	4·4	20·4	1·7	8·6
	100·5	99·5	99·5	100·8

Ries has pointed out that many rocks containing little or no felspar—such as serpentines and gabbros—appear to produce

highly plastic clays, though there is no positive proof of this reaction; nor can it be stated with certainty whether all clays contain essentially the same hydro-alumino-silicate. That the chief constituent of all clays has a composition corresponding very closely to a hydro-alumino-silicate, or an alumino-silicic acid, is undoubted; but it is, at present, impossible to say whether this substance is kaolinite or a mixture of several alumino-silicates of very similar but not identical composition. The latter opinion is rapidly gaining favour.

J. M. van Bemmelen has suggested that clays may have one or more of the following origins:—

- (i) Ordinary weathering causing a decomposition of the rock.
- (ii) Secondary actions whereby new materials are formed from it.
- (iii) Lateritic decomposition in which free alumina is formed, this occurring chiefly in tropical climates.
- (iv) Pneumatolytic or gaseous action proceeding from below upwards.

This investigator has shown that whilst kaolins are practically insoluble in hydrochloric acid, yet many clays yield a considerable amount of soluble matter when boiled with hydrochloric acid and then with caustic alkali. This material—which he considers to be obtained by the decomposition of a silicate or alumino-silicic acid more easily decomposed than kaolin—has an alumina-silica ratio which is never less than 1 : 3 and may rise as high as 1 : 5, and so differs materially from kaolin. The amount of water combined with this substance has not yet been ascertained. (*See* Chap. VII.)

The original rocks from which clays are produced are usually massive, and so hard that it is difficult, even with powerful machinery, to reduce them to a fine powder; the clays, on the other hand (when freed from coarser impurities), are so fine that they will readily pass through the finest silk gauze, and are amongst the smallest particles known. This difference enables clays to be separated from the greater part of the other minerals occurring with them.

Artificial kaolinization must be extremely difficult of accomplishment, even if it be at all possible. It does not appear likely that the necessary conditions can be realized experimentally, as the reactions proceed so slowly as to extend over periods outside all human experience. This explains the fact that, in spite of many attempts at the artificial kaolinization of felspar (by heating with steam under pressure, by electrolysis, etc.), no fully satisfactory result has yet been obtained.

CHAPTER III.

THE SEDIMENTARY ROCKS.¹

So violent and destructive are the agencies described in the previous chapter, that practically all that is left of the igneous rocks in the British Isles are in a few isolated parts of Devon and Cornwall, the coast of north-west Scotland, the Outer Hebrides, and the north-east and south-east of Ireland. Much of these rocks is hidden with a covering of sand and debris many hundreds of feet in thickness.

Most of the other igneous rocks have been carried down to the sea by rivers and streams in the manner already described, and were there deposited layer on layer. In this manner the land which has disappeared from one district forms a new area of land, or diminishes the depth of the ocean in another.

A careful examination of the chief rocks above the present sea-level will show that most of them are not simply igneous, but are of a sedimentary character, and a still further study of the subject will show that the majority of them were at one time below the sea, though they are now above it. These sedimentary rocks usually show the stratified arrangement characteristic of water-deposited materials; some of them have become hardened or indurated by pressure or by the infiltration of water containing salts or gases in solution.

Geologists are now agreed that this great change in the composition of dry land is due to the action of movements similar to earthquakes, though they may have been so gentle that no shocks marked their occurrence. These movements have not been regular, nor have they all been in the same direction, and the result of their action has been (1) to cause the land to rise or fall relatively to the sea or *vice versa*, and (2) to cause the

¹ Sedimentary rocks are those formed by materials which have been carried along by suspension in water and have afterwards been deposited as sediments.

sedimentary or deposited rocks to become folded and crumbled in a most peculiar manner.

Of the cause of these movements no adequate explanation can, as yet, be given, the old theory of the shrinkage of the earth's crust by interior cooling being not so acceptable as formerly. It is almost certain that, as originally formed, the sedimentary rocks were in horizontal layers, but as they now exist they are tilted in all directions, and in some cases have been turned completely over. Some of these folds are of enormous size: the Pennine range, running through Yorkshire and ending at the Peak in Derbyshire, being a good example of a fold nearly forty miles across, and many others, equally impressive, are known. In fact, most of the great mountain ranges are of this character, though they have been so affected by weathering since their formation as to prevent the "fold" being easily recognized.

In larger earth-movements the rocks have snapped in certain directions, and have changed their positions; such displacements are termed **faults**, and almost the whole of the rocks in Great Britain have been displaced in this way, though it is necessary to get some distance below the surface before the displacement can be seen, as the effect of weathering has been to obliterate the surface indications.

Earth-movements are also responsible for the enormous thrusts and lateral movements of the rocks, whereby whole mountains have been moved through a distance of several miles.

The formation of compact shales and slates from loosely-deposited clays is thought to be effected by this means, and as some chemical action has often occurred, and heat has been developed simultaneously with the pressure, the character of the sediment has been altered by the formation of entirely new minerals, each from a corresponding constituent, or mixture of constituents, of igneous rocks. In this way granites have been converted into gneiss, sands into quartzite, and clays into slates, shales, and schists.

The lime dissolved out of felspar and other minerals has been converted partly into limestone by carbonic acid in the air and water, and partly into chalk by the action of living creatures (foraminifera); and if the heat and pressure have been sufficient, marble has been formed.

In some cases rocks have been subjected to the action of several earth-movements, and in this way the study of their formation has been seriously complicated, though the short description just given will, it is hoped, be sufficient to indicate broadly what has occurred.

So far as can be ascertained in the present state of geological knowledge, what happened was, briefly, as follows:—

Natural agencies having slowly removed the igneous rocks to such an extent that almost the whole of Great Britain was at a considerable depth under the sea, beds of limestone were formed, and at a still further depth the remains of the older rocks underwent various metamorphoses, forming schists from the clays and quartzite from the sands and sandstones of the earlier epoch.

The lowest-lying, and therefore the oldest, of the sedimentary rocks in Great Britain are the Torridonian sands and gravels (from Loch Torridon), which are so ancient that they were carved into hills and valleys before the beginning of the Cambrian period. These rocks have, however, suffered so profoundly that their primitive character is almost entirely lost. The fewness of fossils in these rocks further complicates the subject, but in the next series—the Cambrian sandstones and slates—which occur in great prominence in Wales (where they attain a thickness of 12,000 feet in Merionethshire), Shropshire, north-east Ireland and north-west Scotland, fossils are plentiful enough to enable the history of the rocks to be read with greater certainty.¹

The land again subsided, or continued to subside, though not universally, during the Silurian period, when slates and shales—some 20,000 feet thick—were deposited upon the Cambrian bed. During this time a certain amount of folding of the earth's crust must also have occurred and active volcanic eruptions taken place, particularly in Wales and in what is now the Lake District.

The subsidence then appears to have largely ceased, or at any rate the water covering became shallower, and thick masses of coarse sandstone and marl rapidly accumulated and formed the Old Red Sandstone deposits. In Devonshire, however, the land appears to have remained below sea-level, for it was at this time that the Devonshire "marbles" were deposited in the form of limestone, hence the Devonian and Old Red Sandstone periods are largely contemporary.

Further volcanic action occurred—this time in the north—and the accompanying earth-movements caused much of the crumpling and folding of the rocks just mentioned, resulting in the whole land being raised again above sea-level. "Weathering" again occurred, carving down much of the land which had previously

¹ The identification of fossils is properly the work of experts and cannot be satisfactorily completed by people not having the necessary training. Stanford's Atlas and other well-known books on geology will be found useful when the services of a palæontologist are not available. (See p. 45.)

been built up, until a further subsidence—which did not affect the area north of the Grampians—occurred, and the Coal Measures, Mountain Limestone, and Millstone Grits were deposited in the Carboniferous period. As the Millstone sands accumulated, a huge swampy jungle was formed, and alternate periods of subsidence and of elevation of the ground produced the existing veins of coal and clays in the Coal Measures.

Further local risings occurred towards the close of the Carboniferous period, and in the enclosed hollows, which were inundated by the sea, Permian rocks of magnesian-limestone and Red Sandstone were deposited, and the New Red Sandstone with its accompanying red clays was laid down.

To the west of the Pennine range bright red sandstones and clays were alone accumulated, but to the east of it limestone was also deposited. Simultaneously extensive denudation of the Carboniferous rocks occurred, and the waters of the enclosed seas became intensely salt.

After an indefinite period the water-level was again lowered, desert conditions prevailed, further denudation took place, and, later, as a result of further elevation above sea-level, the Upper New Red (Bunter) Sandstone, which is characteristic of the Triassic period, was formed. Subsequently a huge shallow lake formed over Yorkshire and Cheshire and extended very far south, and in this the characteristic bright red Triassic clay was deposited.

After this there appear to have been many changes in the relative heights of land and sea, particularly in the south-east of England, where Lias deposits were formed, and the Oolite and Wealden beds were laid down.

Later still, during the submergence of the centre and South of Europe, vast deposits of greensand and grey ooze of a chalky character were laid down, and the latter now forms the chalk cliffs on our coasts.

At the close of the Cretaceous (chalk) period a general rising of the land again occurred, and the Tertiary period began. In this period the ridge which forms the watershed between the Thames basin and the rivers of the south was produced, the North and South Downs being the worn edges of it. A long series of intensely active volcanoes broke out in the north, and the county of Antrim and several of the western islands of Scotland are covered with their lava.

Protrusions of igneous rocks reached the surface in various districts during many of the changes.

During the following (Pliocene) period, East Anglia was again

submerged, and a considerable lowering of temperature occurred over the whole country, becoming arctic during the Pleistocene period, when the whole of England north of the Thames and Severn was covered with ice which formed glaciers, and during thousands of years ground away the projecting portions of rock until it melted and deposited its burden of rock, gravel, sand, and clay in a huge sheet throughout almost all the valleys.

Since the end of the glacial epoch, the chief changes which have occurred have been due to the action of the weather and of rivers on the materials formed in the manner just described. The destructive action of these agencies has been already detailed in Chap. II. ; a brief outline of their formative influence is given in Chap. V.

For convenient reference, the order in which the most important sedimentary rocks were formed is shown in Table II. on p. 46.

The construction of such a table is based on the fossil remains of plants and animals found in the various rocks, in accordance with the discovery of William Smith, more than a century ago. It is also based on the assumption, now generally accepted, that, with a few exceptions which are readily recognizable, all the strata occur in chronological order, the oldest being below and the newest above them. Members of the series are, of course, constantly found wanting, and in no case is the complete superposition of all the series found ; different rocks of the various periods may come up to the surface, sometimes one, sometimes another. Often this protrusion is caused by the dislocation of rocks by fire or other agencies. In other areas the older rocks are now seen on the surface solely because of the erosion or removal of the later and higher deposits, but the order is rarely disarranged. The oldest is almost always at the bottom, even though the rocks of intervening periods may be absent. For further details on this subject the reader should consult works on Advanced Geology.

Stratigraphical Geology and *The Building of the British Isles* (both by A. J. Jukes-Browne) will also be found of interest in this connection. *Geological Rambles*, by T. Sheppard (p. 78), is an excellent guide to the geology of the Yorkshire coast.

TABLE II.
ARRANGEMENT OF ROCKS AND ROCK-SYSTEMS.

	Systems.	Groups.	Periods.	
RANGE OF VOLCANIC ROCKS.	Post-Tertiary (Quaternary)	Now being formed (<i>cement clay, silt, fluvialite and alluvial clays and sand</i>)	Cainozoic or Tertiary.	
	Tertiary . . .	Recent (<i>brick earths, sand</i>) Pleistocene (<i>brick earths, boulder clay, sand</i>) Pliocene } (<i>brick earths, sand, pottery, and ball clays</i>) Miocene } Oligocene } Eocene (<i>brick clay and sand</i>)		
RANGE OF TRAPPEAN ROCKS.	Cretaceous . . .	Chalk (<i>cement clays</i>) Greensand (<i>brick clays, sand</i>) Wealden	Mesozoic or Secondary.	
	Oolitic (Jurassic)	Oolite } (<i>brick clays, sand</i>) Lias }		
	Triassic . . .	Rhætic shales and marls Saliferous marls (<i>brick clays</i>) Upper New Red Sandstone (<i>sand</i>)		
	Permian . . .	Magnesian limestone Red marls (<i>brick clays</i>) Lower New Red Sandstone		
	Carboniferous	Coal-measures (<i>brick clays, fireclays</i>) Millstone-grit (<i>ganister</i>) Mountain limestone		
		Yellow sandstones		
	Old Red Sandstone (Devonian)	Fossiliferous limestones and slaty shales (<i>brick clays and slates</i>) Red conglomerates, sandstones, and cornstones.		Palæozoic or Primary.
		Grey sandstones, flags, and conglomerates		
	Silurian . . .	Upper shales and limestones (Ludlow and Wenlock)		} (<i>slates</i>)
		Lower grits and flags (Llandovery and Caradoc)		
Ordovician . . .	Sandstones and slates	} (<i>slates</i>)		
Cambrian . . .	Upper slates and flags (Tremadoc) Lower slates and grits (Harlech and Llanberis)			
Pre-Cambrian . . .	Upper series of schists and serpentines	}		
	Lower series of quartzites and schists			
Metamorphic . . .	Clay-slate	}		
	Mica schist and quartzites			
Igneous . . .	Gneiss and granitoid schists	} Azoic or Hypozoic.		
	Granites, etc. (<i>china clays</i>)			

CHAPTER IV.

THE CLAY-FORMING PORTIONS OF SEDIMENTARY ROCKS.

THE various changes just described have produced so complex a mass of material that its separation into its different constituents is a matter of serious difficulty. Although, in all probability, the sedimentary rocks were formed in the order shown on p. 46, they are occasionally found in quite different relative positions, the oldest rocks lying above the more recent, and frequently arranged side by side, like books on a library shelf, instead of beneath each other, as originally produced.

This "rearrangement" has been brought about by earth-movements as already described, and the effect of the weather, rivers, etc., on the rocks so placed has been to produce a large number of "clays," sands, and other minerals of the most varied composition and characters imaginable.

Where the variety and complexity of composition is so great, a really satisfactory arrangement is almost unattainable, and in the following notes the various rocks are mentioned in the order of their formation, as given in Chap. III., commencing with the lowest and oldest.

METAMORPHIC ROCKS.—These are the oldest of the sedimentary rocks, and have been so changed in character that any fossils which may have been originally present in them have been destroyed, hence the term "metamorphic" is used in a broad sense to include all rocks which have undergone important constitutional changes, and in a narrower sense as implying those rocks which are obviously sedimentary, but to which it is impossible to assign any definite place, owing to the absence of fossil remains.

The metamorphic rocks have a generally crystalline structure, and the hypogenic and epigenic changes (p. 21) which they have undergone are so great that it is now impossible to say

which were originally strata of clay, which of sand, or which of gravel.

The chief metamorphic rocks are the crystalline schists, such as gneiss, mica-schist, quartzite, and clay-slate, which have been produced by the action of pressure and heat (probably in the presence of superheated steam and other vapours) on clays and other minerals formed by the action of weather, etc., on the primary, igneous rocks. The *argillaceous rocks* have been metamorphosed into schists and slates; the *sands* have been converted into quartzite rocks.

They are found associated with later igneous rocks (containing hornblende and hypersthene) such as syenite, porphyry, etc., which break through them in a most irregular manner.

The gneiss and mica-schists occur chiefly in the Highlands and Hebrides of Scotland and in North and South Ireland.

Gneiss is an aggregate of felspar, quartz, and mica. On weathering it produces a variety of china clay mixed with undecomposed quartz and mica. The clay is not found in sufficient quantities to pay for extraction from the mixture, but it is important as a source from which rain and rivers obtain clay which is afterwards deposited as described in Chap. V.

Schist is a term applied to crystalline rocks which are laminated and fissile, so that a schist may be regarded as a crystalline shale. It is generally employed in connection with the main constituent; thus **mica-schist** is an aggregate of mica and quartz, **talc-schist** of talc and quartz, **hornblende-schist** of hornblende with some quartz. The only schists which form clay are those containing hornblende or felspar.

Quartzite is a granular aggregate of quartz, formed by pressure and heat from the quartz derived from the primary igneous rocks. Being entirely siliceous, it does not form true clay, though it is often found in clay deposits. (*See* Chap. IX.)

Under the term **Dinas clay**, a quartzite found in the Vale of Neath, it is much used for the manufacture of fire-bricks. The term "clay" is, however, quite inapplicable to this material, which is a comparatively pure silica.

Clay slate appears to have been formed by the action of heat, pressure, etc., on the clay washed out of the primary igneous rocks (p. 2), together with some of the finest particles of mica and quartz. On weathering, clay slate again forms clay, but as it is very resistant, the amount of clay thus formed is too insignificant to be treated separately, though it adds its quota to the many other clay-forming rocks. The clay-slates are chiefly found in the Cambrian and Silurian districts (*q.v.*).

The **PRE-CAMBRIAN ROCKS** form nearly the whole of the Outer Hebrides, and occupy a belt of variable width in the west of Sutherlandshire and Ross-shire in Scotland, Donegal, Londonderry, Mayo, and Galway in Ireland, and irregular areas in Pembrokehire, Anglesea, Caernarvon, and the Midlands.

They consist of massive hornblendic gneiss with bands of schist, felsite, etc.

The **CAMBRIAN ROCKS** are chiefly found in West Wales and are almost entirely formed of slates, sandstones, and siliceous grits, with frequent dykes containing granite, porphyry, and other igneous rocks. The slates and igneous rocks, on weathering, form clay, though in small quantities relatively to other accessory minerals, and the Cambrian rocks are therefore of small importance to the clayworker, though valuable as a source of slate.

Grauwacke rocks—slaty grits—were at one time supposed to form a series intermediate between the Cambrian and Silurian rocks, but the term is now seldom employed (*see* p. 13).

The **ORDOVICIAN ROCKS**—sandstones and slates—attain their chief development in Central and West Wales and in Co. Tipperary, Ireland, several famous slate quarries being in them, especially near Blaenau Festiniog (*see* Table III.).

SILURIAN ROCKS.—Unlike the Metamorphic and Cambrian rocks, the Silurian deposits are clearly stratified, beds of shaly mudstone, clay, and limestone being so distinct as to show the clearest evidence of their formation.

The sandstones are often finely laminated, showing deposition in still water; others have evidently been deposited in slow-flowing streams, or in tidal seas and rivers, as they show ripple-marks; whilst others again are so mixed with pebbles as to form conglomerates.

Silurian clays and shales have shown a similar variety of origin, some having formed a deposit of fairly pure black clay, whilst others contain a large proportion of sand, or of sand and lime—this latter from the shells.

The whole of the Silurian rocks may be said to be composed of dark, slaty shales, calcareous shales, flagstones, sandstones, and clayey limestones; those in England being somewhat more shaly and richer in lime than those of Scotland, which are more sandy and resemble those on the east coast of Ireland in containing anthracite. The Silurian shales are chiefly found on the borders of Wales, in the north-west of Hereford and West Shropshire, including the Malvern Hills, in the south of Scotland, the north of Ireland, and in Cumberland, Westmorland, and north-west Lancashire. They comprise so large a variety of stones that

any general description of them must necessarily be deficient in detail, but the following list gives their chief characters:—

TABLE III.

Upper Silurian.

Ludlow series.	{	Finely laminated, reddish and greenish sandstones, known as "Tilestones." (In part, base of old red sandstone.) Micaceous grey sandstone in beds of various thickness. Argillaceous limestone (Aymestry limestone). Shale with concretions of limestone (Lower Ludlow).
Wenlock series.	{	Concretionary limestone (Wenlock limestone). Argillaceous shale in thick beds (Wenlock shale). Shelly limestone and sandstone (Woolhope and Mayhill). Gritty sandstones and shales (Upper Llandovery).

Lower Silurian or Ordovician.

Llandeilo series.	{	Grits and sandy shales (Lower Llandovery). Thick-bedded whitish freestone (Caradoc sandstone). Dark calcareous flags and slates (Bala beds). Slaty flags and bands of limestone (Llandeilo flags). Slates, flags, and shales (Arenig beds).
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In many places the Silurian rocks have been metamorphosed by igneous rocks which have been formed about the same time, or later, whereby shales have been converted into slates, sands into quartzite, and clays into crystalline hornstones.

Their industrial value is small, but on weathering they form beds of clay and marl which are often of great importance; their precise value depending on the agents causing their deposition.

OLD RED SANDSTONE and DEVONIAN.—The rocks comprised in these terms consist chiefly of sandstones, flagstones, and pebbly conglomerates in the former, and limestones and shales in the latter; but each of the two terms is often used to express the whole group of rocks formed after the Silurian and before the Carboniferous period, though it is better to apply the term Devonian to the special formations of rocks in Devonshire containing marine fossils.

The shales are often termed **marls**, but this term is unsuitable, as they contain no lime compounds. They form the lowest part of the series and are mostly red, with paler bands, and are often badly contaminated with limestone pebbles (**cornstones**).

The chief Old Red Sandstone deposits are the Ochils and Sidlaw Hills, Moray, Caithness, and Ross, with a large belt skirting the Grampians from Stonehaven and the Firth of Tay to the Firth

of Clyde in Scotland, and the hills of Hereford, Monmouth, and Brecknock (Wye and Severn Valleys); the formation occurring in irregular patches from Wales to the north of Scotland.

The south-west of Devon (between Dartmoor and the South Coast) is typically "Devonian."

This formation occurs in a number of small, isolated areas, as at Sedbergh, Strickland in Westmorland, Haycot and Clun in Shropshire, and Presteign in Herefordshire.

Much larger areas occur between Bridgnorth and Ludlow, and practically the whole of Cornwall, Herefordshire, and Monmouthshire, and the west of Worcestershire and Somerset are of this formation, as is the district for some miles around Brecknock and extending almost due west from that town to St Ann's Head and from Abergavenny due south to Cardiff. Red-burning marl of this formation, which is valuable for brickmaking, is much used at Maindy and Whitchurch near Cardiff and all round Newport (Mon.), and may be taken as typical of the best "marls" of this period. It is purple to deep red in colour, and often contains sandstones and nodules of limestone (termed **Cornstones**) which must be removed before the marl can be used.

The chief igneous rocks associated with this series are felstone, porphyry, and other felspathic traps, which occur very irregularly as upheaved masses and dykes.

The bulk of the Old Red Sandstone forms sand on weathering, though the so-called marls are much used by clayworkers.

The **CARBONIFEROUS ROCKS** are clearly distinguished by the abundance of their vegetable remains. They are divided into four well-defined groups: (1) Mountain Limestone; (2) Millstone Grit; (3) Lower Coal Measures; and (4) Upper or true Coal Measures, though all of these are not always present.

Omitting the limestone as being almost free from clay, these rocks present a great variety of composition and include sandstones of many kinds, shales of all degrees of hardness, from soft, laminated clays to dark slaty flags and vegetable matter decayed through all stages to coal. Limestone and ironstone are also abundant. In short, the Carboniferous rocks consist of strata of sandstones, shales (including oil-shales), fireclays, limestones, coals, and ironstone; layers of similar material being repeated at irregular intervals.

They occur in an available form in Central Scotland, in Northern and Central England, in Wales, Ireland, and in other parts of Great Britain, and their structure and arrangement point to the conclusion that their formation is the result of the action of weathering on earlier rocks and the transportation of these

weathered materials by rivers, lakes, and seas. The "soil" thus formed proved fertile, and the trees, etc., which flourished in it, at a later stage formed coal and other bituminous products.

The shales found in the **Carboniferous Limestone** are of no importance to clayworkers.

The **Millstone Grit** is a typical hard quartzose sandstone alternating with shales which constitutes the lower bed of the Coal Measures and so is known to colliers as the "farewell rock." Where it is not so covered it usually forms narrow areas immediately around the great coalfields of Wales, Yorkshire, Derbyshire, the West of England and on the edge of Northumberland and Durham, though small areas of it are distributed irregularly some distance away. Thus to the south of Hexham and Haltwhistle in Northumberland are several such isolated areas, whilst numerous others occur to the north-east of Sedburgh. From Lancaster to Settle and Garstang is a large Millstone Grit area. A large tract of Millstone Grit also occurs in West Devon, extending from Barnstaple to Tavistock and from Bampton to the Bristol Channel. The softer and purer portions are used in the manufacture of silica bricks.

The **Lower Coal Measures** consist chiefly of argillaceous shales, sandstones, coals and grits, or of white sandstones and dark oily shales (as in the Scottish Lothians). They are apparently of fluviatile or lacustrine formation, though there is occasional evidence of marine deposits and of admixture with igneous rocks which have been brought to them by the action of flowing water.

The sandstones may be very coarse and loose, or fine and compact, as in **Ganister**.

The **Middle Coal Measures** consist of grey shales and sandstone with seams of coal, fireclay, and ironstone. The greatest thickness is in North Staffs. Some of the sandstones are red.

The **Upper Coal Measures** are composed of sandstone grits; fireclays and bituminous shales are also abundant, and seams of ironstone, coal, and limestone frequently occur in them.

The shales are usually dark in colour and contain a certain amount of carbonaceous matter—those rich in this material being known as **oil shales** (see Chap. VI.), whilst those rich in pyrites (termed **alum-shales**) are sometimes used for the production of sulphuric acid. (See Chap. VI.).

Some parts of the Coal Measures do not show a shaly or laminated structure; these are sometimes highly plastic clays, often little more than slightly compressed mud. Refractory clays (fireclays) are found immediately below the coal seams.

The clays and shales of the Coal Measures are known by a

variety of local names, such as "clunch," "bratt," and "sklutt," but, unfortunately, these terms have different meanings in different districts, and their use is, consequently, very misleading.

The greatly prized clays of the Coal Measures occur in about a dozen well-defined areas or coalfields. That in Scotland is the most irregular, being broken into areas extending (1) from Kilwinning to the river Nith (Kilmarnock area); (2) north, east and south of Glasgow to Barrhead, Motherwell, Alloa, and Culross; (3) between Dysart and Leven; and (4) near Edinburgh.

The Irish Coal Measure clays are worked in Tyrone.

The Northumberland and Durham Coalfield extends from Coquet Island along the coast to South Shields, thence west of Houghton-le-Spring to Ferry Hill, Bishop Auckland, and Barnard Castle.

The Cumberland Coalfield extends four miles south of Wigton to Maryport along the coast to near St Bees Head; Workington and Whitehaven being the most important places in this district.

The Yorkshire, Derbyshire, and Notts Coalfield is comprised within an area obtained by drawing straight lines between Wilsden or Bingley, Halifax, Huddersfield, Penistone, Ambergate, Stapleford in Notts, Shireoaks, Pontefract, Church Garforth, and Baildon, near Bradford. It is, however, extremely probable that the eastern boundary of this area should be extended into Lincolnshire, where it is buried beneath Permian and Triassic rocks.

The Lancashire Coalfield is roughly triangular in shape and extends from Colne to Huyton on the south-west and to Stockport on the south-east, with a narrower area extending to Macclesfield and east to Chapel-Frith. Between Bury and Blackburn, however, there is an area of 50 square miles of Millstone Grit quite devoid of coal.

On the left bank of the river Dee—from Mostyn to Hapwarden and thence south to Oswestry—is an important Coal Measure area with several outliers on its north-western extremity. To the clayworker Wrexham is the most important town in this district.

The Leicester Coalfield extends from the north of Swadlincote to Normanton, but its most important area is around Ashby de la Zouch.

The North Staffordshire or Potteries Coalfield extends from Congleton to Longton and almost to Stone, its western extremity being Madeley and its eastern one Oakmoor.

The South Staffordshire Coalfield extends due south from Armitage to Walsall and thence to Hales Owen, with Wolverhampton just beyond its western boundary, and Stourbridge just outside its south-western one.

The Shropshire Coalfield extends from Dorrington, almost due south, to Bewdley and Stockton in Worcestershire. Broseley and Iron Bridge form the chief clayworking centres in this area.

The Shropshire Coal Measures are famous for their tile clays. These are mined as a hard rocky mass, which requires blasting, but the lumps soon fall to pieces on exposure to the weather. The Broseley *brick clay*, which occurs as a stratum 8 to 12 feet thick, lies uppermost, and is remarkable for its low shrinkage (under 2 per cent.). The famous red Broseley *tile clay* occurs as a 7-foot stratum interspersed with a grey clay. A Red marl in the same district, but of a different composition and of much greater shrinkage, occurs as a 5-foot stratum about thirty yards above the "sulphur coal"; it is used for the manufacture of encaustic tiles.

In Gloucestershire there are two coalfields, one covering the greater part of the Forest of Dean and the other extending from Wickwar to rather south of Bristol, with three small areas to the south at Chew Magna and Poulton.

The South Wales Coalfield is also in two sections, of which the main one extends from Kidwelly to Pontypool in a direction roughly parallel to the coast, with Tredegar as its most northerly point and Bishopton as its most southerly.

The smaller coalfield—which is chiefly anthracitic—extends due east from St Bride's Bay to Caermarthen Bay.

Taken as a whole, the Carboniferous system is utilised more than any other in this country for obtaining high-class earths for brick and tile-making. The under-clays of the Coal Measures yield excellent material for the manufacture of fire-bricks; the well-known "Staffordshire Blues" are also manufactured from this horizon. Clay and ganister for the lining of furnaces, the magnificent clays of Shropshire used, as at Broseley, for making ornamental tiles, the fireclay goods of Yorkshire and of the neighbourhoods of Newcastle and Glasgow, all come from the innumerable horizons of Carboniferous age.

The Coal Measure clays are of two types: (1) shales, and (2) underclays.

The **Shales** of the Coal Measures constitute the bulk of the deposit. They are essentially siliceous clays which have been laminated by bedding. Their normal colour is grey, but on the outcrop they are often brown or yellow, due to oxidation of the contained iron salts. They range from smooth clays to hard sandstones, and are much used for the manufacture of bricks, tiles, coarse pottery, refractory goods, and sanitary ware. Unlike the underclays, these shales have been deposited in definite

layers; they are apparently derived from the waste of granitic rocks.

Underclays, also known as **Seat-earth**, **Spavin**, and **Warrant**, lie immediately beneath the coal seams. They vary greatly in composition, from an aluminous clay to a siliceous rock (**ganister**), and are generally thought to be the old soils in which the plants grew which later formed the coal seams, or else a marine estuarine ooze which has been repeatedly shifted and re-sorted. They are devoid of bedding, and have not the fissile character of the shales above them. The upper portions of the underclays are usually more tender than the lower ones.

In the Leeds district, the "Better-bed underclays" take the highest rank, the underclays of the Black Bed, which is nearer the surface, being an inferior fireclay.

"The Halifax Hard-bed" clay lies at a lower level than the "Better-bed" coal. Near the outcrop it is rather tender, and is chiefly used for the preparation of slips. The Shipley (Bradford) clay from the same bed is more aluminous, but its refractory nature is often lowered by an increased percentage of iron. (*See* "Fireclays" in Chap. VI.).

The coalfields in Northumberland and Durham are remarkable for the quality of their brick earths, though but little has been published on the fireclays in spite of their extensive use. The more plastic clays have been used for white and brown earthenware since 1730, many potteries formerly existing on Tyneside and Wearside, but the number is now much reduced.

By mixing the shales from various beds together in definite proportions, a wide variety of articles may be produced. Most of the northern fireclays are much improved by weathering.

In the Upper Coal Measures in North Staffordshire is an important series of clays known as the **Etruria marls**. They are chiefly worked by quarrying on the outcrops, care being taken to discard the beds of gritstone which frequently alternate with the clays. To remove these stony layers and the harder portions of the clay, blasting is employed. These "marls" are 800 to 1000 feet thick, and lie immediately below the Newcastle shales, which are 300 to 500 feet thick, but are of much less importance, and above the Black Band series from which the coal is obtained. There are, however, many outcrops, and it is at these that the chief workings are found.

The characteristics of the Etruria marls are more fully described in Chap. VI. ("marls"). They are chiefly red, purple, or mottled, fine-grained, compact, and usually without lamination. The chief impurities are nodular ironstone and limestone layers.

As their name implies, these clays are specially developed round Etruria (Staffs); they run continuously towards Longport. They are also worked at Chesterton, Blurton, Hanford, Trent Vale, Springfield, Fenton, Newcastle-under-Lyme, Madeley Heath, Downing, High Carr, Silverdale, Ridge Hill, south-east of Andley and Crackley, and at several other less important points.

Important workings of the *Black Band* series in Staffordshire are at Hanley, Shelton, Cobridge, Hammel, and near Burslem station. They contain a considerable number of different "marls," and these vary greatly in character in various places, so that very careful selection is necessary if the clays are to be used successfully. The Newcastle (Staffs) series is more shaly.

The *Keele* series are not much used for clayworking in Staffordshire, but there is evidence that these are the principal brick-earths near Ruabon. The Buckley and Ruabon clays have been shown by Dr Gibson to correspond exactly to the Etruria marls, the Newcastle beds, and the Keele series of Staffordshire, though the maps of the Geological Survey do not show this clearly.

This uniformity of character throughout the Midland Coal Measures explains the great similarity of the clay products of Denbighshire, Flintshire, and Staffordshire.

Geologically the Ruabon and Buckley clays are identical in age, though the former may be slightly younger. The Penybont clay worked by Mr J. C. Edwards corresponds to the Keele series. In both districts local variations in the composition of the beds are frequent, and the digging must be carefully supervised, so that the clays may be properly blended, many distinctly recognizable grades being present. For this reason, single analyses of the Ruabon and Buckley clays convey no practical idea of the composition of the beds.

The red-burning clays of this district are famous for the quality of terra-cotta produced from them; the fireclays are equally well known, though, with the exception of specially selected deposits, they are noted for their resistance to acids (making them valuable for chemical works) rather than for their high refractoriness. Owing to the numerous faults and the great variations in the character of these clays, any more detailed description of them could only relate to so small an area as to be of no general interest.

The Coal Measure fireclays of Wales, particularly in the Ebbw Vale district, are highly siliceous, but vary so much in composition that exceptional care in blending is requisite. The "Hard Vein" clay of this series is used for the manufacture of sanitary

ware, sewer pipes, and firebricks; the "Brass Vein" clay for terra-cotta, bricks, and tiles.

The Coal Measure clays of Somerset and Gloucestershire have not been used at all extensively, in spite of their suitability for high-class bricks and firebricks of fair quality and the fact that they are sufficiently rich in bituminous matter to be cheaply burned. This is partly due to the excellent red-burning clays in Somerset, but in any case it is unsatisfactory to have large heaps of good fireclay lying idle.

The **PERMIAN ROCKS** comprise part of the New Red Sandstone and the magnesian limestone formations; but conglomerates, marls, and slates are also abundantly found in them. Their distribution is not well defined, except in North and Central England, East Durham, Central Yorkshire, Nottingham, and Shrewsbury, where the magnesian limestone is prominent, and the formation runs in an almost straight line from Tynemouth to Nottingham.

The **Permian Sandstones** are very irregularly distributed. A somewhat important area occurs in South Cumberland, and extends from Wreay to Penrith, Appleby, and Kirkby Stephen. A narrow strip runs irregularly along the eastern edge of the Durham coalfield from South Shields to Shincliffe. A small area occurs near Thornton in Yorkshire, another near Clitheroe, and various irregular strips near Leigh (Lancs) north and east of Manchester, and extending through Stockport to the Macclesfield Canal.

Numerous irregular and small areas occur in Shropshire, notably (1) around Shrewsbury, (2) north of Oswestry to Gresford, (3) south of Newport to near Kidderminster, and (4) east of Market Drayton. Similar irregularly-shaped areas lie around the South Staffordshire coalfield, particularly between Shareshill, Wolverhampton, Stourbridge, Lickey Hill, and West Bromwich.

A relatively large area extends from Kenilworth to near Atherstone, with unimportant outliers to the north and west.

The southernmost area of Permian sandstone extends irregularly from Nether Stowey in Somerset through Tiverton and Exeter to Torquay, with a westward branch from Silverton to Exbourne.

They consist chiefly of reddish sandstone, of mottled purple, yellow, green, and brown shales, of magnesian limestone, and of calcareous flagstones. When clays occur, they are usually loamy in character, but only the uppermost and the lowermost beds are valuable to the clayworker, and these are of minor importance.

The chief materials composing the Permian series are shown in Table IV., which is based on the assumption of Phillips, that all red sandstones, marls, and magnesian limestone usually grouped under "New Red Sandstone Series" are one formation.

TABLE IV.

Permian.

Palæozoic.	}	Magnesian limestone.	Red and white marls. Laminated limestone, with layers of coloured marls as at Knottingley, Doncaster, etc. Gypseous marls—red, bluish, and mottled. Thin-bedded compact limestone, with very little magnesia and few organic remains. Marl-slate in thin layers, frequently enclosing fishes. Laminated, impure, calcareous flagstones of soft argillaceous or sandy nature. Magnesian limestone :—Yellowish and whitish ; of various texture and structure ; some parts as in Durham, curiously concretionary and crystalline, in others soft and earthy, and in others impregnated with bitumen.
		Yellow or purple sand, and sandstone and marl.	An extremely variable series of sandstones, sands, and clays of various colours, irregular thickness, and much local diversity of character. Plants like those of the Coal Measures.

The Permian "marls" are really shales in a friable and but slightly laminated state. They often contain gypsum and salt, and weather to a reddish clay which, with the weathered sandstone and limestone, forms a red loam characteristic of the Permian rocks.

The red clay used at Bulwell, near Nottingham, for the manufacture of flower-pots, bricks, etc., is of Permian origin. Like most Permian clays it has a high shrinkage and so requires considerable manipulative skill in the manufacture of articles from it.

The **TRIASSIC ROCKS** were at one time grouped along with the Permian ones under the general title of "New Red Sandstones," but they now form a separate group. They are termed "Triassic" because in Germany this formation consists of three well-marked subdivisions—the Keuper beds, the Muschelkalk beds, and the Bunter series, but the Muschelkalk is not found in Great Britain. For this reason the older term—New Red Sandstone—which is still largely retained in England, is in some respects preferable, though it disregards the very important clays in this formation.

These rocks in Great Britain may be grouped as follows :—

TABLE V.

Triassic.

1. Rhætic	{	Red, green, and grey marls, shale, and "white Lias."
2. Upper Trias Keuper	or {	Saliferous and gypseous marls (New Red marls), red and grey shales, and grey and whitish sandstone.
3. Bunter sandstone	{	Various coloured (mottled) sandstones, dolomites, red clays, occasional pisolites, and quartzose conglomerates with red clays.

Both the Bunter and Keuper series indicate sea and desert conditions, with much wind-drifted material.

The **Rhætic beds** follow the upper limit of the Keuper marls (*i.e.* between Trias and Lias). They comprise grey marls, black shales, and white Lias, and are most developed east of Taunton and in Polden Hills at Sedgemoor. The Somersetshire Rhætic beds, formed of black shales and white Lias, lie under the lower or blue Lias, which is extensively quarried for stone, lime, and cement. They consist of thin bedded shales, clays, and sandstones of little value to the clay worker.

The Rhætic or Penarth beds are too irregular and uncertain to be valuable to the clayworker. They are usually rich in pyrites and organic matter, and, once started, may burn for many hours.

The **Keuper marls** or **New Red marls**, which is the most important clay-bearing portion of the Triassic formation, attained a thickness of 3000 feet in Lancashire and West Cheshire, but diminished rapidly toward the south-east. The finer portions and those richest in clay are in the southern half of the deposit, the northern portion being coarser and more siliceous. The Keuper marls are chiefly found in Cheshire, but occur in patches on the west coast of Scotland and the east coast of Ireland, in the Solway basin and down towards the Mersey, where they merge into "that broad belt of red sediments which stretches diagonally across the whole country from Durham to South Devon."

On weathering, the Triassic rocks form a light sand, but more usually a stiff clay loam, and extensive morasses occur in South Lancashire.

The Trias rocks of this country yield earths that are highly prized by the brickmaker. The Red marl of the Midlands is the principal horizon for this purpose. This, as the name implies, is

composed of clay and lime; it frequently is so hard as to require to be blasted.

The uppermost division—the Red Marl—is 3000 feet thick in Lancashire and West Cheshire, 800 feet in Staffordshire, and 700 feet in Leicestershire and Warwickshire.

The Keuper marls extend with some interruptions across the country from Axmouth and Sidmouth to the mouth of the Tees. They form vales of red material in the south and west of England, the Vale of Taunton, and to the east of the Malvern range. A very large clay area of this formation extends over the eastern half of Nottinghamshire, north and north-east from Trent Junction to Southwell and Newark and the west of Lincolnshire, forming a narrow strip near Scunthorpe (which rapidly widens as the borders of Nottinghamshire are approached), and reaching into Derbyshire, Staffordshire, and Leicestershire.

The Isle of Axholme (Lincs) is composed almost entirely of Upper Trias. The Western Upper Trias is included in an area bounded by lines joining the following places: Nottingham, Derby, Ashbourne, Market Drayton, Wolverhampton, Stafford, Lichfield, Tamworth, Birmingham, Bromsgrove, Hagley, Abberley Hill, Newent, Newnham, Tewkesbury, Droitwich, Alcester, Stratford-on-Avon, Lutterworth, and Leicester.

Keuper marls also occur at Wem and Whitchurch in Shropshire, but are extensively covered with gravel and boulder clay. They occupy a large area in Worcestershire, Warwickshire (where they are succeeded by badly-exposed Rhætic beds), the western half of Leicestershire, particularly around Market Bosworth, Hinckley, and eastwards to Leicester, the fringe being at Loughborough and Quorn. In Lincolnshire the Red marls eastward of the river Humber form the base of the low escarpment of the Lias from Burton on Humber to Gainsborough and further south. Red marls of Old Red Sandstone occur in Monmouthshire, and above this, but below the Lias, are Rhætic beds of black shales. In Staffordshire the Keuper marls are often rich in gypsum, especially at Uttoxeter, Fauld, and Tutbury. Much of the red marl is unworkable, however, for clayworkers' purposes by reason of its containing a high percentage of salt, particularly in Cheshire.

The uppermost portion of the Keuper beds—the Red marls—is widely distributed; it can be traced from the coast of Lancashire to the Bristol Channel, and covers a larger area in the Midlands than the rest of the Trias and the whole of the Permian sandstones combined. It also occurs at Budleigh Salterton in the south of Devonshire. Keuper marls are largely of a clayey

nature, but contain thin beds of sandstone and veins and nodules of gypsum. In some districts they consist of sandstones with only irregular layers of clay, so that the formation as a whole is sometimes valuable to the brickmaker, but frequently quite useless, and great caution is required. They often contain common salt, the beds of which are sometimes enormously thick. Gypsum is also found frequently in thin layers and in thicker beds. These impurities cause a whitish scum on articles made from the clay containing them.

The Triassic (Keuper) marls in the Midlands and Cheshire—sometimes known as “New Red” marl—are the most extensive, and are practically all capable of being made into bricks, coarse pottery, etc. (when sufficiently free from salt), but in South Wales they so constantly give place to conglomerate as to be useless for this purpose. Thus in the neighbourhood of Cardiff (where they overlie the Old Red marls) they are difficult to use on account of their conglomerate nature, but if carefully selected and well mixed they make satisfactory bricks.

In Somerset the Keuper marls are much appreciated by brick and tile manufacturers.

The **Bunter** formation, or Lower Trias, is usually divisible into an upper red sandstone, a middle bed of conglomerate, and a lower bed of sandstone. One large tract of this formation extends from Annan in Scotland to Longtown and Brampton, thence southwards to Brough in Westmorland. This formation also extends along the coast from St Bees to Morecambe Bay, West Hartlepool, and Darlington, across the Tees to Northallerton and somewhat south of Ripon, where it is divided by more recent deposits, but covers an area west and south of York and, in an irregular manner, the districts west of Selby and Snaith.

Between Thorne, Doncaster, and Bawtry, and southwards to Nottingham, the Triassic area is broad and important, Retford forming its most easterly boundary and Mansfield its most western one. The Triassic areas in Derbyshire and Staffordshire are irregular—a small one at Morley, and another extending from Repton-on-Trent, through Church Gresley to Nether Seal in Leicestershire.

The banks of the river Trent present many good sections of these strata, as at the junction of the rivers Trent and Soar, where they are pierced by the Red Hill tunnel, on the line of the Midland Railway; and at Radcliff-on-Trent, where they form picturesque cliffs of a red colour covered with hanging wood; and they are exposed to view in many places in the immediate vicinity of Nottingham, as in the cutting for the old road over Ruddington

Hill, in the Colwick cutting of the Nottingham and Lincoln Railway, and Goose Wong Road, leading to Mapperly Plains.

The brickmakers of Nottingham and its immediate vicinity derive their supplies of brick-earth from the strata of red marl overlying the red sandstone on which the town is built, which in its turn rests on the Coal Measures. This marl abounds with loose and thin layers of *skerry*, or impure limestone, and in many places contains veins of gypsum, or, as it is called, *plaster stone*, which are extensively worked near Newark, and other places, for the manufacture of plaster of Paris.

The water from the wells dug in these strata is strongly impregnated with lime compounds.

The colour of the bricks made at Nottingham and in the neighbourhood is very varied. For making red facing bricks the clay is selected with great care, and only certain beds are used; from these beds excellent coloured wares are made. For common bricks the earth is taken as it comes, and the colour is often irregular and unsatisfactory, varying from a dull red to a dirty straw colour. Some of the marls burn of a creamy white tint, and have been lately used with much success in making ornamental copings and other white ware.

A larger area extends from Keddleston to Ashbourne, others around Longton, Whitmore, and Leek being equally significant.

The Triassic area west of the Potteries Coalfield, though nominally in Staffordshire, is really a portion of the large area extending across the northern half of Shropshire and extending southwards to Quatford and northwards to the borders of Cheshire.

A large area of Lower Trias extends from the Mersey (New Brighton and Warrington) through Chester to Ellesmere in Flintshire. A branch of this lies between Rhyddlan and Ruthin. A much extended and irregular area reaches along the west of Lancashire from Cockerham through Preston and Ormskirk to Liverpool, east to Warrington and Manchester, and south to Macclesfield. A large area extends from Stafford to Wolverhampton, Stourbridge, and Stourport, and another from Lichfield to Birmingham, with a small district around Lickey Hill between these two areas.

The **JURASSIC ROCKS** comprise the Lias, the Oolite, and the Purbeck formations, the former being of marine origin and the latter mainly lacustrine or estuarine. The Jurassic system includes a great variety of limestones, sandstones, marls, shales, and clays lying between the New Red Sandstone and the chalk, the Lias forming the lowest group and the Purbeck the upper one.

The outcrops of the clays can be traced in the wide valleys; the limestone composes the low hills and escarpments along the line of strike. They may be arranged thus:—

TABLE VI.

Jurassic.

OOLITE . . .	{	<p><i>Purbeck Beds</i>.—Estuary limestones alternating with sands and clays (formerly grouped with the Wealden).</p> <p><i>Upper Oolite</i>.—Coarse and fine-grained oolitic limestones, with layers of calcareous sand and concretions (<i>Portland stone and Shotover sand</i>); dark laminated clays, with gypsum and bituminous shale (<i>Kimeridge clay</i>).</p> <p><i>Middle Oolite</i>.—Coarse-grained shelly, and coralline oolite, with calcareous sands and grit (<i>Coral-rag</i>); dark-blue clays, with subordinate clayey limestones and bituminous shale (<i>Oxford clay</i>); shelly calcareous grit (<i>Kellaways rock</i>), with subjacent blue clays.</p> <p><i>Lower Oolite</i>.—Coarse, rubbly, and shelly limestones (<i>Cornbrash</i>); laminated shelly limestones and grits (<i>forest marble</i>); sandy layers and thick-bedded blue clay (<i>Bradford clay</i>); thick-bedded oolite, more or less compact and sandy (<i>Bath or great oolite</i>); flaggy grits and oolites (<i>Stonesfield slate</i>); marls and clays, with soft marly limestone (<i>fuller's earth</i>); calcareous freestone, irregularly oolitic, and yellow sand (<i>inferior oolite</i>).</p>
LIAS . . .	{	<p><i>Upper Lias</i>.—Thick beds of dark bituminous shale; beds of pyritous clay and alum shale; indurated marls or marlstone with beds of ironstone.</p> <p><i>Lower Lias</i>.—Dark laminated limestones and clays; bands of ironstone; layers of jet and lignite; beds of calcareous sandstone.</p>

Outbursts of igneous rocks are almost unknown in Jurassic rocks.

The Jurassic formation gives rise to a characteristic type of scenery, the sand and limestones forming long ridges and the clays underlying the level spaces between them. The fossils in it indicate a great number of changes in the earth's crust during the deposition of the rocks of this system.

The **Lias**, as its name implies,¹ is composed of alternating

¹ The word *lias* is a corruption of *layers*.

layers of shales and limestones. It is very extensive in England, as the main mass extends from the Tees *viâ* the Cotswolds to Lyme Regis.

The formation extends along the Yorkshire coast from Robin Hood's Bay to the mouth of the Tees (Redcar), then south-west to Northallerton and south-east *viâ* Thirsk and Pocklington across the Humber and due south through Lincolnshire and East Notts into Leicestershire. In the last-named county the area is much broader—from Leicester to Hambleton in Rutland being the greatest width,—but it narrows again on entering Northamptonshire and Warwickshire, and is much broken up by Trias or obscured by overlying Oolite.

From Warwickshire the Lias extends south *viâ* Banbury to Blethington, and south-west through Cheltenham and Gloucestershire to Bath and Bristol. It narrows down near Dursley, where it runs almost due south into Somersetshire, though in the last-named county it is often rendered inaccessible by alluvium. Here it spreads into numerous isolated areas, but unites again at Glastonbury and extends to the Dorset coast near Bridport and Lyme Regis.

Isolated areas of Lias (usually limestone) occur in several districts; one of the largest extends from Audlem to near Wem (Shropshire), and another, rather smaller, occupies the Welsh coast from St Brides to near Cardiff.

The Lias of the North of Scotland consists in some parts of dark-coloured unctuous clays, in others of greyish black sandstone so fine as to resemble an indurated clay, and in others by beds of black fissile shale alternating with bands of coarse, impure limestone and studded with limestone nodules.

The Lias formations are chiefly of a shallow marine origin, and thin seams of coal are often present—when shales occur. The Lias in East Yorkshire is particularly rich in shales of which alum shale (Chap. VI.) and jet are the most important.¹

The Lias shales near Whitby were also formerly mined for septarian nodules which were made into cement.

The Lias is divisible into three sections, the Upper and Lower Lias being for the most part composed of clay, and the Middle of a calcareous rock known as marlstone, which is used in the manufacture of cement, this industry being extensive in Leicestershire. The Lias clays at various horizons are employed in the manufacture of bricks, tiles, and drain-pipes, the articles for the most part being red. The clays have the disadvantage of being very

¹ For information on the geology of the calcareous rocks of this district, Tate and Blake's *Yorkshire Lias* should be consulted.

variable in composition, even in short distances; some are too calcareous, more especially those which alternate with the limestones in the basement portion of the Lower Lias.

Some of the Lias shales are notorious for the pyrites they contain. This oxidises, forming ferrous and aluminium sulphates (see *Alum Shales*, Chap. VI.), which form scum and discoloration on articles made from these clays.

The dark colour of Lias shales is attributed to lignite or coal derived from Coal Measure cliffs on the edge of the Liassic sea, and eroded during the formation of the Lias deposits.

The **Upper Lias** is mainly composed of clay; it extends, like the others, from Dorset to Yorkshire and the Inner Hebrides. It is particularly exposed near Grantham, and continues to be so further north. The Upper Lias at Lincoln contains a dark blue clay much used for brickmaking.

The Upper Lias clays bordering the Oolitic hills in Rutlandshire have been extensively worked for bricks at Luffenham, Seaton, etc., as they are well exposed in that county.

The Upper Lias, though frequently covered by drift deposits, forms the chief clay for bricks and coarse pottery in Northamptonshire around Wansford, Wallingborough, Brixworth, Moulton, etc.

The accompanying Northampton sand is usually too rich in iron to be used in brickmaking, but is successfully employed at Uppingham, Seaton, and in a few other places.

In Somerset a valuable Upper Lias clay occurs east of Glastonbury.

The Upper Lias is so homogeneous that no further details regarding its composition are necessary.

It is everywhere suited for making good bricks, and, being usually found in the valleys, it offers good facilities as far as carriage is concerned.

The **Middle Lias** is mainly composed of sand and shales overlain with limestone (marlstone). It is often rich in iron ore. The lower portion of the Middle Lias is usually preferable to the upper portion for brickmaking, but the Middle Lias as a whole is inferior to the Upper Lias beds for this purpose.

The **Lower Lias** is chiefly a mass of limestone alternating with clay or shales (Blue Lias), and overlain by other liassic clays and shales. The Lower Lias clays in Northamptonshire are used for brickmaking at Braunston, and were found to be of excellent quality when constructing the tunnels at Kilsby and Catesby; but much of the Lias in Northamptonshire is overlain by limestone and thick beds of blue clay. In Oxfordshire the Lias forms a rich, friable, loamy soil.

Dorset is noted for its development of Lias, particularly between Thorncombe and Lyme Regis. The higher portions are marls and clays; the lower are limestone, which is much used for hydraulic cement. The clays occurring in this district contain too much pyrites to be satisfactory for bricks and pottery.

The most important clays in the Lias formation in South Dorset are stiff clays bordering on marls in some localities, and shaly in others, the shales frequently occurring beneath the others; but they are all difficult to work except by the semi-dry process.

In Somerset the Lower Lias has a particularly prominent outcrop around Shapwick, and a good quality is accessible near Talton. It is brown at the surface and dark blue deeper, and rather stiff. Eastward it is too far below the gravel to be accessible, though the gravel is thinner to the north-east. These Somerset clays require much experience, but beautiful results can be obtained by those possessing the necessary skill.

Around Frome the Lias is associated with Bradford clay (p. 73) and a variety of other brick earths, marls, and sands, so that this district has for many years been very popular amongst brick-makers.

The Lower Lias clay is also important around Hinton Blewet (Glos).

Around Cardiff the Lower Lias shales and clays are also extensive, but are not much used.

In some districts the Lower Lias is of so shaly a character that it must be worked like the clunches and shales of the Coal Measures.

The clays of the Lias formation have yielded excellent clay goods from time immemorial. Bricks, tiles, drain-pipes, flower-pots, and chimney-pots are amongst the chief products. The clays are almost everywhere fairly stiff, but do not yield much water, nor do they shrink much in the kiln, in spite of their fatness. This is not so remarkable as might be supposed, as nearly all the goods made are red, the temperature to which the clay is subjected not being high enough to cause much yellowness except at certain places to be hereafter noticed. The chief reason for the comparative non-contraction is perhaps the presence of the lime, which in greater or less quantity is practically ubiquitous in the formation. When subjected to a sufficiently high temperature, this lime acts as a flux to the siliceous sand grains found sparingly in the clay, and tends to greater toughness and uniformity. In certain localities, as, for instance, at Rugby, the clays and shales contain about 30 per cent. of calcium carbonate, and are not

particularly suitable for brick manufacture, though in the same district, not far off, as at Hill Moreton, the Lias clays furnish a good class of brick.

Again, in certain localities the clay contains "race" and plenty of shells, which, on being burned, by the liberation of the carbonic acid gas, cause the bricks to blow, and the latter are then always unsatisfactory. Speaking generally, however, the Lias clays are amongst the best in the country for supplying good all-round clay goods, including excellent bricks.

They are much valued for their non-absorption. Care should be taken to avoid those Lias deposits which are rich in selenite. This material only exists in certain localities.

There is hardly any part of this formation that is not of use to the clayworker; it consists throughout of clays, except the Middle Lias, which is more calcareous and yields excellent hydraulic limes and cements.

The Lias clays vary in quality in different districts.

The **OOLITE ROCKS**¹ consist of limestones, grits, conglomerates, sands, and clays, the last-named frequently containing lime, but constituting some of the most important clay deposits in the country.

They usually consist of variegated blue, green, yellow, and purplish clays, often containing bands of irregular whitish or pale-green nodules of lime compounds and ironstone.

They form a broad belt above the Lias from Dorset to Yorkshire, and may be arranged as follows:—

TABLE VII.

Oolite.¹

UPPER OOLITE (of Purbeck, Portland, Wilts, Bucks, Berks, etc.).	{	<i>Purbeck Beds.</i> —Blue clays and laminated limestones, exhibiting, according to E. Forbes, alternations of fresh-water and estuary conditions of deposit.
		<i>Portland Oolite.</i> —Oolitic and earthy and compact limestones with marine shells and layers of nodular chert.
		<i>Shotover Sand.</i> —Calcareous sand and concretions.
		<i>Kimeridge Clay.</i> —Thick blue clay, bituminous, with septaria and marine remains; and—especially in the lower part—bands of sandy concretions.

¹ The term is derived from a Greek word meaning an egg, the oolitic rocks having an appearance resembling the petrified roes of fishes. For a similar reason some of the oolites are known colloquially as *roestone*.

TABLE VII.—*continued.*

MIDDLE OOLITE (of Oxford, Berkshire, Yorkshire, etc.).	Coral-Rag.—An upper calcareous grit, with marine fossils; coralline oolite, rich in zoophytes (hence the name coral-rag), and a lower calcareous grit, with bands of clay and marine shells.
	Oxford Clay.—Dark blue and greyish clays, with septaria and fossils; subordinate beds of clayey limestone and bands of shale.
	Kellaways Rock.—A calcareous grit (rarely oolitic), very rich in fossils, with a subjacent bed of blue clay.
	Cornbrash Limestone.—A coarse shelly rock of variable and small thickness, but remarkable continuity.
LOWER OOLITE (in Gloucestershire, Oxfordshire, Northamptonshire, etc.	Forest Marble.—Sand with concretions of sandstone and nodules of fissile arenaceous limestone; coarse helly oolite, in some places slaty; sandy clay and blue clay of Bradford.
	Great Oolite.—A calcareous rock of variable thickness and changeable nature, the upper beds shelly, the lower sometimes laminated (<i>Stonesfield slate</i>).
	Fuller's Earth.—A series of marls and clays, with included beds of soft marly or sandy limestones and shells (<i>see</i> Chap. VI.).
	Inferior Oolite.—A coarse, often very shelly limestone, irregularly oolitic, occasionally interlaminated with sand, especially in the lower parts; ferruginous sand, with concretionary masses of sandy limestone and shells.

The Upper Oolite contains the important clays of the Purbeck and Kimeridge beds.

Purbeck clays are blue clays associated with laminated limestones of estuarine origin, with irregular deposits of marl and sand. They lie immediately below the Wealden deposit, but are usually separated from the Wealden clay by the Hastings sands. They are chiefly used for sanitary stoneware and for pottery in which the colour is of minor importance, but some of the deposits are more valuable, being composed of good ball clay almost free from limestone.

The largest area of Purbeck clays is in the southern half of the Isle of Purbeck, in Dorset, in the Vale of Wardour, in Wiltshire, and near Aylesbury and Swindon.

The middle Purbeck beds on the summit of the southern half of the island are suitable for brickmaking, but the cost of carriage to likely markets is prohibitive.

Three small areas at Brightling and Whatlington in East Sussex contain bituminous shales and limestone. The natural gas at

Heathfield appears to escape from the lower Wealden and Purbeck sandstones, but the Kimeridge clay is regarded as the chief source of natural gas and oil, as it contains much thicker bands of bituminous shale.

The Purbeck series are used near Brill (Bucks) in conjunction with Wealden and Lower Greensand clays for high-class tiles and pottery. Nearer Aylesbury the extensive Kimeridge and Gault deposits are easier to use.

The **Portland Beds** are oolitic limestones and chert with only occasional beds of brickmaking clay, as at Swindon and Hartwell.

The **Kimeridge clays** are dark, stiff, laminated clays (shales) containing septarian nodules of limestone and phosphates, gypsum, and bituminous shale. Some portions are so bituminous that they are used as fuel under the name of "Kim coal." The name is derived from Kimeridge in Dorset, where the deposit is readily observable. In Lincolnshire, Sussex, and Dorset the Kimeridge shales are highly bituminous, and in the two last-named have been used for producing shale oil and as fuel. They are very similar to Gault and are much used in the West and Midlands, the most typical deposits being in Huntingdonshire. The Kimeridge clay forms a series of vales in Dorset and Wiltshire; in the Vale of Aylesbury, north and west of that town, and in Quainton. It is remarkably free from superficial deposits, except in the Thames Valley, and even there they are thin and unimportant. Kimeridge clay in Wiltshire forms a belt of clay land from Westbury to Seend and from Wootton Bassett to Swindon—where it is extensively dug for bricks,—and extends (1) north-east to Leighton Buzzard, (2) south to Westbury, with an extension from Mere to Buckland Newton and east through the Vale of Wardour. A deposit of Kimeridge clay in the Vale of Pickering in Yorkshire has long been worked for bricks.

A large brickworks near Brill utilizes the Kimeridge clay effectively. The Oxford clay lying to the west and immediately below the Kimeridge is, however, more valuable when it is properly understood.

The Kimeridge clay has a broad and important outcrop along the valley running south-west of Leighton Buzzard (Dorset).

The best brick clay in North and West Norfolk is the Kimeridge clay, which occurs between Watlington, Ely, Aldreth, and King's Lynn, though it is much overlain by glacial drift and the Gault which extends from a point east of the Downham Market to Sandringham, and between these places.

At Wicken and Soham the Kimeridge clay is a grey fat marine clay turning almost black when wet. It is improved by

the addition of a little sand, as otherwise it is liable to crack on drying and burning.

There are several excellent Kimeridge brick clays near Market Rasen, Wragby Caistor, and Spilsby. Another brickyard in which this clay is used is just north of Knapwell (Cambs).

At the base of Shotover Hill, Oxfordshire, and above the Oxford clay, the Kimeridge clay is also available.

In East Yorkshire the Kimeridge clay occupies a large area north and south of the railway line from Slamer to Filey, but it is largely covered with drift. It is exposed in several areas, the most northerly being at Speeton cliffs and on the foreshore at the south of Filey. In this county it is seldom available for brickmaking, though it was formerly employed in a brickyard near South Cave, a few miles south of Market Weighton.

The Kimeridge clay in the north of Purbeck Island is black, weathering to dark brown, and, being highly bituminous, should be cheap to burn. When ground with waste Portland stone from the locality it makes excellent clinker bricks. Kimeridge clay is also abundant at Weymouth, but is not much used. It is, there, of a deep, blue-black colour, weathering brown and containing but little pyrites. In places it is sandy.

The Corallian limestones and clays lie beneath the Kimeridge beds and occur in a broad area between the outskirts of Thirsk and Scarborough, running north of the Vale of Pickering with extensions southwards to Grunston. The clays in this deposit are of little value, as they are too calcareous, with the possible exception of that at Ampthill in Bedfordshire.

The **Oxford clays** are dark blue or grey in colour, with subordinate beds of clayey limestone and bituminous shale, and are acted on by air and frost to a remarkable extent.

Oxford clay is one of the most important parts of the Middle Oolite formation. It comprises a mass of stiff clay with septarian nodules and shales with shelly sandstones containing nodules of sand and loam. These clays and shales are known as the Kellaways beds—from Kellaways in Wiltshire. At Chatham it has been proved to a depth of 943 feet. It is always important for brickmaking, but in the neighbourhood of Peterborough, particularly near Fletton, it is used in enormous quantities.

In Yorkshire the Oxford clay extends as a horizontal belt from somewhat east of Thirsk to Scarborough, but it is largely covered with Corallian limestone, grit, and drift, and being very siliceous is of little value.

The cliffs at Gristhorpe show an excellent section of this deposit, with an overburden 120 feet thick.

A lengthy area of Oxford clay extends from Brigg to Bourn, (Lincs) and irregularly south to the borders of Northamptonshire, through the east of this county (*via* Peterborough), over the greater part of Huntingdonshire and Bedfordshire into Buckinghamshire, South Oxfordshire, and Wiltshire, finally ending at Ryeme in Dorset. To a large extent the eastern portion of this area contains too much of the Corallian formation to be useful to the clayworker, and as the limits of this are not clearly defined it is necessary to test carefully before deciding upon the nature and extent of the material found.

Part of the district is covered with glacial drift consisting of boulder clay, gravel, and sand. These are of little value and must be removed before the Oxford clay is reached.

The chief area where this clay is now worked is well defined. It extends from a large outcrop north of Peterborough, with an outlier to the east of Thorney, and a very much larger one at Whittlesea, near which place bricks have been made for many years. The main eastern mass of Oxford clay, however, occurs to the south of Peterborough, extending to beyond Haddon. There are too many places where good bricks are made in this neighbourhood for them to be enumerated, but Fletton, Whittlesea, and Farcet are the most important in this portion of the Oxford clay.

In some parts, as at Whittlesea, the clay contains much pyrites and wood, and at Eyegreen a thin ferruginous stony seam occurs. In some parts of the district the alluvium from the fens covers the clay. Great care must be taken to avoid using the Cornbrash (a variety of limestone which occurs in Oxford clay), and the Cornbrash clays occurring in it are undesirable, as they are irregular and uncertain in composition.

To obtain satisfactory results on a large scale, the clays from several layers should be mixed together in definite proportions, a steam navy being advantageous in this respect.

The Oxford clay in the neighbourhood of Fletton is much more shaly in character than in Central and West England, and has a number of bituminous shales running through it. These contain so much combustible matter that the amount of fuel needed to burn bricks made at Fletton is almost negligible.

The Oxford clay near Stamford is quite as good as that at Peterborough, but is not so much used.

The Oxford clay is the predominating brick earth east of Northampton, and is similar to that at Peterborough, though but little used. It has special commercial advantages north of Harrold towards Huntingdon, but these have not yet been developed. In

Huntingdonshire it is particularly extensive and highly valued, though it is largely covered by useless river gravel around Huntingdon itself, and should be chiefly worked in the higher ground, well above the river Ouse, though most of the existing brickworks in this district are parallel to the river and south of the town.

The Oxford clay covers most of the county of Huntingdon and is especially important at Ramsey, St Ives, St Neots, where bands of limestone occur in the clay, and much of it in this county is covered with boulder clay.

The north and west of Bedfordshire is a broad vale formed mainly of Oxford clay with scattered boulder clay deposits. The lower part of the Oxford bed at this part (the Kellaways beds) is well exposed at Bedford, but is both sandy and calcareous. It extends over north-west Berkshire over a broad vale in which flows the Thames, and as a large clay tract across north Buckinghamshire from Marsh Gibbon to Bletchley, but is covered with drift. In West Cambridgeshire it occurs near Long Stanton, but is usually too covered with drift to be used. In Oxfordshire it forms a belt of low-lying ground along the Thames from Lechlade to Bampton and Oxford and to the north-east of that city, as at Ot Moor.

To the east of Bicester the black, well-weathered Oxford clay forms an admirable material, excellently situated, for the manufacture of bricks, if reasonable prices could only be obtained. The Oxford clay in Wiltshire forms a great clay vale from Trowbridge through Melksham, Chippenham, Kellaways, and Christian Malford to Braydon, Brinkworth, Minety, and Cricklade.

The Oxford clay occupies a large area in the east of Somerset in the vale south of Frome, though it is not much used. It is not so stiff as in some other localities, and is very free from septaria and other nodules.

The Oxford clay is well seen in the cliffs and cuttings near Weymouth, where it is several hundred feet thick and has often been confused with Kimeridge clay, which it closely resembles, both being bituminous, though the Kimeridge is the more so. Its local boundary on the east is Ham Cliff, on the west at Abbotsbury, following the course of the Coral Rag. The presence of much pyrites, septarian nodules, and selenite in this locality is objectionable.

It will thus be seen that Oxford clay varies greatly in composition and value in different districts. In some areas it is little better than an indurated sand, whilst in others it is a valuable clay. It is difficult to manipulate, even under the best conditions, and requires great skill for its employment as a brick-making material to be successful.

Bradford clay is a stiff, blue, brick clay containing numerous

calcareous fossils, and in many respects resembles a thin bed of Oxford clay. It is abundant near Bradford-on-Avon in Wiltshire, Frome and Wolverton (Somerset), and in parts of Gloucestershire, particularly near Cirencester, but is not much used as it is very rich in fossils (lime).

The **Kellaways blue clays** lie immediately below the limey grits beneath Oxford clay, and are often included in the latter. They form sandy irregular bands and were laid in comparatively shallow water, whilst Oxford clay is of deep-water origin. They are used for brickmaking near Oundle and Stamford, and produce a semi-firebrick which is easily dried, being slightly more sandy than the ordinary Oxford clay.

The flat of Ot Moor between Oxford and Bicester is of Kellaways clay, but though apparently well suited for brickmaking it is not much used.

The lowest portion on the west of a vertical strip running from north to south in the centre of Lincolnshire includes sandy Kellaways beds, the clays in this series being worked in several localities for bricks.

The **Great Oolite** in this country comprises an Upper Estuarine series of coloured clays and sands, shelly limestone, and calcareous clays, but most of the available portions are too irregular in character to be of value. Immediately above the Great Oolite in Somerset is a valuable formation of clay containing limestone and sand. It appears along a bold scarp extending from Templecombe *via* Wincanton to Frome.

Stonesfield slate is not a true slate, but a dense sandy laminated limestone. The *Forest Marble* overlying the Great Oolite in Dorsetshire is highly fossiliferous limestone and clay, but in parts it passes into small beds of multi-coloured clays and sands.

The **Fuller's Earth** series extends from Dorsetshire to Gloucestershire, and is a mass of grey clay or marl with bands of soft limestone. The series is comparatively large, but the portions of it which are valuable are small and scattered. In addition to its occurrence in the Lower Oolite at Midford and Wellow in Somerset and near Bath, fuller's earth is also obtained from the Greensand formation at Nutfield, Surrey, near Oxford, at Woburn (Bedfordshire), and occasionally in Silurian rocks, as in the Wenlock shales and Lower Ludlow beds in Shropshire.

"Fuller's Earth Rock" occurs at Thornton, Dorset, but can only be used to a limited extent, as it is deficient in some of the properties of true fuller's earth. In parts of central Gloucestershire "fuller's clays" lie over the solid strata of oolite limestones.

See also under *Fuller's Earth* in Chap. VI.

The **Lower Oolite** extends from Saltburn on the Yorkshire coast, over the York moors and southwards to Acklam. After a gap of some twenty miles a fresh area occurs at Newbald, near Beverley, and continues directly southwards across the Humber through Lincolnshire (Sleaford being its most easterly point in this county), through the east of Rutland to Peterborough and then south-west through Northamptonshire (where it is much broken up by Lias) and skirting Oundle and Thrapston in Huntingdonshire.

This formation also extends across North Oxfordshire, the east and south-east of Gloucestershire, north-west Wiltshire to Bath and the Cotswold Hills, and southwards through east Somersetshire to the Dorset coast at Burton Bradstock. It contains very little useful clay, and the sands in it, with some few exceptions, are too calcareous to be of value.

The **CHALK** or **CRETACEOUS** system comprises the Hastings sands, Wealden beds, Greensands and the various chalks.

Between the Upper and Lower Greensand is a bluish-black tenacious clay of marine origin termed *Gault*, which is often interspersed with layers of green sand and septaria. The chalk deposit also contains greyish marls, and flints are frequent.

The Greensand is not always green in colour, but is frequently yellow or even brown.

Some geologists prefer to include the Wealden beds in the Cretaceous formation rather than in the Jurassic. When this arrangement is followed, the Cretaceous rocks may be arranged as shown in Table VIII.

This table is based on the assumption that the great Wealden river or delta was in process of formation at the same time as the marine fossils of the Lower Chalk were being deposited in other areas. As the sea advanced this delta was also submerged, so that whilst the fluviatile deposits must be older than the marine ones above them, the two kinds of deposits were, to some extent, contemporary.

The *fluviatile deposits* of the Lower Chalk are described on p. 80.

The *marine or Neocomian deposits* reach down to the Jurassic rocks at Speeton in Yorkshire, but in the South of England only the upper division appears, and lies above the Wealden series, indicating the gradual submergence of the Wealden delta beneath the sea.

The chalk extends from a line drawn between New Malton and Filey (Yorks), across the Humber to Alford and Welton (Lincs), and occupies most of the land east of the Vale of York, Brigg, Caister, and Scamblesby. In Norfolk it occupies a broad band

TABLE VIII.

Cretaceous.

Upper Cretaceous.	Chalk.	{	Upper (soft) chalk with flints.	{	Lower (hard) chalk without flints, including red chalk in Yorkshire.	Chalk marl (grey chalk).	Chloritic marl.			
			Greenish grey and brown sand and chert.							
			Gault, stiff blue clay with septaria.							
Lower Cretaceous.	Greensand.	{	Green and brown sands with pebbles, beds of gaults, chert, and limestone (Kentish rag).	{	Lower Green- sand.	Folkestone beds.	Sandgate beds.	Hythe beds.	Atherfield clay.	Upper Speeton clay.
			<p style="text-align: center;"><i>Fluviatile Type.</i></p> Weald clay (p. 79). Hastings beds (p. 80), consisting of— (a) Tunbridge Wells sands. (b) Wadhurst Clay. (c) Ashdown Sand.							

(from Hunstanton to Weybourne) running due south. Norwich forms an important part of the eastern edge of this area, the western extremity of which is Cambridge and Arrington. Thence this band of chalk extends southward through West Suffolk until it is capped by the London clay at Long Melford, Somersham, and Barham. It then turns south-west into Essex, its most southern extremity in this county being Bishop's Stortford. Still further west it enters Hertfordshire, South Buckinghamshire (where its northern boundary is the Chiltern Hills), westwards through South Oxfordshire and Berkshire into the north-east of Wiltshire. It then turns more directly south towards the Dorset coast near Dorchester and broadens out eastwards, occupying the greater part of central Hampshire, but it there divides into two bands, one of which takes a southerly direction along the south coast of Sussex and ends at Beachy Head, and the other runs through Surrey (Farnham, Guildford, and Croydon) into Kent, where it stretches right across to the coast at Dover, Deal, and the Isle of Thanet. Strictly speaking, the chalk underlies a much larger area, but in other districts it is so overlain with other formations as to be inaccessible.

The portion of the chalk formation chiefly interesting to the clayworker is the lowest or *chalk marl*, which is in many places

suitable for the manufacture of Portland cement. It must usually be mixed with clay ("river mud").

Deposits at Grays near Gravesend, and on the Medway above Rochester, are much used for cement. There are also numerous brickyards on the chalk in Hertfordshire. Small patches occur in the West of England and in north-east Ireland.

In some parts it is covered with a stiff plastic clay, as in Wiltshire, but in Sussex and parts of Surrey and East Yorkshire it is overlaid with drift.

The **Greensand** takes its name from the green grains of glauconite (iron silicate) it contains, but the name is somewhat misleading, as the general colour of these sands is dark brown.

The Upper Greensand is so closely associated with the Lower Greensand that the two need not be specially distinguished so far as the needs of clayworkers are concerned, though geologically the distinction is important.

The **Gault** is the chief clay deposit in this system. It is a stiff black or dark blue clay of marine origin, which extends from the seashore near Folkestone in a north-westerly direction through Ashford and to the north of Maidstone, then further westward by Sevenoaks to Reigate and Dorking, forming a well-developed zone east and west of Merstham. After this the outcrop becomes very narrow, owing to the inclination of the beds, but at Farnham it broadens out southwards for several miles as far as Petersfield. It then takes an easterly direction, and the outcrop again narrows towards Midhurst and Steyning, and, after a long stretch south-eastwards, is cut off by the sea in the neighbourhood of Eastbourne, though the latter town is chiefly on alluvium. The outcrop, though hidden in places, is almost everywhere available for brickmaking, particularly near Selborne, Lyme Regis, Shaftesbury, the base of the Chiltern Hills, and in Suffolk and Surrey.

In Norfolk a small strip (about two miles wide at its broadest part) runs due south from Sandringham to Stokeferry.

The Ely and Cambridge gault is of a different geological age, but is a good brick clay, though requiring to be carefully treated. It is improved by the addition of sand.

In Cambridgeshire, gault is the clay chiefly used for manufacturing purposes, and is a black, fat, unctuous material not difficult to work if the phosphatic nodules are removed. Although much covered with drift deposits, these are not used to any noteworthy extent, the gault clay being so superior.

A small area occurs around Soham and Wicken, and south to Thetford, and a much larger area extends from near Upware in

a south-west direction through Bedfordshire, where it has long been used for bricks at Arlesey, Buckinghamshire, Oxfordshire, Berkshire (north of the Chiltern Hills), North Wiltshire, and irregular areas and bands occur in south Wiltshire, Warminster and Dorset (Lyme Regis), and north-east Devonshire (Honiton). To the east of Potton in Bedfordshire the gault clay is very abundant and accessible, though not much used. It is similar to the gault beds at Folkestone, Dunton Green, and other districts where large quantities of bricks are made.

At Burnham and Snodland the shell-beds and phosphatic nodules are much scarcer than in most portions of this formation. The gault also occurs plentifully in the Isle of Wight, but owing to the high inclination of the beds it is not always convenient to work.

Widely extended outcrops of Gault are found along the edges of the London basin in Hertfordshire and Buckinghamshire, where it occupies a large area beneath the chalk in the vicinity of Leighton Buzzard, Princes Risborough, and northwards towards Shefford and Biggleswade. It is, however, largely covered by drift deposits, which often renders it useless. Where it is exposed the ground landlords will not permit it to be used, as it lies below extensive parks. The beds are not usually thick, though in some places they reach a depth of 300 feet.

Gault is generally dark coloured and usually contains sufficient sand to be readily worked. When used alone, it forms bricks of a reddish colour—owing to the 3 per cent. of iron present,—but is more frequently mixed with chalk to produce malm-bricks. It frequently contains about 33 per cent. of chalk and then burns a chalky white, but is much improved by mixing sandy red clay with it, so as to reduce the proportion of chalk to 25 per cent. A similar material may be artificially made by washing a suitable mixture of chalk and red clay of fairly strong texture. The resulting bricks burn a good cream colour resembling bath-stone, or if the mixture is very carefully made they are quite white and are known as “White Suffolks.”

Gault is occasionally sandy and calcareous, and usually contains nodules of pyrites, marcasite (iron disulphide), and phosphate of lime. They should be removed, though the phosphatic nodules are less harmful, and, in most cases, may be ground up with the clay. It breaks up readily on exposure to the weather, and is an easy formation for the brickmaker to use.

Although largely used, gault cannot be regarded as a high-grade brick earth, being limited to the manufacture of bricks, drain-pipes, etc., as it lacks many of the qualities of the finer

clays; nevertheless it is a good all-round brick earth, especially when used with admixture of chalk for the production of light-tinted bricks.

Speeton Clay, on the south of Filey Bay, in Yorkshire, is of little commercial importance, but palæontologically it is of great importance in establishing the geological boundary between the upper and lower portions of the Cretaceous system.

It is a dark-blue shale which weathers to a soft, grey, plastic clay and is seen to the best advantage on the shore below Speeton, where a face about half a mile in length is visible, and presents one of the best sections of the Neocomian (Neufchâtel) beds in the whole of Northern Europe. Between the sea and Speeton it is largely covered with glacial drift, but nevertheless the bed has a thickness of 150 to 250 feet. At Knapton it is found in the slopes below the Chalk Hills and is used for brickmaking. Fossils and septaria abound in it,¹ some of the latter being commonly sold as "petrified tortoises"! Some years ago the upper part of the Speeton clay was quarried for these large calcareous nodules; these were made into cement. Selenite, pyrites, and coprolites (phosphatic nodules) are also abundant.

According to Lamplugh, Speeton clay or its equivalents exist in Lincolnshire as well as the gault of Kent, Sussex, and Cambridgeshire.

At the northern end of the Speeton beds the clays appear to belong to the Kimeridge series (p. 69).

The lowest portion of the **Lower Greensand**—termed *Atherfield clay*—occurs in Surrey to the south of Guildford at Ockley, Horley, and Crowhurst, and produces bricks very similar to those made from gault. A patch of the Lower Greensand around Potton in Bedfordshire has also been much used for brick-making.

The Lower Greensand rises gradually from the Gault vale in Kent, and forms a fine escarpment overlooking the Weald clay, south of Sevenoaks and thence by Ashford to the coast at Hythe and Sandgate. The highest portion (Folkestone beds) is composed of siliceous sands; in some places (Aylesford and Berstead) they are pure enough for glassmaking.

The Lower Greensand is chiefly found in the south of England, in Surrey, north-west and south-west Sussex.

The Lower Greensand also occurs in East Hampshire and in

¹ Over 300 species of ammonites ("snakestones"), belemnites ("spear-points"), and other fossils have been found in the area mentioned. The reader interested in these should consult T. Sheppard's *Geological Rambles in East Yorkshire and Hull Museum Publications No. 29*.



TYPICAL AMMONITE from Speeton Clay.

(By courtesy of T. Sheppard, Esq.)

the form of a narrow strip running through Kent to Hythe, in the Isle of Wight, between Leighton Buzzard and Potton in Bedfordshire (where it has been much used for brickmaking); in the form of sponge gravels in Berkshire (Farringdon) and near Shotover in Oxfordshire and thence north-east to Ely and north and south of King's Lynn in Norfolk.

The glass sands of Godstone (Surrey) and Hartwell near Aylesbury, the Woburn sands, the Sandringham beds and the brick clays of Snettisham are all valuable members of this series. It also occupies a long straggling area from Grassby and Caistor to Spilsby and Alford in Lincolnshire, and a broader area running along the east coast of the Wash to King's Lynn and a little south of Downham Market. Some good beds of clay occur. These strata overlie the Kimeridge clay.

The Lower Greensand in Norfolk is very different to that in South England. At Heacham and Castle Rising the middle portion, used for brickmaking, consists of clay with loamy layers and ferruginous nodules, but the Carstone above it being a good building stone prevents many bricks being required.

An isolated area occurs between Haddenham, Wilburton, and Stretham (Cambridgeshire), and is, with the small outlier at Ely, an extension of the main formation running south-west from Cottenham *via* Caxton, Potton, Shefford, Amptill, and Woburn, to Leighton Buzzard.

Several isolated areas occur in Oxfordshire, one at Cliddesden, one three miles south of Oxford, and another at Nuneham Park; the main mass extends in a thin strip from Shellingford to near Devizes.

In Hampshire the Lower Greensand occurs at Petersfield and extends in a north-west direction along the London and South Western Railway to Guildford and thence almost due east to Maidstone *via* Ashford to Hythe. Another area extends southwards from Petersfield *via* Midhurst to near Eastbourne.

The southern half of the Isle of Wight is largely composed of Lower Greensand, which is in parts (particularly near Ventnor and Chale) overlain by Upper Greensand and Gault.

The nature of the Greensand varies greatly in different areas, but it is mainly a marine deposit of sands with some brown and grey calcareous clays (Atherfield clay) at its base.

The sands are occasionally very pure, as at Godstone and near Aylesbury, where they are dug for glassmaking purposes.

The **Wealden** beds lie immediately above, or may even be said to form part of the upper portion of the Oolite system; the clay

in them is extensively used for brickmaking. It lies close to the Lower Greensand and is largely confined to Kent, Sussex, and Surrey. It is stiff in character, and yellowish grey or bluish in colour, and often contains ironstone nodules with thin layers of impure limestone and sandy flagstone, apparently of fresh-water origin. The Wealden beds are characteristically fluvial in origin and probably formed the delta extending in an east and westerly direction, for at least 200 miles, and north and south for 100 miles, but the present visible area is far smaller than this owing to the superposition of later formations—chiefly chalk. The Wealden beds consist of—

(1) *Punfield beds*, containing a little chalk.

(2) *Weald clay*. Thick blue clays and brown shales, having in the upper part septaria of argillaceous ironstone, and, in the lower parts, beds of the shelly, fresh-water limestone known as “Sussex marble,” “Petworth marble,” or “Paludina marble.”

(3) *Tunbridge Wells sand*, used for tiles and facing bricks in conjunction with local clay. It resembles Ashdown sand.

(4) *Wadhurst clay*, useful only for common bricks—very rich in iron and fossils. It is shaly in parts.

(5) *Ashdown sand*. A soft buff or white sand and sandstone.

(6) *Fairlight clay*, precisely similar to Purbeck clays (*q.v.*).

The chief Wealden area commences rather north of Midhurst, and extends in a north-easterly direction through Surrey, and eastwards through Kent to the borders of Romney Marsh and Hythe, and south-eastwards through Sussex to Eastbourne.

The true Wealden clay—above the Hastings beds—also forms a large vale below the Lower Greensand scarp of Leith Hill and Hindhead (Surrey), and extending to the north, west, and south of Ashdown Forest.

Wealden beds—consisting of alternate clays and sands—also occur in the south of the Isle of Wight and north of Swanage, in the Vale of Wardour (Wilts), and in Berkshire, Oxfordshire, Buckinghamshire, Bedfordshire, and Cambridge, but are of small commercial value. The Wealden clay is really a brown shale, and forms a highly valued brickmaking material.

Hastings Sands.—Fawn-coloured sand and friable sandstone (*Horsham beds*); calciferous sandstones, alternating with friable and conglomeratic grits (*Tilgate beds*); white sand and friable sandstone alternating with clay (*Worth sandstone*); bluish-grey limestone alternating with blue clay and sandstone shale, and some beds of calcareous sandstone (*Ashburnham beds*).

The differences between these clays are not sufficiently marked to need further description.

The Hastings beds occupy the whole of north-east Sussex and the southernmost quarter of Kent. They form the elevated ground in the Weald at Trowbridge, Tunbridge Wells, Crowborough, Ashdown, Mayfield, Heathfield, and Hastings.

The **TERTIARY SYSTEM** includes all the materials deposited after the chalk and before the close of the glacial drift. These deposits are usually well defined, some being of marine and others of fresh-water origin, and of somewhat loose texture. They consist chiefly of clays and sands, with sandstones, grits and marls as accessories; the clays being highly important, though often thin and irregular. They may be arranged as follows:—

TABLE IX.

Tertiary.

PLEISTOCENE	{	<i>Boulder or Glacial Drift</i> , consisting of brick earths, boulder clay, sands, gravel, and boulders.
	{	<i>Mammaliferous Crag</i> of Norfolk and Suffolk.—Consisting of shelly beds of sand, laminated clay, and yellowish loam, with layers of flinty shingle reposing on the chalk, and generally covered with a thick bed of gravel, abounding in the bones of mammals: hence the name.
PLIOCENE	{	<i>Red Crag</i> of Norfolk and Suffolk.—A deep ferruginous shelly sand and loam, with an abundance of marine shells, frequently rolled and comminuted.
	{	<i>Coralline Crag</i> .—A mass of shells and polyzoa in calcareous sand; or compact, and forming flaggy beds of limestone, with bands of greenish marl. Some of the harder portions are used as building-stone.
MIOCENE	{	Supposed, on palæontological grounds, not to be represented by any of our British strata, unless the leaf-beds of Mull, the lignites of Antrim, and the lignites of Bovey Tracey in Devonshire belong to this period. This is extremely doubtful.
OLIGOCENE	{	<i>Fluvio-Marine</i> , or <i>Marino-Lacustrine Beds</i> of Hampshire and Isle of Wight.—Consisting of clays and marls, sometimes indurated, of sandy clays and subordinate layers of siliceous limestone, some of which (the Hamstead Beds, etc.) are now regarded as the base of the Miocene.
	{	<i>Upper Marino-Lacustrine Period</i> .—Fresh-water and marine deposits of Hamstead, Osborne, and Bembridge in the Isle of Wight (Miocene?).
	{	<i>Lower Marino-Lacustrine Period</i> .—Fresh-water and marine deposits of Headon Hill.
EOCENE	{	<i>Barton Period</i> .—Marine sands and clays.
	{	<i>Bracklesham Period</i> .—Sands and clays, with lignite beds.

TABLE IX.—*continued.*

Eocene— <i>contd.</i>	<i>Bagshot Sands.</i> —A marine series of loose sands and sandstone with valuable clays.
	<i>London Clay.</i> —A brown or dark blue or blackish tenacious clay, with layers of argillo-calcareous nodules. Layers of greenish sand and masses of gypsum and iron pyrites not infrequent.
	<i>Oldhaven and Blackheath series.</i> —Sands and pebbles with laminated clays of marine origin.
	<i>Woolwich and Reading series.</i> — Gravels and black loams and clays in the upper part (<i>Woolwich Beds</i>), and mottled plastic clays in the lower (<i>Reading Beds</i>). Greenish sandy clay and fissile marls.
	<i>Bognor Beds.</i> —Occur towards the base of the London clay, and consist of calcareous and siliceous nodules, or of coarse green indurated sand, with septaria and numerous marine shells.
	<i>Thanet Beds.</i> —Marine and fluviatile deposits, lignite, pebbles, coloured clays, and sands, shingle, and loam, with beds of rolled flints and marine shells.

In England, the Tertiary rocks have suffered no internal change from igneous action, though they have been much displaced since their formation; they now chiefly occupy the basins of London and Hampshire and are represented by the steeply inclined strata of the Isle of Wight. There are no important Tertiary clays in the North of England, though indications of their having been present may be found in the "pipes" in the chalk of East Yorkshire. Apparently the greater part of such Tertiary clays as exist north of the Humber have been almost entirely swept away.

The clays of the *Pleistocene* formation are described on p. 104, under the caption "Boulder or Glacial Drift."

The *Pliocene* formation is practically useless to the clayworker, though some of the alluvial clays on its surface are employed with success in Norfolk and Suffolk. As a formation, the Pliocene deposits are too calcareous and fusible to be really valuable.

The *Miocene* formation in Great Britain does not contain any clays of any importance, the Bovey Tracey clays—which were at one time considered as Miocene—being now included in the Bagshot series, of Eocene formation.

The *Oligocene* formation occurs in the north of the Isle of Wight and on the Hampshire coast. It consists of fresh-water and marine limestones, and clays known as Headon, Osborne Bembridge, and Hamstead beds.

It was formerly included in the Eocene formation, and is of

little commercial importance, owing to the relatively small quantity and unsuitable situation of the clays. Apart from this, the clays of this formation are excellent for bricks and tiles.

The Oligocene deposits can be most easily studied in the Isle of Wight, as they are there more accessible than on the mainland. Commercially, the clays in Hampshire generally and in the Isle of Wight are valuable, but are not nearly so much used as they might be. Thus there is no exportation of bricks from the island, and the local wants are very small. Unfortunately the clay beds are very steeply inclined and are difficult to work in large quantities.

The most important clays in this district are the Hamstead, the Bembridge, the Osborne, and the Headon series, though the Barton, Bracklesham, Bagshot, London, and Reading beds also exist in the Isle of Wight.

The *Hamstead* clays are most prominent about one and a half miles to the east of Yarmouth (Isle of Wight), where they are covered with a gravelly sand. The clay is blue, but turns yellow on weathering and contains calcareous nodules. Below this are laminated clays and shales also containing lime, and still deeper is a 40-foot bed of shaly marls. These clays would not be profitable; they are too inaccessible.

The *Bembridge* clays also include marls and calcareous shales with intervening layers of sand. The proportion of lime and the sudden changes in character make these clays of doubtful value.

The *Osborne* series consists of blue and red shales rich in lime nodules, together with calcareous sands and marls. These are readily accessible between Ryde and Cowes and in the west of the island, and are suitable for common bricks of uneven colour. The formation is too irregular for well-coloured bricks to be produced in large quantities.

The *Headon* clays are calcareous and of small value, though the sands are used for glassmaking. They underlie much of the New Forest and the north of the Isle of Wight.

The main Upper Eocene strata lie from Chertsey and Weybridge, west towards Woking, Aldershot, Chobham, Bagshot, Ascot, and Sandhurst, and again between Reading, Newbury, and Kingsclere.

In the Hampshire basin the beds occur over much of the New Forest and west to Wareham, and extend right across the Isle of Wight in a narrow strip.

In Dorset the formation yields the famous pottery clays.

The Eocene formation is, agriculturally and industrially, the

most important of the Tertiary deposits. It is chiefly comprised in two large areas: (*a*) the London basin, which is enclosed in a triangle, two of whose sides are formed by two lines drawn from a point twenty miles west of Reading, one passing through Norwich and the other through Canterbury; (*b*) the Hampshire basin, which comprises the Isle of Wight and a triangular area extending on the north to Salisbury, on the west to Dorchester and east to Newhaven.

The clays in this formation are of deep-sea origin and are very extensive, particularly in what are known as the Hampshire and London basins, though largely covered with gravel and sand; curiously enough, those portions which are the least suitable for the growth of crops are often the most valuable to the clayworker. This is particularly the case with the South Hampshire and Bagshot beds.

Eocene clays (pipe clays) are found near Lough Neagh (Ireland), but are so much covered with drift and alluvium, and are so impure, as to be relatively unimportant.

In the following notes only those portions of the Eocene formation which are valuable for the clays they contain will be noticed.

The *Barton* bed in Hampshire and the *Bracklesham* beds on the east and west of the Isle of Wight consist chiefly of marls and loams, which are suitable for small quantities of hand-made bricks. In Hampshire and north-western Surrey they occur as extensive loams, which are well developed between Lymington and Christchurch, near Portsmouth and Gosport, round Southampton, and in the Bagshot district. They are but little employed; indeed, if used alone many of these materials would prove failures, though the remedy is usually at hand.

The **Bagshot Beds** (Table IX.) lie normally above the London clay, but are less widely distributed. The main mass of this formation occupies a large area from Chertsey and Weybridge westwards towards Woking, Aldershot, Chobham, Bagshot, Ascot, and Sandhurst, and again between Reading, Newbury, and Kingsclere. In the Hampshire area the Bagshot sands extend over the New Forest and westwards to Wareham, and across to the east of the Isle of Wight. In Dorset the deposits contain the very valuable "ball clays." Though known as sands, they are rich in clays of a loamy character, and the more sandy portions are excellent for mixing with the tougher London clay. Curiously enough, in spite of the ease with which they may be made into bricks, most of the clays of the Bagshot series are entirely neglected. When they are used it is seldom desirable to mix chalk with them, though some brick-makers do this. If used alone, and heated rather more strongly

than usual, they produce excellent bricks of a bright red or purple-red colour.

They are divided into Upper, Middle, and Lower beds, but the line of demarcation between each is often difficult to define, though the central portions of each of the beds are clearly distinct in character.

In Essex the Bagshot series are limited to outliers near Brentwood, Rayleigh, east of Epping, Highbeech, Laingdon Hill, and a few smaller patches. The outlier extending from north of Rayleigh to just south of Hadleigh, and south-west to Benfleet, is of a very irregular shape, being surrounded by the London clay. Around Hadleigh it is covered with pebbly gravel, but the remainder is practically free. The material is much more argillaceous than might be expected, some of the clay being almost as good as the Dorset pipeclays of the same formation, but requires selection on account of interruptions of gravel. For brickmaking, the brick earths of Rochford, Shopland, and Southend are so extensive as to prevent the Bagshot beds being much used.

The outliers of Bagshot sands at Highgate, Hampstead, and Harrow Hills are important and characteristic.

In Surrey, to the south of Esher, the Bagshot sands crop out on the higher ground and are very valuable deposits, though used to a limited extent only. In this district the area they cover is a rough triangle, with its apices at Esher, Ockshot Street, and Cobham. The lower Bagshot beds consist chiefly of fine yellow clayey sands, with irregular beds of multicoloured clay which are 100 to 150 feet thick near Woking, Horsley, and Egham. They are also well developed to the east and south of Weybridge, but are much covered with gravel. There is a small outlier at Wimbledon.

In the Middle Bagshot beds in this area the clays are brown, sandy, and laminated, and are most abundant near Addlestone, Chertsey (where they are 10 feet to 20 feet thick), thinning off gradually towards Winchfield. They are covered with a thick layer of Greensand and thin useless beds of yellow clay.

They are also prominent on the high ground forming St George's Hill and Red Hill, and in both localities are much used for brick-making.

The Bagshot beds are most conspicuous in the district from which they derive their name, lying between Ascot and Woking and extending north-westwards beyond Bracknell. The last-named place has long been famous for "rubber bricks." Some portions of this area are, however, quite useless to the clayworker. The

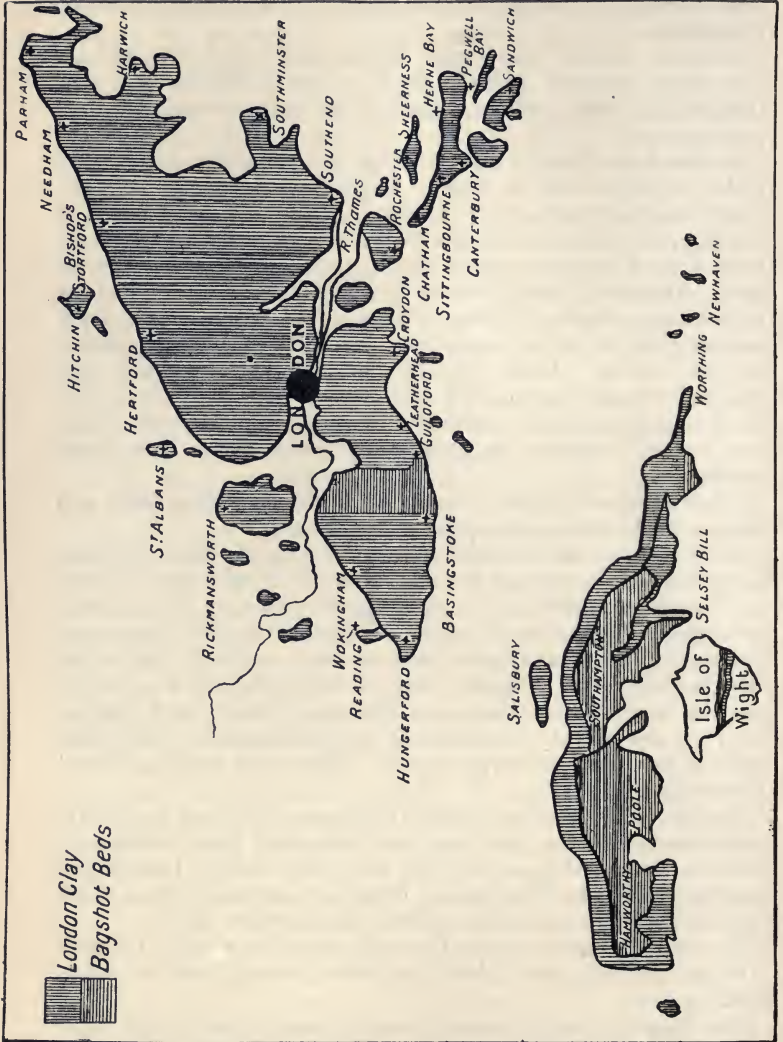


FIG. 2.—Sketch-map of London Clay and Bagshot Beds.

lower beds are the most important, and consist chiefly of a sandy loam which can only be heated to what brickmakers regard as rather a low temperature, but carefully made goods have a

remarkably uniform red colour. It is not a little curious that the present brickyards do not, by any means, occupy the best portions of this valuable deposit; the latter are further south.

The most suitable sites for brickyards in this area are at the points where the London clay joins the Bagshot sands on the east and south of Esher Common. Further west, there are several important outliers of Upper Bagshot beds near Long Cross, Staples Hill, Fox Hill, King's Hill, Long Down, King's Beeches, and Brick Hill; loams in the two last-named being used for brickmaking in conjunction with the Middle Bagshot beds there.

The Upper Bagshot beds west of Aldershot are extensive, but too sandy to be useful.

The Middle Bagshot beds are also well developed to the north-east and north-west of Aldershot, beyond an outlier of Upper Bagshot sand. They are free from all gravel or sandy cover, but the clay is in rather thin strata between layers of good sand. Hence only moderate quantities of a good mixture for brickmaking can be obtained. Further west towards Crookham they are equally useful. Pottery clays are also found in various parts of this area; pipeclay and what is sometimes regarded as china clay also occur, though the latter is not of much value.

At the extreme west of the London basin, near Marlborough, the Bagshot sands cap the outcrop of the Reading bed between Oare and Bucklebury, but are better developed to the south of the river. The clays are, however, of only medium value, being very sandy and readily fusible.

The Middle Bagshot beds also form good brick-earths in places, particularly at the bases of the higher ground. In this area, the Upper Bagshot beds, capped by gravel, occur on the higher ground, from Easthampstead Plain southwards to the further end of Chobham Ridge and westward to Edgeburrow Hill, with three prominent outliers—one at Duke's Hill and the others on Bagshot Heath; but the clays in them are scarce and of relatively little value, though some portions in this district make good "rubber bricks." Some of the Upper beds in this district are capable of yielding a high-class refractory brick, although a little lacking in strength unless mixed with a flux such as lime.

South and west of Wokingham, the Middle and Lower Bagshot beds are also extensive, and the town itself is built on an outlier of the latter. Surrounding this outlier, the London clay comes to the surface, and it is on the junction between this and the Lower Bagshot beds that the most valuable brick-earths occur.

The Upper beds are scanty in this district. Eastwards towards Windsor the Bagshot beds pass gradually into the London clay and are frequently capped with a stony deposit.

Around Aldershot, the Lower Bagshot beds run in a north-easterly direction, and westward to the Horns and Ewshot, but are too sandy for the clayworker.

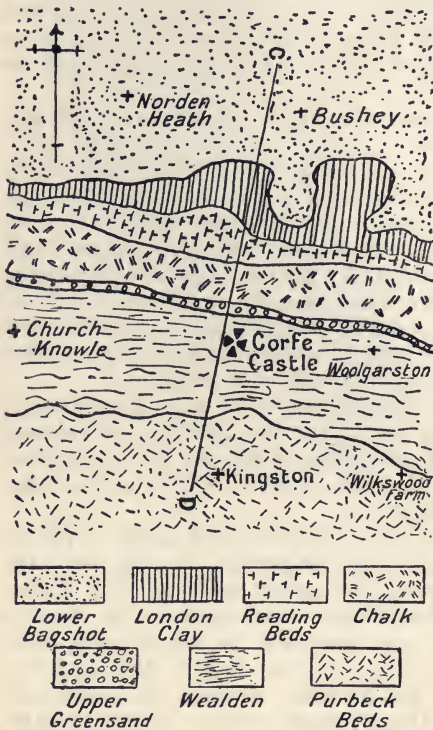


FIG. 3.—Corfe Castle District. (G. Harris.)

The Lower Bagshot beds, which are richer in clay than the Middle or Upper ones, are specially developed around Esher, Weybridge, in the Bagshot area, and in the Isle of Wight.

The Lower Bagshot beds occupy the greater part of the Tertiary area in Dorsetshire, and are famous for the ball clays and pipe clays found in them, particularly in the neighbourhood of Wareham, Norden, Goathorn, Creech Grange, Corfe Castle, and in the northern portion of the Isle of Purbeck. They occur in alternation with thick beds of sands of various colours. Fig. 3 is a sketch-map of the "Corfe Castle" district, indicating the various positions of the strata, and fig. 4 is a section across the district showing

that the Lower Bagshot beds under Bushey and neighbourhood, as well as the other Tertiary beds resting on the chalk, are much inclined to the north, and that the whole of the beds, including the Purbeck, partake of this dip, though at Matcham they have exactly the reverse inclination.

The ball clays found around Poole, Parkstone, and Bournemouth are seldom sufficiently white in colour when burned to be

used for whiteware, but are much used for cream and ivory goods and for drain-pipes.

In the "trough of Poole" they are very extensive.

These ball-clays are all shipped from Poole, and hence are frequently termed "Poole clays." Their characteristics are more fully described in Chap. VI., under the heading *Ball Clays*. Another enormous deposit of ball clay occurs around Kings-teignton, Teigngrace, Homers, Decoy, and Newton Abbot in South Devonshire, and near Mariond and Merton (Torrington) in North Devonshire; their respective shipping ports being at Teignmouth, Bideford, and Exmouth. In consequence of this, ball clays are often known as Poole clay or Teignmouth clay, though they do not occur naturally in either of these places.

The ball clays obtained from South Devonshire are all comprised within the Bovey basin, which is a depression about 10 miles by

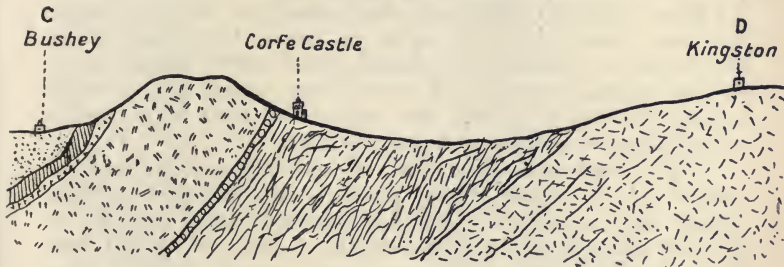


FIG. 4.—Corfe Castle District, section on line C D.

2½ miles extending from Bovey Tracey to about 2 miles south of Kingskerwell, watered by the Teign and the Bovey, which have their sources in the granite rocks of Dartmoor. According to J. A. Key, who surveyed this district very carefully, "commencing on Knighton Heath, and running down the eastern side of the basin, are three principal parallel beds of muddy clay, silt, sand, and gravel, all having a western inclination or dip. The bed to the east is the pipe clay (called locally 'white body'); the two western beds are potter's clay (or 'black body'); and there are parallel beds of coarse clay, sand, etc. South of the Newton Railway Station the beds of fine clay thin out to a mere trace, but occur again at the Decoy as a well-defined and regular deposit, but here the dip is changed from west to east, the pipe clay now being found to the west, and the potter's clay, accompanied by seams of lignite, to the east. Further south, the beds of fine clay thin out again, still keeping their eastern inclination;

become again well-defined at Aller, especially as regards the potter's clay and lignite (the pipeclay having here lost its distinctive qualities, being mixed with sand and stained with ochreous matters).

"Fig. 5 is a section across the beds of pipe and potter's clay, on the eastern side of the basin, near New Cross, which represents the stratification of the continuous clay deposit from near Knighton, on the north, to the Newton Railway Station; with the difference that at the commencement of the deposit the seams of fine clay are thin, somewhat irregular, and to some degree mixed with quartz gravel. The dip is also greater than in the section; and in several cases the clay-beds show the action apparently of running water, portions of the fine material having been evidently washed away, so that the fine clay runs down to a considerable depth almost perpendicularly.

"From Knighton southwards the beds of fine clay increase in thickness, purity, and regularity, to below New Cross, where they begin to diminish in thickness until lost to the south of Newton Railway Station. In two or three places, narrow bands of clay, generally stained, run across the finer clay; and in several places the pipe clay forms two beds.

"Fig. 6 represents a section of the beds of clay, etc., at Decoy. All the seams of clay shown in the section have been worked for considerable distances longitudinally, from 60 to 100 feet transversely, and two depths of from 30 to 90 feet. The inclination of the strata here is much greater generally than, and in the opposite direction to, that in the section fig. 5, but the superposition of the beds is almost identical with that in the last-named section, taken in the upper part of the basin. Here and there a smooth water-worn stone, generally of quartz, but sometimes slate, is found embedded in the clay; nodules of iron pyrites, of all sizes, from that of small shot to that of a hen's egg, are in some places abundant.

"The clay and accompanying beds at Decoy rest against the Greensand hills surrounding this portion of the basin; and the strike of the beds forms a segment of a circle, somewhat conformable in direction to the shape of the hills.

"No fine pipe clay has been found at Aller; instead are rough clays, highly stained with ochre, all having an eastern dip.

"The clay-beds throughout the deposit show no signs of disturbance by slips or faults; they seem perfectly unaffected by any other power than that of water."

In North Devon, Marland Moor, Merton Moor, Greenings Moor, Clay Moor, and Bury Moor, on the banks of the river Muir near

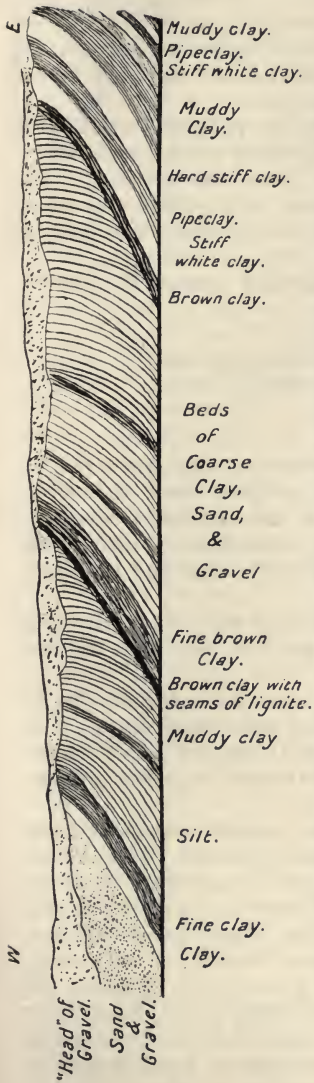


FIG. 5.—Section of the Clay beds near New Cross. Scale, $\frac{3}{8}$ inch to a fathom. (After J. A. Key).

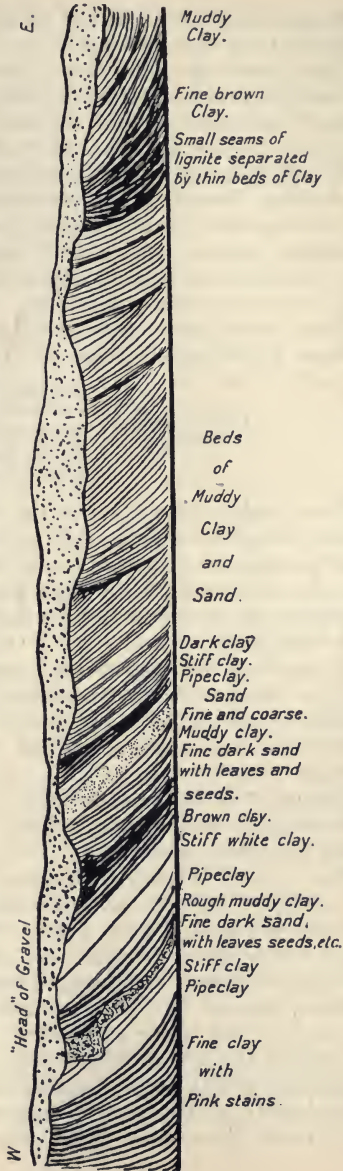


FIG. 6.—Section of Clay beds at the Decoy. Scale, $\frac{1}{8}$ inch to a fathom. (After J. A. Key.)

Torrington, all of which are on the slopes of Dartmoor, are the centres of the clay-workings.

The deposit resembles that of the Bovey Basin. The extent of these clays towards Dartmoor, which is eighteen or twenty miles distant, has not yet been definitely proved, the workings being chiefly at the northern extremity of the basin.

The first use of Devonshire ball clay for pottery is attributed to Astbury (about 1715), previous to which it was used solely for the manufacture of tobacco pipes. There is usually an overburden of common clay 6 or 8 feet deep, below which the white clay extends to so great a depth that in some places the bottom has not yet been reached.

The Lower Eocene formation (sometimes termed the **Lower London Tertiaries**) includes :—

Lower London Tertiaries	{	London clay. Oldhaven and Blackheath beds. Woolwich and Reading beds. Bognor Beds. Thanet beds.
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These beds are included in the London and Hampshire basins, which commence on one side on the northern coast of Suffolk, and pursue an irregular course in a south-westerly direction through Hertford (St Albans), Essex, Kent, Surrey, and South Middlesex, Buckinghamshire to Berkshire (Windsor and Reading), and Hampshire.

In the north the formation is much covered with alluvium, which may be mixed with other materials to act as a light flux, but can seldom be used alone.

In the south-eastern portion of the basin the chalk is partially covered with brick-earth, loam, and clay containing flints, all of which are used for brickmaking. These clays are usually mixed with chalk to form "white bricks" or "malms," any flint present being previously removed.

The Lower London Tertiaries also extend south-east from Charminster (Dorset), and north east along the edge of the Upper Eocene which lies over them, through Cranbourne, Downton (with an outlier at Salisbury) to Tycherley, then south-east through Bishops Waltham, Bursledon, Fareham, Porchester, Portsea, Havant, Chichester, Arundel and Worthing to St Lancing. Several outliers occur at Seaford. A narrow strip ($\frac{1}{2}$ mile wide) lies across the Isle of Wight from the Needles to Culver Cliffs. Commencing with several outliers at Great Bedwin, the beds also extend south of Hungerford, eastwards through South Berkshire and North Hampshire (with large outliers at Great Fawley,

Winterbourne, Chieveley, Bradfield, Reading, Mapledurham, Ship-lake, and Wargrave) to Windsor, Beaconsfield, with outliers at Turville, Taplow, Rickmansworth, Chesham, Abbots Langley, St Albans, Uxbridge, through the greater part of Middlesex to Hertford. There are further outliers at Digswell, Dutchworth, and Sacombe.

Almost the whole of Essex, except the coast and the chief river valleys, is of this formation, as is also North Kent. In the last-named county, however, the main mass ends at Dartford, and the remainder consists of a series of irregular areas, all of which are to the north of the railway lines from London to Canterbury.

To the north of Essex the formation continues into Suffolk through Sudbury, Hadleigh, and Ipswich. South and east of Ipswich the formation becomes straggling and much overlain with Pliocene deposits until it ends at Woodbridge and Orford.

The **London Clay**.—Material suitable for brickmaking is obtainable from London clay in almost every part of the London basin, except in the immediate vicinity of the Thames, the Wey, and the Mole, where it is hidden by other deposits. The formation is often so thick that it is impossible to get at the sands beneath. Where this sand is accessible, the quality of the bricks made is considerably improved, and the difficulties are correspondingly reduced. The brickyards scattered over the whole area are chiefly engaged in the manufacture of "stocks," which are very durable, though lacking the accuracy of shape demanded in the Midland and Northern counties. It is exposed in many parts of Essex, as at Romford, but in others it is capped by other deposits such as boulder-clay, drift, gravel, Bagshot beds, as at Brentwood, or alluvium as at Southend. In North Middlesex and eastwards it is largely covered with drift.

Considered by itself, the London clay is usually too contractile to be of great value¹ unless mixed with at least one quarter of its weight of sand or other non-plastic material, but along its edges excellent brick- and terra-cotta-clays are often found.

When near to outliers of Bagshot sand, the London clay tends to become sandy, and is then more valuable for brickmaking. The two deposits are worked together in many localities.

True London clay is a particularly treacherous material and is not, alone, suitable for brickmaking; and as it is seldom found

¹ The inexperienced clayworker must guard against being persuaded to work the richer portions of the London clay. Though sticky and strong this clay is not really plastic, and failure will probably attend efforts to make it into bricks. It is only of value for this purpose when adjacent to accessible beds of Bagshot sands.

associated with other materials which can be mixed with it, it is often quite useless. Many failures have resulted from this fact not being fully appreciated. Many of the most successful of the users of London clay have been fortunate in also possessing considerable quantities of other deposits, but there are many brick-makers who imagine they are using true London clay, whereas, in reality, they are working one of the many superficial deposits

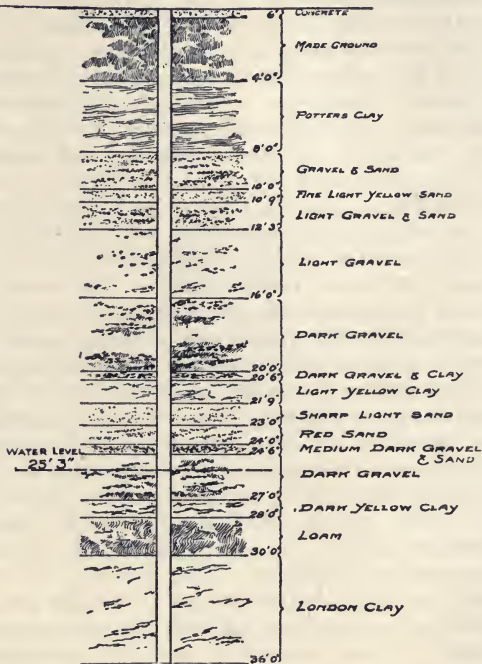


FIG. 7.—Section of No. 1 Borehole in the Crypt of St Paul's Cathedral.
(By courtesy of Messrs Duke & Ockenden, Ltd.)

of brick-earths which are scattered about the London basin and have but little connection with the London clay (which is a marine deposit) beneath.

True London clay cannot well be mistaken, as it is easily recognized by its blue-black colour turning brown on exposure, by its soapy conchoidal fracture, by its toughness, plasticity, and by the selenite crystals it contains. Marcasite is also common, and septarian nodules are frequent and characteristic.

In the east of Kent, the London clay consists of a large mass of dark-blue tenacious clay, which turns brown on weathering, and a bottom bed of stiff laminated loam too irregular for use.

In Essex and in the part of Suffolk immediately north of Ipswich it forms the most important of the clay deposits, and in the former county it occurs in broad sheets, covered with a blanket of brick-earths, chiefly of glacial origin and (within the usual limits of variations of this material) reasonably uniform over the whole of the area in which they occur in this county.

To the east of the outcrops of the Reading beds at Chipping Barnet, Wrotham Park, Potter's Bar, Northaw, East Barnet and Southgate, Hornsey, Friern Barnet, Enfield and Waltham Cross, the London clay might form the chief brickmaking material, being well developed and valuable at its many outcrops; but as it is difficult to use and is often covered with glacial drift and river drift the latter are much used for brickmaking, though in South Essex and in some other districts, in spite of the disadvantages, the London clay is often preferred by brickmakers to the superficial earths, though these are really more suitable for their use.

Over a large portion of the London basin the London clay lies above the Reading beds (p. 97), in some places being very thick. A good instance of this occurs between Harefield and Rickmansworth in the northern part of the London basin, where it is comparatively free from overburden. At Harefield it is about 12 feet thick, with an additional 6 feet of sandy marl, and throughout this portion of its formation it is usually more sandy and softer than nearer London, and is, consequently, better for brickmaking, if carefully blended with the sandy portion of the Reading beds found below it.

The deposits of this clay south and east of Aldenham, particularly on the higher grounds, are not much used for brickmaking, though very suitable for this purpose. At Watford Heath brickyard they are about 24 feet thick, with some 16 feet of clean sand below. Rather further west, to the south of Amersham, at Cold Harbour and Frog Hall, there are two outliers of London clay and Reading beds which have long been used in spite of the capping of gravel. For a large area east and north-east of Uxbridge as at Northholt, Ickenham, Kingsbury, Harrow (where it is capped by Bagshot sand), Hanwell, Pinner, Whitchurch, Stanmore (where it is spoiled by gravel), Elstree, etc., the London clay is well developed at the surface, and, within the usual limitations of this clay, is well adapted for brickmaking.

Further to the south, as at Hillingdon, Cranford, Bedfont, Staines, and Feltham, it is too much covered with gravel and sand,

though a large patch of exposed loam (seven miles and two miles) stretches from West Drayton by Hayes to Greenford, and if carefully selected, so that the grit and pebbles are avoided, it makes good, light-red bricks without requiring to be washed. There are smaller patches near Brentford, Hounslow, and Ealing, the deposits being very thick at the last-named place, though so interstratified with sand and pebbly gravel as to be of little value to the clayworker.

At Esher, the London clay is still present, but its upper portion is more sandy and therefore more workable.

Near Easthampstead Plain, between Woking and Aldershot, the London clay is very free from a covering of gravel, its upper portion being rather sandy and good for red bricks, and the remainder—the usual stiff, plastic material—for “stocks.” Mixtures of this clay and the Bagshot sands found above it make excellent bricks.

At Wokingham, an outlier of London clay forms a good brick-earth when mixed with the lower Bagshot beds which occur just above it, and is so used by several brickyards in that district.

Near Windsor, the London clay has been much used for brick-making. It extends over a wide area from Stoke Poges southwards over a great portion of Windsor Great Park, and then to the west; a boundary being reached near Dorney and Farnham Royal.

In the southern portion of the London basin, the London clay occupies a large area between Norbury, Croydon, and Beddington Park, and forms the chief brick-clay in that district, though covered with a bed of gravel which is particularly thick at Norbury and Thornton Heath.

At Epsom also—where it forms the most recent of the solid beds—the London clay is very uniform in quality, though somewhat sandy towards the base. Between it and the Reading beds there is a good red-brick loam which is useful though very irregular. This district is important because of its proximity to London as well as on account of the excellent clays at or near the surface.

In the direction of Aldershot, it extends as a band with an outcrop one and a half miles wide from north to south, widening to the north of Guildford and extending for a few miles towards Woking, where it is buried beneath the gravel and silt of the river Wey. To the south of Ripley and Ockham it becomes wider, but at Stoke D'Abernon and Cobham is partly covered by the gravel and silt of the river Mole. Between these places and Mitcham is a large area of remarkably uniform composition, though near its junction with the Bagshot beds it becomes more sandy.

All around Aldershot the London clay is important, particularly in the low undulating ground on the south, as at Weyburn, Aldershot Place, Tongham, Ash, Poyle House and West Wood, the most useful material being found in a zone which is bounded by a line running east and west through Ash, and a similar line half a mile south of Weyburn and Tongham. It is in the more southerly part of this zone that the best clays of this formation are found; the others are tougher and closer, and would require relatively large quantities of non-plastic material to be added, and even then would only make common bricks. Further west, and to the north of Crondall, the London clay is very extensive and useful, though hard and stiff. It could apparently be worked satisfactorily at Redland, Hare Farm, Rye Common, Velmead, and Dogmersfield, particularly to the south of the first three places, where it joins the Reading beds and becomes sandy.

The London clay also extends westward from Worthing (Sussex), forming a syncline at Chichester, and between these towns is concealed by brick earth. At this part it contains hard bands of calcareous sandstone, which form the Bognor Rocks.

In Berkshire, the most accessible portions of London clay are between Twyford and Ruscombe and the outliers at Ashley Hill, the former being gravel-covered, but the last-named free. The higher ground at Tilehurst, near Reading, is an outlier of London clay, the importance of which is obscured by the more valuable Reading beds so abundant in the neighbourhood.

Further west, near Marlborough, the London clay runs very thin and sandy, and is comparatively unimportant as loams and stiff clays abound, the best brick earths being found on each side of the valley.

The *Oldhaven and Blackheath* beds form a band of sands and pebble beds. These beds occur near Blackheath, Bromley, and near Oldhaven Gap east of Herne Bay. They are of small commercial value.

Woolwich and Reading Beds.—These beds comprise a series of mottled clays, coloured sands, and pebbles of a very irregular formation. At Reading and in the Hampshire basin they are mainly of fresh-water origin, but east of London they also contain estuaro-marine remains. They appear to have been deposited by a great river discharging into the Eocene sea near Woolwich, the estuary being occupied alternately by fresh and salt water. As the beds are traced westward they show increasing evidences of fresh-water origin, whilst eastward they become of an increasingly marine nature. These beds are most noticeable in the neighbourhood of the towns whose name they bear, the mottled clays of

the Reading series being highly valued for tiles, finials, and other modelled work (terra-cotta). They are naturally fat, and are often improved by the addition of loam and sand from the same formation.

The Woolwich beds are far less extensive, and whilst well developed at Charlton near Woolwich, near Chiselhurst and Upnor near Rochester, are not found further west than Croydon. They are useful for brickmaking, when sufficiently accessible and free from gravel, but are, unlike the Reading beds below them, of no value for terra-cotta and pottery. Eastwards they develop into the Oldhaven-Blackheath series, and are thickly covered with buff and white sands, though they are used for brickmaking in spite of this overburden.

The Woolwich and Reading beds consist of—

- (1) Reddish, mottled plastic clays, devoid of fossils.
- (2) Alternating layers of sand and grey clay, rich in fossil remains.
- (3) False-bedded sands rich in marine fossils.

The last-mentioned clay is the only one which is well developed in the eastern portion of the basin. It is much used for brick-making near Richborough, Wingham, and Sandwich, the surface sand being first removed.

In Essex these beds occur only at the extreme south (being used in connection with the Thanet sands for the manufacture of bricks and cement). They also extend in a thin, irregular line from Ware (Herts) to Ipswich (Suffolk).

In Suffolk the fine sands and loams of the Reading beds form an admirable material for mixing with London clay, though the loams are often used alone. Material derived from the Red Crag (limestone) formation is often a source of trouble to brickmakers in Suffolk. It is a curious fact that the solid beds of clay in Suffolk are scarcely touched by brickmakers and potters, superficial drift beds only being used. The same remark applies to Norfolk.

On the northern portion of the London basin, between South and North Mimms and Hatfield Park brickyard, there is about 20 feet of London clay, 7 feet of loam of less value, and 23 feet of Reading sand with layers of clay (the whole being capped with several feet of gravel); but, with the exception of three small old brickyards in this district, these have not been developed.

Reading beds between Aldenham and Radlett are sandy and laminated, the mottled clays being thin and not so stiff as in other districts. These sandy clays make good bricks where they are free from "race" (limestone), which is often abundant in

this portion of the deposit. Five miles to the north-east of Rickmansworth are three outliers—at Abbots Langley, Redmont, and Levenstock—of Reading clay, which have been used for brickmaking. About four miles to the north-west of Rickmansworth are three other outliers—covered with gravel, but otherwise excellent brick earths—at Micklefield, Sarratt, and Dars Lane.

There are other outliers at Chesham, Digswell, Braintfield, Sacombe, and St Albans.

In the brickyard near Bricket Wood is a layer of about 40 feet of boulder clay and 15 feet of gravel and sand, resting directly on the chalk. This clay requires washing to remove the stones and lime compounds; it then makes good bricks.

Between Rickmansworth and Harefield, the Reading beds lie on the higher ground, though with a stragglng outcrop, and run northwards on the hillsides. Near Perry's and Moor Park there is a large patch of Reading beds (about two and a half miles long), which—unlike most of the formation of the district—is entirely free from a capping of London clay.

A little further south, at Harefield, the Reading clays consist of 8 feet of grey loam and 15 feet of mottled grey and red clay, with alternate layers of sand and clay beneath, but the layers vary considerably in thickness. If carefully blended with the sands, these clays are admirable, the large variety of materials enabling sandy bricks or clearly ringing tiles to be equally well produced.

Somewhat further west, and immediately south of Amersham, two outliers of Reading beds and London clay at Cold Harbour and Frog Hall occur. They are covered with gravel, but have, nevertheless, been used for many years for brickmaking. To the east of Chalfont St Giles several other large outliers of Reading beds again crop out, but the London clay and superficial earths are of more commercial importance.

The Reading series is remarkably well developed around Beaconsfield, though much covered with gravel in places, except in the south, as at Hedsor, Brook End, and near Poyle, and intermediately at Hickenham. The beds here are 15 feet to 20 feet thick, and are composed of mottled grey, brown and yellow clay, passing down into bright ochreous, grey and brown clays, and chalk. About one and a half miles east of Beaconsfield is a little pipeclay in an 8-foot layer of sand.

Still further south—between Mumford and Edgerly Hill, and expanding to both east and west—the Reading beds are extensively exposed, and, near Hedgerley, these clays are about 30 feet thick,

and overlies a 5-foot seam of refractory earth suitable for domestic fire-bricks.

At Windsor, the Reading beds crop out in the centre of the town, and there is an important boundary of the series between Bray and Burnham, but the local brick earths are covered with gravel.

South of London, the Reading beds are covered; they were formerly accessible on the north and west of Croydon, but building operations have stopped their use near this town.

From a line joining Hog's Back, Merrow Downs, Great and Little Bookham, Ashted, Epsom, and Ewell the beds run in a southerly direction. In this part of Surrey the formation presents its usual character of mottled clay, sand, and loam. Near Guildford the mottled clay is red, green and yellow, but near Leatherhead, Ashted, and Epsom the beds are less mottled and more sandy. (A refractory clay is found at Epsom and Ewell which has a good reputation for gasworks purposes.) There is a large outlier at Knowle Hill. Large outliers of Thanet sand occur to the south-west of Banstead at Walton-on-the-hill, Warren Farm, and on Mickleham Downs. These are capped by mottled Reading clay.

The Woolwich and Reading beds run almost due north and south at Epsom, and may swell out to many feet in one locality and decrease rapidly in another. These consist (as usual) of plastic mottled clays, loams, and sands, the first two being excellent for red bricks, tiles, terra-cotta, and coarse pottery. Few stones are found. At Ewell the total thickness of clay in these beds is about 20 feet, the intermediate sand layers about 10 feet; but, as already noted, the beds vary considerably in thickness in other parts of the same district.

In the district around Aldershot, the Reading beds of mottled plastic clay are also well suited to the manufacture of coarse pottery, bricks, and tiles, though they are but little used. They crop out in a narrow band running east and west about a mile from Weyburn and Tongham.

In Berkshire the Reading beds usually lie too far below the London clay to be available, except for an inlier near Mount Scippot to the south of Maidenhead, which brings them to the surface.

The greatest development and most famous portions of these clays are in the immediate neighbourhood of Reading, though their extension further west to Hungerford and Marlborough is important.

In the Reading district these well-known mottled clays and

sands are of such value that their name is synonymous with good earths for bricks, tiles, finials, moulded work, etc., and in this area they form one of the best red-burning earths in the country.

The main mass lies to the east, west, and south-west of the town, but large outliers occur on the chalk downs to the north at Caversham Park, Chause Heath, Rotherfield, Peppard, and between Whitchurch and Woodcote. The higher ground around Tilehurst is an outlier of London clay. The alluvium running east and west on the north of the town is practically useless. Most of the clay has a superficial covering of useless gravel and stones.

Although the general characters of the different beds are tolerably constant, they vary continually within small limits, and many sections would be necessary to convey an adequate idea of these variations, but a classical section which gives the best obtainable average is that shown in fig. 8, at Katesgrove kiln. Owing to this great variety each stratum must be kept distinct, and they must be blended with great care, as if mixed indiscriminately, the goods will vary too much in colour.

To the east of the town of Reading the beds are somewhat different in character, the mottled clays being covered with a thicker layer of brown and red clays and sand, all of which are of little value.

Around Marlborough the plastic clays of the Reading series lie in patches on the highest ridges on the chalk downs, and form the remnants of the main Reading series which once covered the chalk. In Marlborough Forest the beds are too thin and too disturbed to be valuable, though clayworking has been carried out there for many years in spite of difficulties. To the south-east of Marlborough and south of Hungerford they will probably prove more useful in the future than in the past, though many brickyards have been opened there at various times.

In this district, the Reading beds consist chiefly of a sandy clay, slightly mottled in parts, with light mottled clay above, separated by a 5-foot layer of sand; but nearer Newbury the beds become richer in mottled clay and less sandy. The largest outcrops are at Thatcham, Oare, and Bucklebury; between these they are capped by Bagshot sands, though these sands are best developed to the south of the river Thames. This district forms the western limit of these important clays.

In the Isle of Wight the most valuable clay is the Reading bed, which occurs in a narrow strip running right across the island a little to the south of Newport, and is much used for bricks and tiles. Parts of this deposit are even more plastic than the mottled clays at Reading itself, and are exceptionally free from sand. With

care, they form an admirable material for most articles made of red-burning clay.

The best portions of the Reading clays are exceptionally plastic

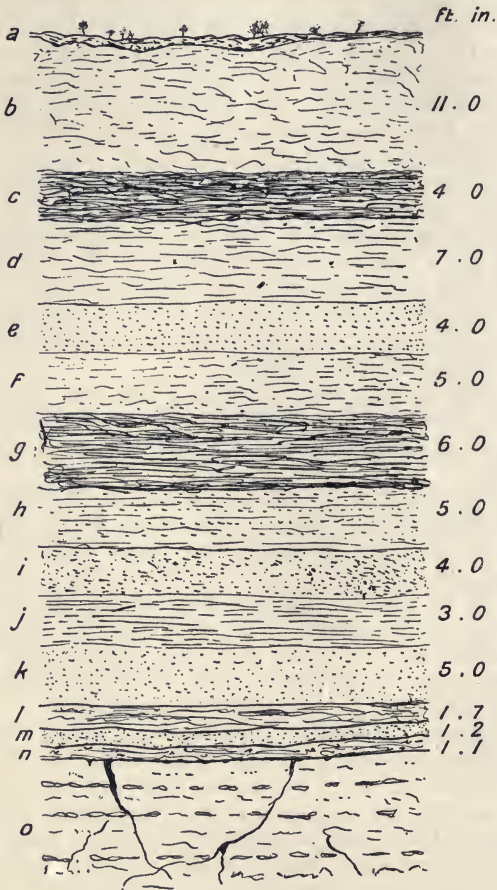


FIG. 8.—Section at Katesgrove Kiln, Reading. (Harris.)

a = clay, sand, and gravel.
 b = soft loam used for "rubbers."
 c = dark red clay, partly mottled.
 d = light red brick clay.
 e = fine sand used for tiles.
 f = white sand used for bricks.
 g = dark red clay mottled with blue,
 used for bricks.

h = lowest brick clay and sand.
 i = white sand used for bricks.
 j = "fuller's earth."
 k = yellow sand.
 l = clay with selenite.
 m = sand with green grains.
 n = brown calcareous clay.
 o = chalk.

(far more so than most Midland clays), require to be very carefully burned, and can only be advantageously worked by those who will take the trouble to study them very fully, and who realize that exceptional care is needed to obtain the best results.

These clays are not suitable for making large numbers of common bricks—in fact, they are too good—but for producing modelled work and tiles they are extremely valuable.

The *Bognor* beds are chiefly composed of loams of marine origin. When carefully selected they may be made into excellent bricks, but they have been somewhat neglected by brickmakers.

The **Thanet Sands** are, as their name implies, well developed in the Isle of Thanet. They are largely composed of quartzose sand with irregularly distributed layers of clay and glauconitic loam, particularly in the lower portions. They are not much used except at Grays (Essex) and Sittingbourne (Kent).

In East Kent they are characteristically sandy above, but pass downwards into thin beds of good brown clay and loam, and in some parts to a useful sandy marl.

Between Erith and Crayford they are less noticeable, and contain sandy and gravelly portions at Crayford, but are nevertheless the best exposure of the “Kent Valley deposits,” and are used in large quantities. At St Mary Cray they again thicken, but the abundant Woolwich beds above them are naturally preferred. Much of the apparently sandy matter is, however, used for brick-making, as it “binds” well in the kiln on account of the fluxes present.

Owing to the frequent occurrence of “pipes” or “swallow holes” of clay in the chalk, care is necessary in boring, lest an entirely erroneous idea of the extent of this deposit is obtained, as the depth varies with remarkable suddenness in some places.

Around Faversham the Thanet sands are of little value, but they are covered with an alluvial brick-earth of good quality, though much of that close to the town has been removed and used.

A little to the east around Boughton-under-Blean is a large area of good clay, covered with about 4 feet of useless gravel in the Woolwich beds which overlie the Thanet sands at this place.

At Sittingbourne and west of Teynham the loams lying above the Thanet sands and chalk have long been used for brickmaking. They are covered with a useless gravel-layer of very variable thickness, which is sometimes a source of trouble.

In Essex the Thanet beds only occur in the extreme south and in a thin irregular line from Ware to Ipswich. At Grays and

Tilbury they are specially suitable, and much used for brick and cement manufacture, but in other districts they are often missing.

Towards the south and west of the London basin the Thanet sands become of small importance, the only valuable outliers occurring in Surrey from the south of Croydon to Beddington (where it is covered with gravel), and to the south-west of Banstead, at Walton-on-the-Hill, Warren farm, and on Mickleham Downs. In Berkshire their place is taken by a loamy deposit known, geologically, as the "basement bed" of the Reading series.

The **Boulder or Glacial Drift**, which is the chief Pleistocene deposit, forms a "blanket" over a large part of the country, particularly in Northern England (fig. 9), Scotland, and Ireland (see *Boulder Clay* in Chap. VI.). It is much used in Lancashire, at many parts on the Yorkshire coast, near Cleveland, and at other places where no better clay can be obtained. It is a product of the period known as the Great Ice Age, when, according to a theory at one time generally held, the land was gradually submerged to the extent of several thousand feet, during which the surface was covered with a thick and heavy ice mantle, which, in its seaward descent, smoothed and grooved the rocks over which it passed, forming the lower boulder clay, while masses laden with boulders and gravel from other regions were dropped by icebergs over the submerged surface. A gradual elevation then appears to have taken place, and glaciers flowed periodically over the land. The newly exposed surfaces were wasted by waves and formed, with the material brought up by the sea, the upper or "pebbly boulder clay." The material so deposited varies enormously in composition, but is readily recognized by the peculiarly marked boulders and other stones found in it.

The mode in which boulder clay has been formed is really far more complex than appears at first sight, and some eminent geologists maintain that it has not experienced submergence beneath the sea, but that, on the contrary, it is entirely the product of land-ice, and that throughout the glacial epoch the British Isles generally stood at a high level, so that the ice which almost buried them flowed out on to the beds of the North and Irish Seas, the boulder clays representing its moraines, and the stratified sands and gravels being deposited in lakes formed by the rivers which were dammed up by ice-sheets.

According to the "land-ice" theory, prior to the glacial period, the climate grew gradually colder and snow accumulated, forming glaciers which descended into the Irish Sea from several directions, viz. Ireland, North Wales, the Lake District, and the Clyde. As

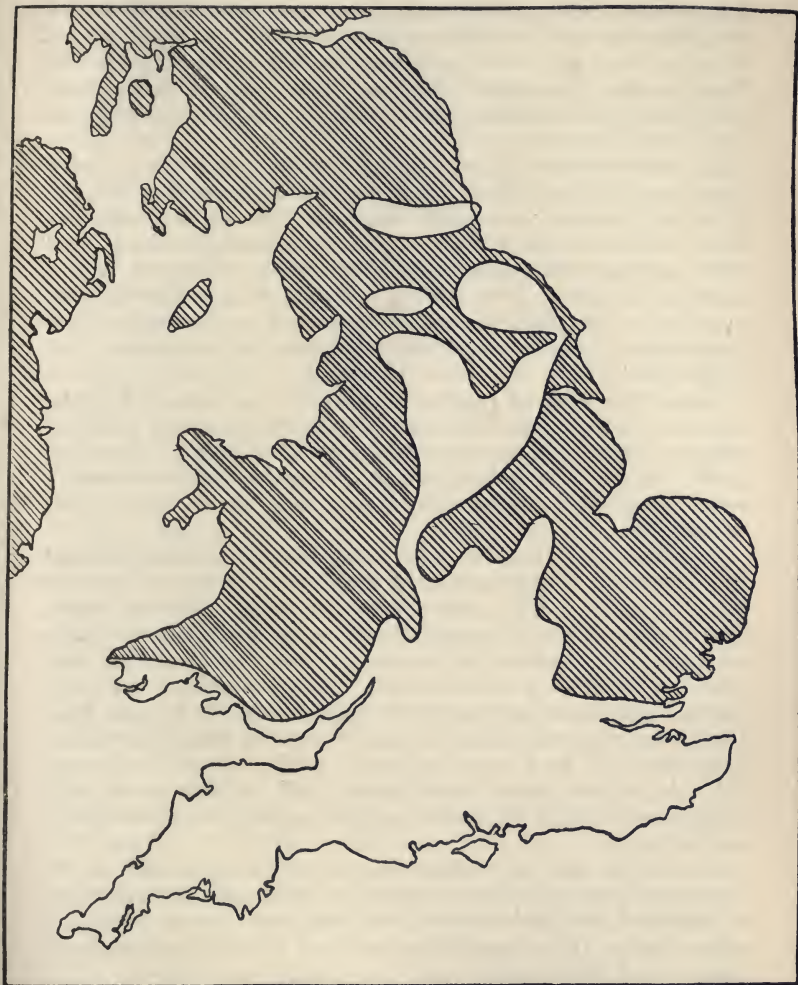


FIG. 9.—Distribution of Boulder Drift. (*After Wright and Bonney.*)

the glaciers increased, they filled the Irish Sea, covering Snaefell in the Isle of Man, and were eventually diverted, one part flowing down Teesdale and another into the North Sea. Simultaneously a

huge glacier from Scandinavia appears to have occupied the bed of the North Sea, and on reaching our shores united with the glacier from the west and flowed southwards, thus accounting for the Shap granite "brockram" and other Lake District rocks being found mixed with Scandinavian granite in the glacial deposits of East Yorkshire, etc.

The erosion caused by such glaciers is not alone due to direct pressure of the ice, but rather to the sand, stones, and boulders which fall between the ice and the rocks over which the glaciers move. These materials become partially embedded in the ice and effect a powerful cutting and grinding action as they are carried or pushed forward. The softer rocks are ground to gravel, sand, or clay, but the harder ones are smoothed and scratched with characteristic lines or striæ which indicate the direction of flow of the glacier.

Most of the material removed is carried at the sides and on the surface of the glacier, and when deposited forms a long irregular ridge or *lateral moraine*; some material falls through the ice on to the bed and, with other material occurring there, is termed a *moraine profonde*; the material deposited at the end of a glacier is called a *terminal moraine*.

The drift left by the ice sheet usually has an undulating surface with mounds and depressions, the latter being the sites of earlier lakes or marshes. The mounds are composed chiefly of stones, gravel, and sand, with some clay. In some cases the bulk of the clay is near the surface, the interior "cores" being almost clean gravel and sand. A series of these mounds—part of the great terminal moraine of the North Sea glacier—extends in a line from Bridlington to the Humber, those at Barf Hill, Coney Garth, and Brandesburton Barf being specially good examples. Though valuable for the gravel they contain, such mounds are of little importance to the clayworker except as sources of non-plastic material.

One of the best sections in this country may be seen in the massive cliffs of Filey Bay terminating in Carr Naze, which attain a height of over 200 feet and are composed almost entirely of glacial drift. Other equally fine sections are to be seen between Kilnsea and Withernsea.

In addition to its erosive action a glacier may, in its passage, crumple the rocks beneath it and fold them in various ways. It may also lift a huge mass of material bodily, transport it for some distance, and may then deposit it; several large masses of Lower Lias shale in the glacial drift in Filey Bay appear to have been placed in their present position by this means.

The "land-ice" theory has now obtained general acceptance (particularly since Lamplugh's work on the *Drifts of Flamborough Head*), so far as the North of England is concerned; as an explanation of the origin of the glacial drift in some other districts the "submergence theory," previously mentioned, appears to be more probable; but, as Professor Bonney has shown in the following examples, both hypotheses involve serious difficulties. For instance, the thickness of the chalky boulder clay alone not infrequently exceeds 100 feet, and though often much less, may have been reduced by denudation. This is an enormous amount to have been transported and distributed by floating ice. The materials also are not much more easily accounted for by this than by the other hypothesis. A continuous supply of well-worn chalk pebbles might indeed be kept up from a gradually rising or sinking beach, but it is difficult to see how, until the land had subsided for at least 200 feet, the chalky boulder clay could be deposited in some of the East Anglian valleys or on the Leicestershire hills. That depression, however, would seriously diminish the area of exposed chalk in Lincolnshire and Yorkshire—where there is little or no evidence of such subsidence, but rather to the contrary—and the double of it would almost drown that rock. Again, the East Anglian boulder clay frequently abounds in fragments and finer detritus from the Kimeridge and Oxford clays. But a large part of their outcrop would disappear before the former submergence was completed. Yet the materials of the boulder clay, though changing as it is traced across the country, more especially from east to west, seem to vary little in a vertical direction. The instances, also, of the transportation of the boulders and smaller stones to higher levels, sometimes large in amount, as in the transference of "brockram" from outcrops near the bed of the Eden valley to the level of Stainmore Gap, seem to be too enormous to be readily explained by the uplifting action of shore ice in a subsiding area. Such a process is possible, but rather exceptional. Submergence readily accounts for the above-named sands and gravels, but not quite so easily for their occurrence at such very different levels. On the eastern side of England gravelly sands may be found beneath the chalky boulder clay from well below sea-level to three or four hundred feet above it. Again, since, on the submergence hypothesis the lower boulder clays about the estuaries of the Dee and the Mersey must be a deposit from Piedmont ice in a shallow sea, the mid-glacial sand (sometimes not very clearly marked in this part) ought not to be more than 40 or 50 feet above the present Ordnance datum. But at Manchester it reaches over 200 feet, while near Heywood it is

at least 425 feet. In other words, the sands and gravels presumably (often certainly) mid-glacial, mantle, like the upper boulder clay, over great irregularities of surface, and are sometimes found, as already stated, up to more than 1200 feet. Either of these deposits may have followed the sea-line upwards or downwards; but that explanation would almost compel us to suppose that the sand was deposited during the submergence and the upper clay during the emergence; so that with the former material, the higher in position is the newer in time, and with the latter the reverse.

Towards the close of the glacial epoch the deposition of the boulder clay ceased and its denudation began. On the low plateaux of the eastern counties it is often succeeded by coarse gravels, largely composed of flint more or less water-worn. These occasionally include small intercalations of boulder clay, have evidently been derived from it, and indicate movement by fairly strong currents. Similar gravels are found overlying the boulder clay in other parts of England, sometimes at greater heights above sea-level. Occasionally the two are intimately related. For instance, a pit on the broad, almost level top of the Gogmagog Hills, about 200 feet above sea-level and four miles south of Cambridge, shows a current-bedded sand and gravel, overlain by a boulder clay, obviously rearranged; while other pits in the immediate neighbourhood expose varieties and mixtures of one or other material. But as true boulder clay occurs in the valley below, these gravels must have been deposited, and that by rather strong currents, on a hill-top, a thing which seems impossible under anything like existing conditions; and, even if the lowland were buried beneath ice full 200 feet in thickness, which made the hill-top into the bed of a lake, it is difficult to understand how the waters of that could be in rapid motion. Rearranged boulder clays also occur on the slopes of valleys, which may be explained, with perhaps some of the curious sections near Sudbury, by the slipping of materials from a higher position. But at Old Oswestry, gravels with indications of ice action are found at the foot of the hills almost 700 feet below those of Gloppea.

From the mode of its formation and accumulation, glacial drift is, necessarily, a heterogeneous mass of stones, gravel, sand, and clay, some portions of which may be of a sufficiently uniform character to be of value (Chap. VI.). Usually some means of removing the stones and gravel must be employed before large quantities of the clay in the material can be made into anything better than common bricks.

At Ewloe, in the neighbourhood of Buckley, and to a less extent

in some other districts, the deposits of clean clay are so large that they may be satisfactorily used for coarse pottery without any preliminary purification.

Its characteristics and distribution are more fully described in Chaps. V. and VI.

The **POST-TERTIARY** or **RECENT** deposits include all those which have been formed since the "drift,"¹ and include the products formed by the action of the weather on many of the older rocks. They cannot be classified according to their position, but are preferably arranged according to the chief agent concerned in their origin, thus:—

TABLE X.

Recent.

- (a) Accumulations of sand, gravel, and alluvial silt in river valleys. (See *Alluvium*, Chap. VI.).
- (b) Terraces of gravel, etc., in valleys, marking former water-levels. High-level and low-level gravels.
- (c) Deposits of sand, silt, shell-beds, and vegetable drift in estuaries; forming deltas.
- (d) Ancient deltaic deposits, forming alluvial plains, corses, etc., partly of fresh-water and partly of marine origin.
- (e) Lacustrine accumulations now in progress.
- (f) Lacustrine or lake silts filling up ancient lakes.
- (g) Shell and clay marl formed in ancient lake-basins.
- (h) Littoral silts, sand-drift, shingle-beaches, etc. Raised or ancient beaches; submerged forests.
- (i) Pelagic or deep-sea deposits and accumulations, as foraminiferal ooze, red-clay, burden of icebergs, etc.
- (j) Calcareous deposits, as calc-tuff, travertin, etc.
- (k) Siliceous deposits, as siliceous sinter, etc.
- (l) Saline and sulphurous deposits from hot springs, volcanoes, etc.
- (m) Bituminous exudations, as pitch-lakes and the like.
- (n) Vegetable matter, peat-mosses, jungle-growth, vegetable drift.
- (o) Animal matter, shell-beds, coral-reefs, osseous breccia, etc.
- (p) Soils—admixtures of vegetable and animal matters.
- (q) Elevations and depressions caused by earthquakes.
- (r) Displacements produced by volcanic eruptions.
- (s) Discharges of lava, scorixæ, dust, and other matters.
- (t) Aerial or wind-blown deposits, as the sand dunes of the Lancashire and other coasts, and the material deposited under desert conditions.

The more important of these superficial deposits are known as "brick earths." See *Brick Earths*, Chap. VI.

As the same forces which formed the recent deposits have been at work during the production of all other rocks, it is convenient to

¹ As there does not appear to have been any glaciation in the south of England and Ireland, the term "Post-Tertiary" is preferable to "Recent" in these areas.

describe their action in a separate chapter (V.), provided that the reader bears in mind the fact that in recent deposits the action is simply that of the weather and the means of transport or deposition, whereas in the earlier deposits subsequent reactions have taken place as the result of pressure, of contact with freshly produced volcanic lava, etc., so that a compacting of the mass, often accompanied by partial conversion into crystalline minerals, has resulted.

According to the extent to which these secondary actions have affected the materials originally deposited by rivers, lakes, or streams, the rocks produced are (1) clays, (2) compacted clays or shales, or (3) crystalline materials which must be "weathered" and decomposed before they can form clay.

In this way two main classes of clays are produced, and are termed primary and secondary respectively. The **primary clays** are those which are produced by the decomposition of feldspar, and other minerals as described under "Kaolinization" (p. 34), and these clays are usually obtainable in a relatively pure state by washing them away from any other minerals with which they may be mixed. The purest of these primary clays are the kaolins, and they are distinguished by their white colour, their composition, which approximates to aluminosilicic acid ($H_4Al_2Si_2O_9$), and their relatively low plasticity.

The **secondary clays** are far more abundant, and have, apparently, been produced from primary clays by the action of rivers, lakes, or seas, earth movements, and a variety of other forces, which have all tended to the removal of the primary clays to some distance from their place of origin, and have deposited them in beds of widely varying thickness and purity, and of a density varying from dry mud to the most compact shale or slate. These shales may be broken down mechanically and used as clays, or they may have been subjected to weathering, and by the action of rivers, lakes, or seas, fresh beds of clay may be formed. Owing to the treatment they have undergone, these secondary clays are often highly plastic, but the cause of this plasticity is by no means clearly understood (see Chap. IX.).

Secondary clays are seldom obtainable in so pure a state as primary ones, and frequently they contain so much sand or gravel as to be quite useless without undergoing some process of purification. They are often accompanied by a non-plastic material of great fineness, which cannot be removed by washing on a large scale. This is particularly the case with glacial deposits, the "silt" in which is often in so large a proportion as to prevent these deposits being used even for brickmaking. Other impurities in the secondary clays are described in Chap. VIII.

CHAPTER V.

HOW RECENT CLAY BEDS WERE FORMED.

ALTHOUGH in a previous chapter the *destructive* action of water on rocks has been chiefly emphasized, its *constructive* influence is equally important. The grains of clay and sand which have been produced by the decomposition of rocks are gathered together by the small streams formed by the rain, and are carried away by rivers to lakes or seas, and are deposited according to the density of the particles and the special features of the district through which they are carried.

In the case of rocks rich in felspar and similar clay-forming minerals, clay substance is formed by kaolinization, as described in Chap. I., but this (represented industrially by china clay) is quite different in many ways from other clays. The total amount of "clay" present in the mineral mass (china-clay rock) is seldom large, and is frequently only one-fifth of the whole; the remainder being quartz, mica, undecomposed felspar, and other minerals.

By the action of water and other natural agencies the smaller particles are removed from this mass, and are carried away—often for long distances—before they are sorted out and deposited so as to form a new bed.

There is some evidence that pure "clay" is of approximately the same composition wherever it may be found, but, as it never occurs perfectly pure in nature, the effect of other materials occurring with it is of the greatest importance. The great differences in the characteristics of clays thus appear to be due in large measure to the treatment which the materials composing them have been subjected to since the original kaolinization occurred, than to differences in the primary material. These differences are, however, so great as to warrant the belief that the original material from which many secondary clays have been formed is quite different from that from which the china clays are derived.

Providing the currents of water have their beds in rocks which are too hard to be sensibly affected by their course, the materials in suspension may remain free from any admixture, and on deposition will form beds of almost pure china clay or of plastic clay. But, usually, the clay particles are carried over sandy, calcareous, or ferruginous ground, or mingle with mud of various compositions or with decomposed vegetable matter, or with water containing cementing materials. At a later stage, all these materials are deposited simultaneously and form beds of very varied composition. In this manner are formed ferruginous, calcareous, peaty, and other secondary clays. It is therefore essential in studying clays to examine carefully the nature of their treatment previous to and during their formation into definite beds. A general description of these formations has already been given, but a more detailed account of the characteristics of the clays produced by the special conditions in which they have been deposited is desirable.

These various beds of secondary clay may be conveniently classified according to the chief agent in their deposition, viz. :—

1. *Fluvial*, or deposits formed by rivers.
2. *Glacial*, or deposits formed by glaciers.
3. *Estuarine*, or *Fluvio-marine*, or deposits at the mouths of rivers.
4. *Lacustrine*, or deposits formed by lakes.
5. *Marine*, or deposits formed by seas.
6. *Æolian*, or deposits formed by air (wind-deposits).

Secondary clays deposited by other agencies are not of sufficient industrial importance to merit description here.

Fluvial Beds.—The action of a river in forming deposits at various parts of its course has already been described (p. 26). Such deposits vary in composition according to the nature of the material carried by the water, but at certain parts of all lands through which a river has flowed or flows, there are deposits of "clay," though these are often too impure to be of commercial value.

Such deposits are seldom thicker than 20 feet, and are usually much less, running out in some places to veins of a few inches in thickness. Their composition varies greatly, owing to the irregularity of their deposition, to the material which the streams gather in their course, and the character of such a deposit may change completely in the course of a few feet.

Thus in the district comprising the ancient basin of the river Thames, an examination of the brickyards will show at one place a series of stiff brown or bluish clays, intermediate to sandy clays

or loams; at another, the earth will become much lighter and more sandy; whilst at a third brickyard it may show much gravel, and a fourth may be using a marl or clay rich in chalk. In some places these different materials may be found together, lying on each other in well-defined layers or "strata," and, on sinking several pits into the ground, first one and then the other material will be found, the thickness of each strata varying in a most irregular manner. Fluvial deposits consist chiefly of

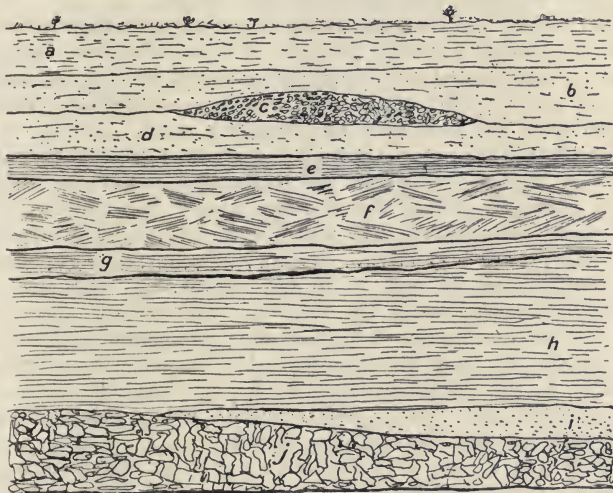


FIG. 10.—Section of Fluvial Brick Earth. (After Harris.)

- | | |
|-----------------------------|------------------------------|
| <i>a</i> , soil. | <i>f</i> , sand and pebbles. |
| <i>b</i> , very sandy clay. | <i>g</i> , laminated clay. |
| <i>c</i> , gravel. | <i>h</i> , stiff clay. |
| <i>d</i> , very sandy clay. | <i>i</i> , sand. |
| <i>e</i> , chalk marl. | <i>j</i> , gravel and sand. |

clay, silt, sand, and gravel, and these materials are sorted out according to their densities, so that masses of strong clays of considerable purity are found, but in such close proximity to other deposits as to cause a difficulty in working (fig. 10). In some other cases the sorting out of the materials has been so complete, that the clays are so far removed from sand deposits as to be unsuited for many industrial purposes on account of their excessive shrinkage.

The larger the river (in past ages) the more likely is it to sort out the materials and to deposit them in sufficiently large

quantities to make them commercially useful. As rivers all tend to cut a channel of increasing depth, unless the land is sinking, it is only natural that clay deposits should be found above the present level of the water; and as the course of a river often changes greatly, it frequently happens that there is a considerable distance between the present watercourse and some of its earlier deposits; though the remains of fresh-water shells, etc., in the deposits and the general contour of the district remove all possibility of doubt as to their fluvial origin.

The twisting and winding course of a river prevents the sorting out of the various minerals borne by it from being very complete, so that at one part of the deposit clay, stones, and gravel may all be quite close to each other, and even mixed together, whilst at another part the clay may be relatively pure. If the earlier reaches of the river flow through materials capable of forming a clean clay, the upper deposits will probably consist of very strong plastic material, and in the deposits nearer the mouth of the river these strong clays will have been diluted with sand and other non-plastic materials. It may easily happen that some of the deposits are so rich in highly plastic clay that they are practically useless, being too "strong" for making bricks and tiles, and yet too impure to be used for pottery manufacture.

If plenty of sand or other suitable non-plastic material is available in the neighbourhood, such clays may be used after careful admixture; but if such material is not obtainable at a sufficiently low cost, the clays are useless.

This is one reason why London clay is so troublesome and dangerous to brickmakers. It shrinks so much on heating, and it is so difficult to dry bricks made from it, that many men have been ruined in the attempt to work it. In addition to this, it has a peculiar stickiness—quite different from true plasticity—which makes it appear to be richer in true clay than is really the case.

In selecting a site for brickmaking to use fluvial clay, it is desirable to keep as near the original mouth of the river as possible, as the higher reaches often contain clays which are too plastic to use alone, and are not profitable to work in the absence of a natural supply of non-plastic material. River deposits are so irregular in composition, however, that no definite rule can be formulated to meet all cases.

Owing to the irregularity and the difficulty of avoiding unsuitable portions of the deposits when working on a large scale, river-deposited clays should be avoided when others are available. When no other clay is convenient, constant supervision of the

men in the pit must be exercised, and some method of removing undesirable ingredients from the clay must usually be adopted. Thus it is often necessary to continue the action imperfectly begun by the river, and to wash the deposit in a "mill" so as to remove the greater part of the stones, sand, and gravel by a process of sedimentation. A typical mill for this purpose is shown in fig. 4 in the author's *Modern Brickmaking*.

In times of *flood* the character of the material carried may be greatly changed, coarser material being borne along—sometimes for great distances—and spoiling any clay deposits with which it may mix.

Glacial deposits are closely related to those made by rivers, and are formed in a similar manner, but the materials composing them are often much coarser, as the solid ice which forms the glacier is able to carry much larger fragments. The proportion of true clay in glacial deposits is often very small, and large boulders (sometimes weighing several tons each) with stones, sand, and gravel, are very abundant. The different materials are often separated into fairly distinct masses and pockets, so that, with sufficient care in excavation, glacial deposits often prove very useful sources of brick and tile clays, though they are always liable to change their character very quickly. At the same time, there is seldom or never any regular stratification, the materials occurring sometimes in masses, and at others are spread over wide tracts, the clays in them being rarely or never laminated.

A characteristic of glacial deposits is a number of "pockets," "nests," or filled-up "ponds." These are usually richer in stones, sand, gravel, or clay than the main deposit, and were probably formed by the ice melting slowly at the places they occur, so that a better sorting of the material has been effected; but no completely satisfactory explanation of their origin has yet been published.

Another characteristic feature of these deposits is the peculiar scratched and grooved surface of the boulders, as if they had been dragged forcibly over each other in one direction, which is generally parallel to the hill ranges and valleys in which they occur (p. 106).

In some districts, *e.g.* eastern counties of England, the glacial drift forms an open, gravelly drift consisting of fragments of all the older rocks, from granite to chalk. In others, as the middle counties of Scotland, large areas are covered with a thick dark tenacious clay ("till") enclosing rounded boulders, as well as angular fragments of all the older and harder rocks, granite, gneiss, greenstone, basalt, limestone and the more compact

sandstones, which are distributed irregularly throughout the mass. In other localities, both in England and Scotland, large areas are covered by loose, rubbly shingle and sand, forming mound-like ridges or flat-topped irregular mounds, as if the originally gravelly deposit had been subsequently furrowed and worn away by currents of water. In other districts the boulders rest on bare rock formations, without any accompanying clays or sands; and at times a single gigantic boulder will be found "perched" alone on some height.

Some clayworkers and many geological writers refer to glacial deposits as "boulder clay." This term is misleading and should be avoided, especially as the word "drift" is now in common use among geologists. If the term "boulder clay" is used at all, it should be confined to that portion of the deposit which has the essential characteristics of a clay, and should not be employed indiscriminately for the whole deposit. Want of care in this direction has occasionally led to much useless expense and annoyance.

The clays and sands in glacial deposits partake of the mineral character of their respective districts; thus the boulder clays of the coalfields are usually dark-coloured and contain fragments of coal, shale, and other carboniferous rocks; in the Old and New Red Sandstone districts the clays and shingly beds are usually red; and in oolitic and chalk tracts they are yellowish or grey.

The clay deposited by glaciers is always troublesome to use, on account of its very irregular character and the large proportion of sand, silt, gravel, and stones it contains. The stones and gravel often consist, in part, of limestone, which is particularly detrimental, as it becomes quicklime in the kiln when the clay is heated, and afterwards swells on exposure to damp air and may disintegrate the bricks or other goods into which it is made. It is, of course, possible to use stone-separating machines, but, as these require the material to be first made into a paste, they are not very practicable unless the larger stones have been previously removed by hand. If the material is fed directly into the paste-producing machine, some of the larger stones are sure to cause serious damage. In any case, stone-separators do not remove the sand, so that for some purposes the material must be washed before use. This treatment is quite effective, but is too costly for most brickmakers, though it is used by some makers of flower-pots and other coarse pottery.

For further information see *Boulder Clay* in Chap. VI.

Estuarine beds are those formed at the mouths of rivers in such positions as have not been materially affected by the sea;

the deltas of the Nile in Egypt and of the Ganges in India being the two best-known examples. Every river has its own estuarine bed, however, though in some cases the sea may have washed much of it away from the shore, and on this account the term **fluvio-marine** deposit is often used. Such deposits consist chiefly of clay, silt, sand, and gravel, with accessory deposits of animal and plant remains, shells, etc. They are of no value industrially unless the sea-level has been lowered since their formation, when they form the edge of marine deposits and may sometimes be employed for brickmaking. The great variety of materials they contain, and the manner in which these are mixed together, renders them of little value, however, as their composition is too irregular to be satisfactory for a brickmaking material, the more so as they are often rich in silt (which is non-plastic), but are deficient in plastic clay.

In Lincolnshire and Northamptonshire estuarine clays of Jurassic formation are used for brickmaking.

The upper estuarine clays north of Great Weldon (Northamptonshire) are remarkably uniform and extensive, though they have not as yet been much utilized in spite of their great value for brickmaking and for tiles, or, when mixed with the Oolite limestone, for cement. Around Kettering and Wellingborough they are better appreciated, though not as much as they deserve. They are blue-black, unctuous clays, usually devoid of stones and well suited for brickmaking.

Loess or *Lehm*, which are abundant in some parts of the United States and in the Rhine Valley, are probably of estuarine or diluvial origin, but may be of æolian formation (see *Loess* in Chap. VI.). They do not occur in commercially important quantities in Great Britain.

Lacustrine beds are those formed by the sedimentation of matter in lakes. They are characterized by a much greater uniformity of composition than beds formed by deposition from rivers, and are usually valuable. The muddy river-water enters the lake and its velocity is rapidly diminished, so that, on flowing out again, it has deposited all the suspended matter and becomes quite clear.

Lakes thus become the great "settling tanks" in which the rivers discharging into them may deposit their burden of clays, sands, and other minerals. The deposit is deepest and coarsest at the inlet of the lake, the finer particles being carried nearer to the centre. As the deposition of the material continues, the lake gradually becomes full and forms "dry land," with a stream running through a portion of it. If the stream be diverted as

the result of some earth movement, a dry lacustrine deposit is formed.

As the deposition of material in a lake is a function of the speed of the water and the size of the particles, the separation of the clay from the sand and gravel is often very complete, the strata of each being clearly defined so long as the flow of the river feeding the lake is fairly constant. In times of storm, on the contrary, the speed of the water is greater, the coarser particles are carried further, and in this way a little sand may be deposited in the clay and a considerable amount of gravel in the sand forming a diluvial deposit (p. 169).

A lake-deposited clay is very difficult to distinguish from one formed by a river, as the fossils may be the same in both cases, and the separation of the materials is not a sufficient guide unless a large area be investigated. Yet the lake deposit is far superior to the other in most cases, as it is more likely to remain constant in composition, and is less likely to be contaminated with sand, etc. A careful study of the shape of the deposit and the disposition of the different materials form the safest means of identifying a lake deposit and of distinguishing it from that of a river.

The "Reading mottled clay" on the edge of the London basin and in the Isle of Wight and Hampshire is a typical lacustrine deposit, and is easily recognized by its striking red-mottled appearance when moist. Another typical lake-deposited clay of great purity is that at Bovey Tracey near Newton Abbot, which is of uniform thickness and differs from most other lacustrine deposits in being apparently derived directly from the granitic rocks of Dartmoor, thus partaking somewhat of the chemical composition of a primary clay with the plasticity of a secondary one.

"Marl" or "marly clay" occurs as a characteristic constituent of many lacustrine deposits, and varies from an almost pure clay to a mixture containing 80 per cent. of chalk. The calcareous material in it is probably formed partly from springs rich in lime compounds, the waters of which find their way into the lake, and partly from fresh-water shell-fish.

Marine beds are of three kinds: (1) those under the sea, or Pelagic beds; (2) those formed on the seashore, or Littoral beds; and (3) those now above sea-level, but originally below it and generally referred to when the term "marine" is applied to clays.

Recent **Pelagic** deposits consist chiefly of fine material, usually rich in clay, silt, and lime, though beds of all kinds occur beneath the surface of the oceans. The soft material brought up from great depths by dredges consists chiefly of calcareous mud or marl (known as ooze) and of red clay, with volcanic dust, decayed sea-

weed, and here and there gravel and sand. These materials are distributed irregularly over the ocean-bed, and a certain amount of sorting-out has occurred, as in lakes, though the ocean and tidal currents disturb these deposits to a certain extent. At a depth of about 800 yards, matter derived from rivers ceases, and the deposit consists chiefly of chalk in process of formation; but at still greater depths this material disappears—possibly being in solution—and an impalpably fine red clay is found below 6000 yards. The recent Pelagic deposits being under so great a depth of water are not available for industrial purposes, but a study of them is essential to a knowledge of those marine-deposited clays which are now above sea-level.

Littoral deposits consist chiefly of sand and pebbles, such as the well-known sea-sand and shingle on the coasts. Recently deposited silt is found somewhat further from the shore, but large littoral deposits of silt are found in the “warp” of the Humber, in the fens of Lincolnshire, Cambridge, and Huntingdon, in the flats of the estuary of the Severn, in Morecambe Bay, and in the reaches of the Solway (see Chap. VI.).

Elevated marine deposits of clay, or those now above sea-level, frequently form one of the most valuable sources of brick and terra-cotta clays. By the slowness with which the material forming them has been deposited, and the large amount of water through which it has travelled horizontally, it has passed through a very thorough process of sorting, and is, consequently, very free from sand and other coarse particles. It may still contain a moderately large proportion of silt, but this is almost as fine as the clay particles themselves and cannot be mechanically separated.

Such deposits are remarkably uniform in character, and, when they have been laid in very deep water, they form a bed of such a nature that, when once the best method of treating it has been ascertained, the operations of making bricks and other articles may usually proceed in an almost automatic manner. This is very strikingly different from river-deposited clays, the composition of which changes every few yards and necessitates a corresponding alteration in the subsequent treatment.

The best known marine-deposited clays in Great Britain belong to the Oolite period, the Oxford clay being perhaps the most famous industrially. They are usually very extensive and of great depth.

Some marine deposits are quite useless for brickmaking, as they contain too much lime, whilst others are too plastic and would need the addition of a large proportion of sand. Hence the

commercial value of such a deposit depends on its containing a certain proportion of non-plastic material, such as silt, or on its being found in a district where sand is cheap, as well as on the uniformity of composition and the absence of deleterious ingredients. Good marine-deposited clays are of great value, but those of an unsuitable nature are worth less than fluvial deposits, for the latter may often be rendered useful by the judicious mixing of the different strata—a remedy impossible with the more extensive marine deposits.

The fear that a marine-deposited clay, such as the Oxford bed, may contain salt, which will spoil goods made from it, is quite unfounded. Although of marine origin, such deposits have been above sea-level for so many thousands of years, that any excess of salt originally present has been washed out ages ago. Clays obtained from the present seashore or from beneath existing oceans are quite different from the marine deposits of the late Lias and Oolitic periods.

Æolian or wind-blown deposits are chiefly of an arenaceous nature, and are represented in Great Britain by the sand-dunes in various parts of the coast. No clays in this country are definitely known to be æolian, though it is not improbable that—were it possible to identify them—some portions of the Triassic and Ordovician clays are of æolian formation. The *Loess* (p. 117) of some areas appears to be an air-transported silty clay, but more usually it is of subaqueous origin.

CHAPTER VI.

THE CHIEF CHARACTERISTICS OF VARIOUS CLAYS AND SHALES.

THE number of different clays is so large as to be practically infinite, and a complete and detailed classification is therefore impossible. In the present chapter some interesting particulars of the most important clays are given, and from these, and a consideration of the site and probable mode of formation, the characteristics of other clays may, to some extent, be predicted. It should, however, be remembered that the word "clay" taken by itself has not the limited meaning which many people attach to it, and no really satisfactory definition has yet been published. The varieties of clays are so numerous—forming an apparently infinite series from "pure clay" itself to the very complex materials into which pure clay only enters in a small proportion, and about which there is some hesitation in classifying them under the head of clays at all—that it is not wise to attempt any hard and fast lines of demarcation. It is generally agreed that the chief constituent of all clays is a hydrogen aluminosilicate corresponding to $H_4Al_2Si_2O_9$, and composed of about 46 per cent. silica, 39 per cent. alumina, and 14 per cent. water, for which the name "clay substance," as originally proposed by Seger, is convenient. Recent researches have indicated that a number of different hydrogen aluminosilicates may form different kinds of clay, but as long as they correspond approximately to the composition just given, so far as the ratio of alumina to silica is concerned, they need not, for ordinary purposes, be differentiated. For this reason, and owing to their really forming the finer debris resulting from the decay of many different kinds of rocks, clays naturally differ greatly among themselves in composition and in properties.

The existence of "clay substance" is due to its remarkable resistance to the action of water and other natural forces—both

physical and chemical,—and this property has played an important part in its production from granite and other rocks.

The chief characteristic of most clays is their plasticity — (though in china clays this is only slight), and their power of becoming non-plastic and stone-like on heating. It is not, however, sufficient to use these properties alone in defining clay, as is frequently done in popular dictionaries, etc.

A definition of clay having fewer objections than most others is : Clay is essentially composed of one or more hydrogen aluminosilicates containing approximately 46 per cent. silica, 40 per cent. alumina, and 14 per cent. water (or an alumina-silica ratio corresponding to $Al_2O_3 \cdot 2SiO_2$) possessing the capability of becoming plastic when mixed with a suitable quantity of water, and losing this plasticity on being heated to a dull redness. It is seldom found pure, but so long as the other materials with it do not interfere with its use for certain industrial purposes, such as the manufacture of bricks, it may, for convenience, be termed "clay."

Broadly speaking, a material which contains less than half its weight of hydrogen aluminosilicate ("clay substance") can scarcely be termed "clay," unless with some qualifying adjective. Thus, a marl may consist of 70 per cent. of chalk and 30 per cent. of clay, or a loam of 55 per cent. of sand and 45 per cent. of true clay, and yet neither of these could be properly known by the name of their less abundant ingredient. In this case the terms "marl" and "loam" are sufficiently comprehensive, but where there is no special ingredient—as frequently happens—disputes of an unpleasant character are liable to arise, especially in connection with the purchase of land for clay working. It is then desirable, as being alike fair to vendor and purchaser, that the deed of sale, or other agreement, shall contain a clause defining the clay as a material capable of being made into bricks, or whatever may be the desired articles, under ordinary commercial conditions. This suggested definition is by no means an ideal one, but it has proved commercially valuable on several occasions, where, in the absence of even so crude a limitation, serious litigation would have resulted.

A rough and ready method of separating clay from the other constituents of a bed is to mix a weighed amount of the dried material with a large volume of water, and to pass as much as possible of it through a sieve having 200 meshes per running inch. The residue is treated repeatedly with clean water until no more material will pass through the sieve, after which the residue on the latter is dried and weighed. The loss in weight represents

the clay and silt with, possibly, some extremely fine sand. It does not, therefore, show the true amount of clay present, but it enables the observer to ascertain the maximum quantity which could possibly be present, and consequently is very useful as a rough sorting test. By allowing all the material that has passed through the sieve to settle, and pouring off the clear water, a slimy mass is obtained, which, on drying, will show in an interesting manner the clay portion of the whole mass, though this will still contain a certain amount—in some cases half its weight—of silt and other (non-clay) material.

Clays vary so greatly in plasticity that definite figures cannot be followed too closely, relatively to their characteristics, but it will usually be found that a "clay" which gives a residue of more than 30 per cent. when treated as above will be of very small value.

This method is not applicable to the harder shales, as these would not be broken up sufficiently by simple treatment with water.

A still further separation may be made by subjecting this fine portion to the so-called "mechanical analysis," but the final product is, even then, not "pure clay," though it is the nearest approach to it attainable with some clays. Thus, "pure clay" does not contain any iron oxide and is white in colour, yet the finest portion obtainable by washing most red-burning clays always contains a considerable quantity of iron and burns to a red colour. With primary clays such as china clay, and to a less extent with pure secondary clays of the ball clay type, the final result of "mechanical analysis" is very similar in composition to Seger's ideal "clay substance," but other clays produce materials of very different composition owing to the other ingredients which are in too fine a state to be removed mechanically.

If all clays were ultimately referable to a standard composition, just as iron ores may be valued by the proportion of available iron oxide they contain, the work of the clay-user would be made much easier. The estimation of the proportion of "true clay" in a material is, in fact, a matter of great difficulty. It is not right to assume that the final product of mechanical analysis is "true clay," as is sometimes done, for some "silts" which are quite free from plasticity would then appear as excellent clays! The best results are obtained by a preliminary separation of sandy particles, as just described, followed by a chemical and microscopical analysis of the finer portion. A determination of the tensile strength of the dried clay, whilst not essential from a

chemical point of view, will often supply valuable information, though not really a measure of the total true clay present. Thus, a mixture of china clay and ball clay may show a low degree of plasticity or a low tensile strength, and yet may be composed entirely of pure clay.

The methods of analysis and testing most suited to the purpose cannot be detailed here. It may, however, be stated that an ultimate chemical analysis of the finer material in conjunction with a rigorous microscopical examination of both the coarse and finer portions will supply sufficient data for the mineralogical composition to be given with sufficient accuracy for industrial purposes, such accessory information as plasticity, shrinkage, fusibility, etc., being ascertained from other tests.

Many attempts have been made to utilize the comparative ease with which china clay and ball clay are decomposed by boiling sulphuric acid to separate them from mica, felspar, and quartz, but the results of this so-called "rational analysis" are not reliable.

Whatever classification is used, it must be remembered that clays which differ greatly in colour and texture may be really similar as regards the burned product, whilst other clays, though apparently very similar in composition when their analyses are alone considered, turn out entirely different when used in actual manufacture. Many clays are of such exceedingly complex composition that their ultimate constituents may appear to be in similar proportions; yet the great variety of ways in which these constituents may be combined makes all the difference in working on a large scale. Thus, to take a simple case, a sample of clay may be divided into two equal portions, one of which is heated to a high temperature so as to burn it completely, and, after cooling, sufficient water is added to make it up to its original weight. If this wet "biscuit" be compared with the unfired clay, the two will appear to have nothing in common except their solidity. One will be gritty and hard, feeling very much like wet sand; the other will be soft and of a silky touch, with sufficient cohesion to form a single mass, whilst the first cannot retain its shape. One will be plastic, the other not; one can be worked as a clay, but the other is quite unsuitable for modelling; yet their composition would be identical if only the ordinary methods of analysis were employed, and the total percentages of silica, alumina, lime, etc., given.

In such a case (which is admittedly extreme) a practical man seeing the two materials could give a far more accurate opinion of their respective values for brickmaking than could a much

better educated chemist who had only the results of analysis upon which to base his judgment.

In other words, practical acquaintance with the materials under widely varying conditions is an essential requirement of the would-be clayworker, and without this experience he cannot reasonably hope to succeed, for the usefulness of a clay does not depend on a single characteristic, but on several, some of which cannot be expressed numerically.

It was at one time thought that clays might be classified as (1) kaolins or primary clays, (2) secondary clays, and (3) clayey earths or rocks, but this classification is not accurate enough to be satisfactory, though it has several advantages where it can be used. There is the further objection to the term "Kaolin" that it already has several meanings, and to add to them would only increase the confusion.

A classification based on the geological formation of clays has little or no value to practical clayworkers.

A classification according to resistance to heat is also unsatisfactory, and, as no scientific arrangement sufficiently simple and comprehensive has yet been devised, the author considers that the interest of most of his readers would be best served by describing the most important clays without reference to any particular method of grouping according to properties.

This is the more necessary as the terms used by clay miners and merchants are in many ways peculiar and even confusing. Thus, "gladyeye," "mediums," and "seconds" worse than "firsts," but "thirds" better than "firsts," etc.; or "cutty" used for making churchwardens, and "pipeclay" never used for pipes, but jam jars; "fine top," used for stone gingers and whisky bottles, always found at the bottom of the pit; and "surface," or rough "bottom" (or "hard ram"), invariably found on the top; "blue ball," among the least blue of all clays; "round" meaning almost square; "square" meaning oval; "best white," which is almost black as coal, but which burns to a snowy whiteness; and a ton, which is not a ton at all, but $22\frac{1}{2}$ cwts., consisting of 70 "balls," which may be of any form except what is generally supposed to be ball-shaped.

Clay-substance, or "true clay," is a term suggested by Seger to indicate the material which forms the characteristic constituent of all earths possessing actual or potential plasticity. It is obtained in its purest form by washing high-class china or ball clays, and collecting the finest particles. Even then it always contains small quantities of iron oxide, lime, magnesia, potash

and soda, but if obtainable in a perfectly pure condition it would, apparently, be composed of—

Silica	46·64	per cent.
Alumina	39·45	„ „
Water	13·91	„ „

which corresponds to $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, the formula of a hydrogen aluminosilicate,¹ the chief crystalline variety of which is **kaolinite**. Many clays are, however, destitute of matter which can be identified as crystalline.

Other hydrogen aluminosilicates may, however, enter into the composition of the purest clays yet obtained, and are considered under the same head as those other substances which, mixed with “pure clay,” form the numerous varieties of “natural” clay.

Dilute acids have no influence on pure clay, but, in a concentrated form, hydrochloric acid and sulphuric acid displace silica from its combination at a temperature of 250° to 300° C. They act in the same way, but more slowly, on any hydrogen aluminosilicate. This “clay substance” is highly refractory (cone 36); its presence in large proportions indicates, therefore, a refractory clay. If much other material (including silica as sand or quartz) is present, the fusion point of the “clays” will be correspondingly lowered.

If the proportion of “combined water”¹ present in the purest sample obtainable is lower than is indicated above, it suggests the co-existence of other materials with similar proportions of alumina and silica, but with less water.

Microscopical investigation of purified clay shows the presence of a well-defined crystalline body with a composition similar to that of the formula just given, known as **kaolinite**, together with a far larger quantity of amorphous material or **kaolinitic matter**. Mellor has suggested the term **clayite** for this amorphous material, which is of the same composition as the other. It is usually more fusible than the kaolinite crystals, and becomes plastic more readily on rubbing with water (p. 158).

A material obtained in such a manner as this kaolinitized matter must always be difficult to identify and describe fully, and it is

¹ Although, on analysis, clay substance appears to contain water, it is improbable that it really does so. As far as can be ascertained, four hydroxyl (OH) groups are present, and these produce water when the clay-molecule is decomposed by heat (see p. 154). As, however, clay substance when heated appears to behave as though it were composed of silica, alumina, and water, the formula given in the text is convenient.

not surprising that different investigators have given widely differing accounts of its properties. This conflicting evidence is largely due to the exceptional smallness and irregularity in the size and shape of the particles.

In the present state of knowledge it is impossible to identify it satisfactorily, and in some ways it does not appear to possess definitely chemical characteristics.

The "kaolinized matter" obtained by washing ordinary clays, such as brown and blue London clay, Oxford clay, "brick earths," etc., has very little in common with that in china clay. The microscope shows that in the majority of such clays scales of true kaolinite are few and far between, that opaque mud-particles (clayite) are more frequent, and that pieces of highly decomposed felspar are also present. Eliminating all other foreign substances from such clays, the whole of what would commonly be called kaolinized matter, taken together, is still of very varied chemical composition, and is in some places fusible; whereas the corresponding material derived from china clay is quite infusible at any temperature used in the industrial arts. From this it will be seen that the term **kaolin**, applied to the finest particles of clay, is very ambiguous and unsatisfactory as a technical term, as, indeed, is any single word used to indicate matter of so varied a composition.

For these reasons any definition of "clay" must be to some extent unsatisfactory, as, unlike certain ores, clays do not contain a single substance of definite chemical composition to which they chiefly owe their value. Nevertheless, there appears to be in all clays one or more substances possessing the general properties of "true clay" ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), though often with an added plasticity, and it is not improbable that it is this material or "kaolinized matter" which gives impure clays their value to the clayworker; though in some cases the presence along with it of iron oxides, lime, silica, and other materials, may alter its properties so greatly that such clays may be commercially valueless. This is one reason why such troublesome difficulties arise in dealing with certain clays, as many clayworkers are unable to overcome the influence of some characteristics met with in the raw materials which they wish to use.

The nearest approaches to any single constituent which may be regarded as the essentially characteristic one in a clay are: (1) the material which is obtained by carefully washing the purest clays in a stream of scarcely moving water, and (2) the hypothetical clay-substance obtained by calculating the impurities in a clay into their probable mineral-forms (as felspar, mica, sand), on

the assumption that any true clay present will have a composition corresponding to $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

Both these are open to the objection that the material obtained by washing is never pure hydrogen aluminosilicate, and a hypothetical substance is an unsatisfactory basis for valuation, particularly if care is not taken to ascertain the precise mineral-forms in which the impurities exist. Thus, it is usual in this country and in Germany to express the impurities in china clay in terms of felspar, but in France they are represented as mica. As the best commercial china clay rarely contains felspar, but usually contains a little mica, the French method is preferable; though the only reliable one is to ascertain, as far as possible, what minerals are present. This is often a matter of considerable difficulty.

The method proposed by Seger (decomposition of the clay by treatment with boiling sulphuric acid) is less satisfactory than the method suggested by Fresenius, of calculating the various bases into appropriate minerals from the results of an ultimate chemical analysis. If this latter method is applied to the material obtained by washing commercial clays, the errors involved are usually too small to be of commercial importance.

The purest clays obtainable commercially are "selected" china clays, which are but slightly plastic, and "selected" ball clays, which are highly plastic but not quite so pure. For most purposes these may be taken as fully typical of the two chief types of pure clay—the slightly plastic or lean (china clay) and the highly plastic or fat (ball clay).

Adobe clay is similar to "Loess," and is a silt mixed with coarser calcareous matter. It is chiefly found in countries in which streams occur which are usually rapid, but which periodically slacken speed and so carry off only the clay and a few heavier particles to other places.

Adobe clay is seldom found in Great Britain, though the term is not unfrequently used by men who have visited South America or Spain as a general synonym for any mud capable of making rough bricks.

In Devonshire, Cornwall, and parts of Somerset the term *adobe* is used for a mixture of earth, stones, and straw or hair used for the construction of farm buildings. Occasionally the term is applied to the grey clay or earth used in this mixture.

Agglomerate clay is of little value. It is the clayey material which cements together angular fragments of rock—usually of volcanic origin,—and cannot be separated at a sufficiently low cost to make it commercially useful. If the clay is exceptionally plastic, it is sometimes possible to grind up the whole mass and

make it into common bricks, but in this case the stony ingredients must be free from lime.

Alluvial Clay.—All matter washed and collected by the natural operation of water is alluvial. Hence most surface soil is of this nature and is termed *alluvium*, though the term is occasionally used for deposits of considerable thickness, as at Tilbury Docks, where the Thames alluvium is nearly 60 feet thick. Alluvial clay is found near or on the surface of meadow lands, dales, etc., on the site of former lakes and river-beds. Such "clay" often contains a large amount of silt, fine gravel, and other non-plastic material. It is usually highly calcareous, and produces yellow, buff, or white bricks. The phrase is chiefly used to distinguish finely divided clay from shale or other rocks.

Recent alluvial deposits are found chiefly in East Yorkshire, Lincolnshire, Cambridgeshire, Nottinghamshire, around the Wash and on the coasts of Suffolk and Essex, and in Kent and Sussex, Somerset and Lancashire. In Ireland the peat-bogs and the clays below them are largely alluvial in character.

Portions of the following alluvial deposits are suitable for brick and roofing tile manufacture, though in some districts the presence of superior clays prevents their being used. The Vale of Pickering, *i.e.* from Helmsley due east to near Filey, and from Pickering due south to New Malton, is entirely alluvial, the former being separated from Holderness by a strip of chalk. Alluvium in the Vale of York extends from a little west of Thirsk to York, forms the southern bank of the Tees, and thence south to Saltburn. From York it covers an area widening out to Market Weighton and Monks Fryston, and thence extending south-eastwards to the north-west of Lincolnshire and north-east of Nottinghamshire, except along the coast of Yorkshire and for some distance inland, where the glacial drift predominates. Alluvial clay also covers the whole of Holderness and the area on the north bank of the Humber from Beverley to Hull, and then south of the railway to Skeffing. Bricks made from the alluvium found between the Witham and the Humber swell badly on burning. On the south bank of the Humber, alluvial clays occupy a roughly rectangular patch of country extending from Goole to Haxey and completely surrounding the Isle of Axholme. Another long strip of alluvium occurs on the banks of the New River and extends to within six miles of Market Rasen.

The drier portions of the Fen districts of Lincolnshire, Cambridgeshire, and parts of Norfolk (from Eccles to Beccles), extend (with some irregular patches of Oolite) as far south as Cambridge, east to Methwold and west to near Stamford. In

Nottinghamshire the alluvial clay is largely confined to the north-east, on the banks of the Idle and the Trent. The latter river has formed a long strip of alluvium about two miles wide, extending south to south-west from Gainsborough to Newton Solney near Burton-on-Trent. At Trent station the strip widens northwards to near Derby (though this town is chiefly on the Trias formation), and south to include about five miles of the river Soar.

The north-west of Somerset between Clevedon and Ilchester is largely alluvial, but large runners of Lias and Trias give this part of the county a very irregular structure.

Wales is practically free from alluvium of notable depth, except for a small patch at the south of the mouth of the Dovey near Llaneyfelyn, and the northern coast of the Bristol Channel from Portskewet to Cardiff. In Suffolk, deep alluvium deposits only occur to a very limited extent on the coast between Aldburgh and Bowdsey, but they continue in an irregular manner along the banks of the Crouch, the Blackwater, the Thames, the Medway, in the southern portion of the Isle of Sheppey, at Faversham, in an irregular-shaped area extending from Oldhaven to Deal and the Marshes between Hythe and Rye, where they are specially valuable.

Another alluvial area of some importance occurs at Eastbourne, extending northward from the coast at Westham to near Hurstmonceaux.

Alluvial clays vary greatly in composition, and may be either valuable or worthless to the clayworker, according to the nature of the material, some being highly calcareous. Unfortunately the term alluvium gives no idea as to the composition of the material, but only as regards the manner of its accumulation. As will be seen from the frontispiece, brickworks exist in all the areas mentioned above. Agriculturally, alluvial clays usually form good, rich soils.

In numerous instances of vales filled with glacial drift or boulder clay, the latter is termed alluvium, though a closer examination will show that it is of glacial origin. Hence the term "alluvium" when used by some writers must be understood as referring to superficial deposits as distinct from solid beds, rather than to those of definitely alluvial origin. Thus the thick deposits of clay in the neighbourhood of Filey are commonly termed "alluvial," yet the ice marks (*striae*) on the boulders in them and the nature of the boulders themselves clearly indicate that this material is of glacial and not alluvial formation.

Further information on alluvial clays will be found under the caption *Brick Earth* (p. 144).

Alum shales are described under *Shales*.

Alumine clay, both white and black, is used for the manufacture of ultramarine, alum, etc. It may be regarded as an inferior quality of Devonshire ball clay, but the term is sometimes extended to cover any clay used for the manufacture of alum. It is sometimes termed alum-maker's clay.

Ammonite clays are those in which ammonite fossils occur in noticeable quantities. They are chiefly found in the Middle Oolite and Lias, and are geologically important in the identification of clays and other rocks. The ammonites derive their name from their resemblance to the horns on the statue of Jupiter Ammon. In East Yorkshire they are known as *St Hilda's Snakes* (p. 79).

Ball clays are chiefly of Tertiary origin (see p. 81), though in North Wales and Derbyshire there are considerable deposits of black and white ball clays which are distinctly different from those of Dorset and Devonshire.

The principal deposits of Devonshire ball clay are in the south of the county, near Newton Abbot and Kingsteignton; those of Dorset are in the district known as the Isle of Purbeck, where the river Frome and its tributary stream, Poole Harbour and the English Channel, practically enclose Hamworthy, Wareham, Goathorn, Corfe Castle, and Swanage. The Purbeck strata (p. 68) include three marine beds, four surfaces which have been dry land, and a large number of what were once fresh-water beds, due to a long and wide river coming from the far north, which at one time flowed over this district. In addition to these, there are Oolite sands, limestone and marl beds, chalk beds with and without flints, and beds of clay.

Ball clays are remarkably plastic, and contain so little iron that they are largely used for the manufacture of white ware. The Devonshire ball clays are usually slightly lower in iron than those from Dorset, but the difference in the colour of the fired ware made from each is not great.

Before firing, ball clays are dark-coloured—sometimes approaching black,—owing partly to the organic matter they contain, which probably has some connection with their extraordinary degree of plasticity. Ball clays often contain 3 or 4 per cent., or even a larger proportion,¹ of carbon in the form of lignite or other organic matter, chiefly of vegetable origin, though this is seldom reported separately in analyses, being included in "Loss on Ignition."

The upper beds of the clay frequently contain a considerable amount of sand, and the best quality is only found at a considerable depth. The latter is unctuous, and is free from sand and

¹ Some of the black Devonshire clays contain as much as 15 per cent.

grit. A good ball clay will always pass readily through a 100×100 sieve when made into a slip with water, and most of the best qualities will leave only an inappreciable residue on a 200×200 sieve. When heated moderately, it becomes white and remains absorbent, but when subjected to intense heat it is rendered as hard as steel, becomes yellowish in colour, and sufficiently vitrified to be non-absorbent.

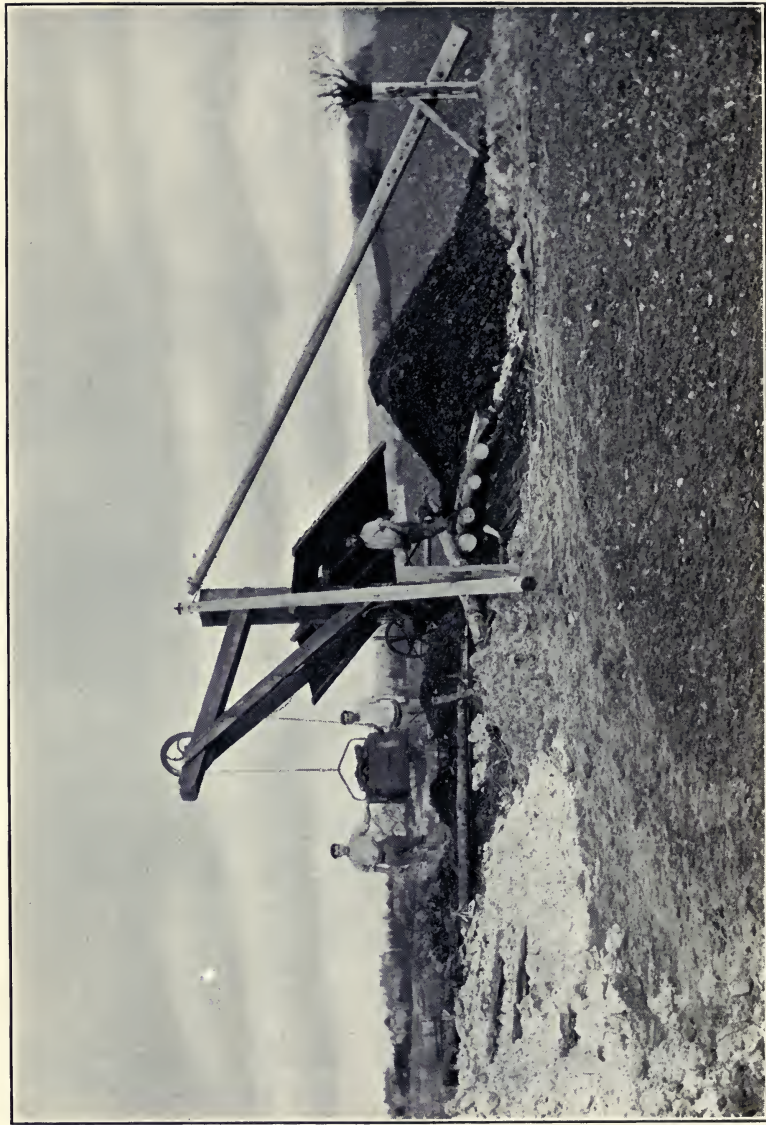
In chemical composition the ball clays do not differ greatly from the china clays, except that they often contain a rather larger proportion of alumina and iron, are more vitreous when fired, but do not burn so white as the china clays. When freshly dug they contain upwards of 30 per cent. of water,¹ of which about 20 per cent. is removed on drying at 100° C., but the remainder only at a dull red heat.

As ball clay is usually stored in open sheds, the quantity of water will vary much, according as the season is summer or winter. The difference between the ball clays and china clay is much more in their relative plasticity than in chemical composition. Though ball clays are somewhat richer in alumina, it is generally thought that china clays have been formed at the place where they are found, or have only been carried a short distance away. Ball clays, on the contrary, are found away from the granitic rocks from which they are supposed to have been primarily derived, and have, in the course of their travels, been so treated that they have gained enormously in plasticity without any noticeable change in composition.

G. Maw and others consider, however, that the ball clays are not derived from the Dartmoor granites, but from the chalk to which they are in close proximity, the chalk itself having been removed from them by the action of carbonated water.

The conversion of china clay into ball clay (if it ever occurs) is a process requiring several hundred years, and it has never been successfully imitated artificially. Various experimenters have been able to increase the plasticity of china clay slightly by drastic methods of treatment, but these methods are too costly to carry out on a commercial scale. Ball clay may sometimes be found in so pure a state that it cannot be distinguished chemically from china clay, but its enormous plasticity (which is a physical characteristic and has nothing to do with its ultimate composition) cannot be reduced to make a true china clay, though a material remarkably similar may be obtained with a mixture of burned and raw ball clay. Physically, ball clays differ from china clays in their great plasticity and in their shrinkage when heated.

¹ See footnote on p. 126.



Mining Black Ball Clay at Newton Abbot.

(Photo, by G. C. Bishop, Esq.)

They are also more fusible than china clay, and as they differ greatly amongst themselves, it is advisable to test each consignment before use.

Ball clays are frequently quarried in open workings, but sometimes the overburden of soil, sand, and other useless material is so great that mining is preferred. In some cases, even when the overburden is very great, it pays to remove it with a steam navy so as to obtain greater accessibility to the ball clay, the cost of removal being less than that of mining and timbering. This is particularly the case where old pits are being re-worked.

When these pits were first cut, the clay men saved but a small proportion of their "get," and the pit when "cut" was filled with clay which, though useless then, is to-day eagerly sought after. Some of these old pits have been cut in shelves, and ledges of clay still remain. Some have been mere surface workings; a horse and cart has been driven down an incline after the clay, and "legs" of clay have been left for supports. Now ledges and legs are all cut and shipped. At the present day the clay is heaped at the pit's mouth, on a bed-place formed of a few slabs of wood, easily moved from pit to pit. Once the bed-places were made of good clay, two balls thick, and containing perhaps twenty tons of clay, and a fresh bed-place was made for every pit. These old bed-places are also searched out. Some of the old pits have only been cut a few feet, and so small a quantity taken that it seems strange they should have been cut at all. In some case the first "batch" has been cut half way across. That the remaining half is "corney," or that there is "iron in the clay," throws some light on why the pit was not cut right down, but does not prevent it from being worked now.

On each side of their big pits the old miners left about 12 feet of clay, partly for safety and partly to keep their pits clean. These four sides of the old pits are now worked. Great ingenuity is often shown in tracing out a "foreside," as the position of the old pit must be accurately determined, for, if a half of one side and a half of another side is mistaken for a complete side and worked, a true foreside might be cut in half and a good patch of clay spoilt. The old pit is usually traced by the "wreath" that has been used on its sides. In some of the older pits the "wreath" was largely willow, etc. This has taken root, and many pits are marked by curious square hedges.

In spite of the difficulty in locating the old foresides it pays to search for them, for they yield some of the best clay, as the old workers took the largest bites in the very best of the clay. Those firms which work the foresides have, however, the dis-

comfort of old works around them. Sometimes old pits have been pumped out and large quantities of clay found. They had been deserted in consequence of water troubles, but with improved facilities can now be worked satisfactorily.

The clay, which occurs as a stiff plastic mass, very difficult to dig, is cut into rectangular or cubic blocks or "balls" weighing about 36 lbs. each, and measuring about 9 inches by 6 inches by 5 inches. It is from these that these clays derive their name. The men work in three sets, one cutting lengthwise ("long scoring"), another cutting at right angles ("thwarting"), and the third (diggers) following and cutting at a depth of about 8 inches with a wide, heavy tool, kept lubricated by now and again dipping its blade into water. These balls, selected according to quality, are raised to the surface by hand or steam power, and are then taken to the stores by sliding them down a shallow trough or toboggan, or by means of tipping waggons hauled mechanically.

The practice, adopted in coal mines, of a central shaft with many horizontal headings is only seldom adopted in mining ball clay; the commoner practice is to sink a fresh shaft as soon as the distance to which the clay has to be carried underground becomes inconveniently great.

After mining, the clay must be stored in heaps to weather, or in warm cellars, some clays being improved and others damaged by frost. It is important that the heaps should not be placed near hedges or trees, and before being "heaped" the clay balls must be pared and scraped. The alleged inferiority of modern ball clays is sometimes attributed to the employment of youths for this clay-paring in place of the much older and more careful men who did it in past years.

During the formation of the heaps the clays are blended or mixed, some firms priding themselves on the skill of their workmen in this connection; and some curious tales are told by the mixers with regard to the "strange" requirements of the potters.

In Devonshire, the thickness of clay is so great that the bottom has not yet been reached in some districts; but in Dorset it is more usual to find deposits of 15 to 20 feet, or even less. In some parts the total depth of clay is far greater, but much of it is too impure for potter's use and can only be employed for drain-pipes and coarse stoneware.

At Wareham, where the best Dorset ball clays are obtained, mining is necessary. At Messrs Pike Bros.' "Furzey Ground," for example, the shaft is about 120 feet deep, and the "cuttings"—which are generally about five feet high—extend beneath a large

pool of water of considerable depth: consequently the mining operations are attended with great difficulty. The clay, on being extracted from the mine, is conveyed further down the sidings to the "heaps," where it is "weathered" for at least two years, being turned over periodically to admit of better seasoning and to ensure evenness throughout.

Some of the better qualities are also obtained by carefully washing the clay and passing it through a No. 200 sieve and then into settling ponds before shipment.

The stoneware ball clays, which occur nearer the surface, are worked by open quarrying.

Ball clays are largely used by potters to produce a plastic and easily worked body. They are really the foundation of most pottery, other clays and non-plastic materials being added to correct any excessive shrinkage or other defects in the ball clay, or to give the mixture special properties. In the manufacture of the best white ware, however, the chief use of ball clay is to impart the necessary toughness, adhesion, and plasticity to the body mixture, only sufficient being added to produce these effects, and an excess being avoided on account of its deleterious effect on the colour.

The colour of ball clays in their natural raw state has no connection with their colour after firing, as the blue (or black) colouration from which the clay derives its name is chiefly due to (carbonaceous) matter which burns away entirely in the kiln, leaving a white or very pale creamy-white mass. Ball clays are, however, never quite so white as china clays.

Some years ago ball clays constituted half the mixture used for making white bodies, and the small amounts of impurities in them prevented pure white effects from being obtained; but more recently they have been largely replaced by the purer china clay, thus making it easier to obtain perfectly white goods.

Ball clay cannot, usually, be substituted for china clay or *vice versa*, because the two give somewhat different results on burning. Thus china clay is used entirely to produce a white material, whilst ball clay (being less pure) tends to produce a yellower shade. For this reason, it is advisable—where colour is important—to use china clay and flint to form the bulk of the material, only sufficient ball clay being added to give the necessary plasticity. The plasticity of ball clay also makes it invaluable in certain cases, whilst the leanness of china clay has advantages in other instances.

The "best selected" varieties of Devonshire ball clay are perfectly black, with a bright, glossy appearance owing to their being impregnated with carbonaceous matter (resembling lignite)

and organic remains, and an ordinary observer would never think they would burn to a good white body. The clay is stacked in rough open sheds with rough wattled sides of heather or straw, or it is placed in heaps on paved floors, on the canal side and wharves, until ready for conveyance by barges to the mouth of the river, whence it is sent to the Staffordshire potteries and elsewhere. It thus undergoes no preparation except slight exposure to weather.

Owing to the small differences in chemical composition and the enormous staining and discolouring effects of small traces of some impurities in ball clays, it is not desirable to rely solely on direct analysis, but to test their softening-points and their colour and general appearance after firing. This latter is best accomplished by making a small saucer or large tile and heating this at a suitable temperature, preferably somewhat higher than that at which the material is ordinarily used. After allowing to cool, the appearance of the fired piece is carefully examined, and any notable differences between it and a similar piece made of clay known to work satisfactorily is duly recorded, and the tested clay selected or rejected accordingly.

The fusibility of the clay is best tested by making a cone similar to Seger cones, and heating it steadily until it bends or fuses as do Seger cones. A convenient method of doing this is described in Chap. IX. and in *The Clayworker's Handbook*, p. 306. When ready for use, ball clays, like the kaolins, should be in a fine state of division, and when made into a slip with water should leave no appreciable amount of residue on a sieve having 120 to 150 meshes per linear inch, when the slip has been worked gently backwards and forwards over the surface of the sieve with a soft brush and an ample supply of water.

For most purposes, that ball clay is the best which will form a paste of convenient plasticity when the ball clay is mixed with the largest proportion of china clay and flint and the smallest proportion of water. Clays which require much water in order to form a plastic paste shrink excessively on drying. A linear drying shrinkage of 12 per cent. on a tile made by casting should be regarded as the maximum ordinarily permissible for any ball clay.

Blue ball clays are the finest in texture, the most plastic, and the purest of the ball clays. When freshly obtained they are yellowish white to drab in colour, and some of them, after exposure, do not show a brown scum or "rust," but become somewhat paler in colour. Sometimes they are spotted or mottled. If allowed to dry partially, they have a smooth, polished surface

when cut. Nodules of pyrites are common, and, unless extracted by careful sifting after blunging, will cause objectionable blotches. The chief characteristics sought in a blue ball clay are freedom from colour when burned, extreme fineness of the particles, great plasticity, absence of impurities, and moderate refractoriness and strength when burned. Blue ball clays, which are not sufficiently pure to be used for "white ware," are largely employed in the manufacture of stoneware. These "stoneware clays" are worked by quarrying where possible, but the system of open shafts is still used by many firms on account of the overburden of sand, which in some districts is 20 feet thick.

Black Ball Clay.—This term is applied to certain white-burning, plastic clays of Tertiary origin, very closely allied to the blue ball clays, but so deeply stained with dark brown carbonaceous matter as to be black when found, and often containing pieces of lignite. The stain is entirely of vegetable or organic nature, and disappears completely on heating, so that some of these very dark brown or black clays, after heating in a biscuit oven, become whiter than burned blue ball clay on account of the carbonaceous matter reducing the iron oxides, also present, to ferrous oxide, which has a less staining power than ferric oxide. Some black ball clays contain over 10 per cent. of carbon, and are difficult to fire, as some of the carbon remains unburned in the pores of the material in spite of the air also present.

Mundic or pyrites occurs as in other ball clays, and should, as far as possible, be removed.

The most valuable black ball clays are found in South Devon and Dorsetshire, the latter usually burning rather less white, unless very carefully selected. They are generally mined from underground workings, only the best parts being removed, but some firms employ a combined method of mining and quarrying (Chap. X.).

Ivory ball clays are found in Dorsetshire, on the north of Poole Trough, Newton, Kinson Park, Branksome, and Parkstone, in Dorset, and near Torrington in North Devon. They are creamy, drab, or blue-grey in colour, and are very similar in many respects to blue ball clay, but contain so much iron that they burn to a yellowish buff-colour. Hence they are quite unsuitable for the manufacture of best white ware, but are in great demand for cheap white ware and for goods of a creamy or ivory tint, such as tiles.

Pyrites occurs frequently, and sometimes makes the clay useless. The characteristic sulphurous odour of these clays when newly cut is probably due to this substance becoming oxidised.

In selecting ivory clay, the degree of fineness and plasticity, the purity of the material, and colour when burned are all-important, and as they are liable to sudden variation, these clays must be carefully tested from time to time in all cases where a uniform tint is desired. Ivory ball clays may usually be distinguished from blue ball clays by their production of a scum or "rust" on exposure, due to the oxidation of the iron salts.

Bath-brick clay is a clay which, when burned, produces soft cream-coloured bricks much used for scouring metals and other cleansing processes.

Modern bath-bricks are made in the neighbourhood of Bridgewater, and have no connection with Bath except that the bricks are similar in colour to Bath stone.

They are made from a slime or alluvial deposit left on the banks of the river Parrett at certain seasons by the ebb of the tidal wave. They are never used for building purposes.

Binding clays play an important part in the manufacture of fireclay and other goods. They are so plastic that they enable a quantity of non-plastic or less plastic material to be mixed with them to form a single mass of such plasticity and mechanical strength as will make a useful product. They are chiefly used to bind together the refractory grog and the lean clays used for the manufacture of refractory blocks, bricks, crucibles, and in the form of ball clay are an essential constituent of earthenware, etc. In foundries binding clays are used to mix with the sand of which cores are made, in order to increase its adhesion and produce a stronger core.

A good binding clay will not only enable a lean clay or grog to be worked readily, but will give to the mixture containing it a greater strength both before and after burning than it would otherwise possess.

Some binding clays only possess one of these characteristics, and, whilst facilitating the shaping of goods of lean material, produce, on burning, so brittle and tender a product as to be practically useless. On the other hand, some china clays have but little influence on the plasticity of the mass, yet greatly increase the strength of the burned product.

Binding clays are usually fat, plastic clays which cannot be used alone for the manufacture of refractory goods; but simple inspection will not indicate whether a clay is a good binding clay. The only way of ascertaining this is to make trials with various proportions of grog, and then to make porosity, tensile, and "fusion" tests on these mixtures. For a binding clay to be satisfactory it must be highly plastic, and not too refractory or

so fusible as to seriously lower the heat-resistance of the mass of which it forms a part (see *Binding Power*, Chap. IX.).

In Great Britain, fire-bricks, retorts, and other refractory articles are chiefly made from raw fireclay, but in Germany a superior article is obtained by the use of non-plastic grog or "burned clay" and a plastic binding clay of the ball clay type. Ball clays which are not sufficiently pure to be used for white ware, but are otherwise of high quality, are, in fact, very representative of the best binding clays.

Binds.—In many collieries the term *bind* or *band* is used as the name of a material; thus "white bind" and "grey band" indicate shales of the colour named, whilst "stony bind" is a sandy shale, and some structureless clays are known as "soft binds," the terms really referring to layers or strata of material, just as miners use the term "seam" to mean a layer or stratum of coal. A "bind" is not a binding clay.

Bituminous clays are, strictly speaking, those which contain appreciable quantities of bitumen, but the term is often used for shales and clays rich in organic matter. This organic matter burns away when these clays are heated in a kiln, but may easily cause overheating, spots, or other defects in the goods. For this reason, clays of this nature should be heated with great caution; apart from this they present no special difficulties in working.

Bituminous shales are often distilled so as to recover the oily matter they contain, as this has a considerable commercial value (see *Shales*).

Black and blue clays are so called from their colour when freshly mined. They owe their colour to the organic matter they contain, this frequently being their chief impurity (see *Ball Clays*, p. 131).

Some clays which become black or blue on heating owe their colour to iron compounds or to manganese. The famous "Blue Bricks" of Staffordshire owe their colour to iron compounds which are largely reduced to ferrous oxide or silicate during the special method of firing adopted in burning these bricks. Several other districts contain clays eminently suitable for the production of blue bricks, but they have not been commercially developed to the same extent as in Staffordshire. On the Continent, "blue" bricks and tiles are obtained by feeding tar or oil into the kilns just before the firing is finished. These materials form a highly reducing atmosphere, and any red iron compounds are, consequently, converted into black ones.

Boles are of a red or yellow colour, and have a composition similar to ochre (*q.v.*). They appear to owe their colours to

hydrated oxides of iron, and are distinguished by their conchoidal fracture.

Boulder clay, as already explained (p. 104), is one of the chief products of the Glacial Age, and is a large deposit of material consisting of boulders, small stones, gravel, sand, and clay, known as "glacial drift" or "till." The clay itself is the most direct product of the ice, the sands and gravels being usually due to streams and floods caused by the melting ice. This clay has usually been held to be deposited from ice, but there are those who adduce good reasons for it being looked upon as a marine formation. The term "boulder clay" is sometimes used for the whole of this heterogeneous mass, but should be reserved for that portion of it which possesses the characteristics of clay. It is also confused with alluvium by some writers (p. 130).

In most districts the "drift" may be divided into two portions, the lower one being a coarse, tenacious clay, containing many rounded boulders and but little gravel or sand, and the upper portion containing relatively few boulders and comparatively little true clay, but rich in silt, gravel, and sand. It is generally supposed that this upper drift is the result of a re-arrangement of the lower one. In Yorkshire, Wood and Rome have found three distinct divisions of glacial drift, usually separated by beds of sand and gravel; a good section of these may be seen at Dimlington. They comprise—

- (i) An *Upper bed* of a bright red colour and loose texture with small boulders. This formation is very abundant near Hessle and is sometimes known as *Hessle clay*.
- (ii) A *Middle bed* of purplish tint, rich in boulders and chiefly seen on the coast.
- (iii) A *Lower bed* or basement clay of dark grey colour, rich in fossil shells.

The most important deposits of boulder clay (fig. 9) are in East Anglia, the Midlands, north-western England, the south of Scotland, and many parts of Ireland. In some parts of the Midlands it is 200 feet in thickness, and at Newport, Essex, a thickness of 340 feet has been reported. In the eastern counties of England a variety known as "chalky boulder clay" is common, and is used for brickmaking; but at its best it is not satisfactory, though, when mixed with the stiffer solid clays found beneath, bricks of fair quality may be made.

Glacial drift is found alike on upland and vale, especially in the Midlands; but further south its progress appears to have been barred to some extent by the Chiltern Hills, and more definitely by Edgehill and the Northern Cotswolds, though there is a large

tract of boulder clay between Dunmow and Epping, with an apparent extension southwards to Hornchurch, where it lies below the Thames gravel. This drift covers the greater part of Lancashire and Yorkshire; it is well seen in cliffs at Blackpool, Filey, and Withernsea. The boulder clay above the Lias occupies the eastern part of Leicestershire. The absence of outliers along the Lincolnshire cliffs is noteworthy, many large masses of Lincolnshire limestone and marlstone in the boulder clay to the south being probably relics of outliers which formerly existed to the north.

The boulder clay occurs plentifully in the north of Lincolnshire, along with much glacial sand. Around Ponton the clay is good for bricks, but contains large Oolitic boulders.

Norfolk is largely covered by boulder clay except in the west, and the same material is scattered irregularly over Suffolk. North-east Norfolk has many fertile loams, with lighter lands of sand, gravel, and marl.

Boulder clay and gravel also cover much of Warwickshire and most of East Shropshire, but it is absent in Oxfordshire, except on the north-eastern border where it joins Buckinghamshire.

Boulder clay and drift cover large parts of the Welsh valleys, but usually contain too much gravel to be of value.

In Scotland the boulder clay is very extensive in Aberdeenshire, particularly to the east, where it is frequently more than 100 feet thick. It also occurs extensively in Banffshire, particularly at Blackpots. The drift clay at Kilchattan in Bute has long been used for brickmaking. Much boulder clay occurs in Caithness and Dumfriesshire, Midlothian, Fife, Inverness-shire, Perthshire—in short, all over Scotland.

Ireland formed the western boundary of the British glacial drift, but also appears to have been the centre of another ice-sheet radiating from Fermanagh. The east and central portions of Ireland are extensively covered by drift up to 100 feet and more in thickness, but the deposits are not rich in clay, though some of the ridges termed "drumlins" are capable of being used for brickmaking. The Green Hills or "Eskers" in the central plain are, on the contrary, exclusively sand and gravel. Indeed, the glacial drift covers so much of the industrial portion of Ireland that the solid beds, with the exception of the Coal Measures, are seldom worked for clay.

There has been much denudation since the boulder clay was first spread over the land, as valleys have been scooped through it, the drift thus being separated into outlying masses.

In the northern counties the boulder clay has filled many old

valleys, but subsequent erosion by rivers sometimes makes it difficult to trace precisely what has occurred, and occasionally has caused a curious dislocation of material. Thus the Vale of York from Bawtry through Doncaster and Thorne to Selby and York is largely covered by thick drift deposits and alluvium, both of which are valuable for brickmaking. A remarkable exposed patch of boulder clay about 40 feet thick overlies the Bunter sandstone at Balby, near Doncaster. It is a hard, tough, unstratified mass with many stones, but if carefully selected makes excellent bricks which are much appreciated locally.

The "boulder clays" of the Midlands are not clays at all, but gravel beds and gritty loam. They are sometimes used for brickmaking, but the abundance of better material in the same localities often precludes their extensive employment. The boulders in the "till" of southern Scotland may be readily removed, and it then forms a good brick earth.

Boulder clay is objectionable for brickmaking on account of the large proportion of stones with which it is associated, though if the clay itself is strong and the stones are chiefly composed of silica, the whole may often be ground up together and a good class of brick produced. In most cases, however, some of the stones must be removed before grinding. When lumps of limestone or dolomite are present, their removal is especially necessary in the semi-dry and the semi-plastic methods of brickmaking, as it is then almost impossible to grind them sufficiently small and to mix them sufficiently with the clay particles. For the removal of boulders and other stones, stone-separating machines are employed, in which the material is made into a stiff paste with water, and passed through some form of riddle which separates the smaller particles of clay and stone from the coarser stone; or the material may be washed.

Boulder clays are probably more variable in composition and properties, and more difficult to work than any other variety of clay used in commerce. Occasionally a deposit of this material is found which is sufficiently uniform in composition and texture to furnish an abundant supply of high grade clay, but this is unusual. The conditions under which they are deposited usually make the boulder clays exceedingly variable, as they occur in pockets rather than in large deposits.

The general characteristics of these materials are described on pp. 106 and 115. If carefully sorted, they often make excellent brick and tile clays, particularly when washed, but for this purpose they must be free from coarse particles of limestone, which, if present, are liable to split the goods made from them.

Many clays of glacial origin are seldom recognized as such by those who use them, the chief means of identification being the characteristically marked stones occurring in the deposits. These blocks of stone are often polished and scratched, and are indicative of the agency of ice in some form. Seams of sand and clay containing arctic shells are associated with these deposits.

Boulder clay is sometimes very difficult to excavate, and may even have to be blasted. There is always a further difficulty in dealing with boulder clay in that it may die out or reappear at any time, this being due to the fact that it has filled up old hollows. The use of boulder clay is, in fact, always speculative because of the uncertainty as to its precise nature. It is not possible to go to a particular spot and predict its value, as its very nature and the manner in which it has been accumulated prevent this.

Brick clay is a general term given to almost all the coarser clays. Formerly, it was sufficient if bricks had a reasonably good shape and colour, but builders and engineers are now specifying vitrified and non-absorbent bricks, or those in which the absorption is within certain limits, and are much more exacting as regards shape and colour. This greater strictness in specification is narrowing the range of clays which can be commercially used for brickmaking and is bringing a better burned, more durable, and higher class of brick into general use. Most superficial clay deposits which are not contaminated with lime compounds can be made into bricks, though the tougher clays may require the addition of so much non-plastic material as to make their manufacture unprofitable.

Clays and shales from a considerable depth below the surface are also used successfully where they may be obtained at a sufficiently cheap rate. Hence the term brick clay covers a very wide range of materials. Some geologists use the term "brick clay" in contradistinction to boulder clay. Low-grade brick clays are only suitable for inferior bricks; medium-grade brick clays are suitable for the manufacture of common building bricks and common red ware. High-grade brick clays are suitable for the manufacture of facing bricks, ornamental bricks, and terracotta. These clays are often prepared from lower grade clays by washing.

Owing to the large proportion of material other than clay usually present in so-called "brick clays," it is generally preferable to use the term "brick earth" (*q.v.*).

Where the clay is sufficiently abundant, a material suitable for making high-grade bricks may be employed when a much inferior material might be used, if it were available. Hence no narrow

definition of the term "brick clay" can be given; it must include all clays capable of being used commercially to produce bricks.

Brick earth is any material of an earthy nature suitable for making bricks. The term is often confined to certain superficial deposits in the London basin (p. 86), but may be conveniently extended to include all materials used for brickmaking with the possible exception of unmined shales and rocks. In this wider meaning the term "brick earth" includes the following:—

1. Plastic clays.
2. Loams or sandy clay.
3. Marls or calcareous clays.
4. Vitriifiable clays (for engineering bricks).
5. Fireclays (for fire-bricks).
6. Silica rocks (for silica bricks).

The two last-named may, however, be excluded as being "rocks" rather than "earths."

The materials for which the term "brick earths" is at present chiefly used in the south of England are largely superficial or alluvial (p. 129) or drift deposits (p. 140). They vary so much in different localities, and even in different parts of the same locality, that it is impossible to describe them fully. Briefly, their composition depends largely on that of the lower beds from which they are derived. The following brief notes on the more important superficial "brick earths" of the London basin (which is the area in which this term is chiefly used) may, however, be useful, particularly in connection with the information in other parts of this volume.

These alluvial deposits are widely spread over the lower reaches of the Thames and form the marshes of the Wash, the Humber, and the Lincolnshire coast, where they vary in thickness from a few feet to twenty yards or more. Many of these marshlands are useless even for brickmaking, but some of the oldest of them are valuable. Thus in the Cambridgeshire fens they are worked both for bricks and cement manufacture.

Brick earth deposits (with gravel) occupy the broad valley of the Thames from Uxbridge to Southall, Ealing, Paddington, and Islington southwards to the Thames; further east along the Lea Valley to Tottenham and Enfield.

There are many brickyards between West Drayton and Southall. Similar clay tracts occur from Regent's Park to Camden Town and north-westwards to Kilburn, Harrow, and Edgware.

The alluvium outlining the county of Essex is chiefly composed of silt with irregular streaks of gravel, and is an impure clay suitable for the manufacture of bricks, but is improved by the

addition of sand. It varies so greatly in character that its use is very speculative and requires constant supervision. The most extensive areas are at the entrance to the river Crouch, near Walton-on-the-Naze in the east, and at Canvey, Tilbury, and Little Thurrock in the South. The brick earths at Copford and Marks Tey are also important.

Between Cranham and Upminster the brick earth on the surface is very free from gravel, and rests directly on the London clay, with which it may conveniently be mixed. It has been used extensively for many years. Several patches to the west of Upminster have been used, but the earth is rather too sandy if employed alone.

To the east of Ilford is another large area of brick earth, though with the rapid growth of the population it has been nearly all used. Still further west it has been used at Epping. At Tilbury this alluvium has attracted much attention from geologists. It consists of mud or silt alternating with layers of peat. The material is rich in iron oxide and lime, but relatively poor in alumina, so that it is a marly-loam rather than a true clay and must be burned at a comparatively low temperature. It should seldom be used alone, being too fine in texture, too fusible and with too high a shrinkage, but if mixed with sand it is excellent for common bricks.

The Tilbury loam is also peculiar in that nearly half its alumina is soluble in hydrochloric acid, and this, with the chalk and iron oxide, which are also soluble, produces a material which, when dried, is composed of about 25 per cent. of clay, 50 per cent. of sand, and 25 per cent. of chalk, iron oxide, and other matter soluble in acid. The alluvium of the river Medway and of parts of the Thames has long been valued for the manufacture of cement.

The loam between East and West Tilbury is typical of the true brick earth of Essex, though near the latter place it joins the Thanet sands and becomes more arenaceous; but the alluvium is more generally used.

Though true, superficial brick earths abound in Essex and in other parts of the London basin, the "solid beds," except the blue London clay lying beneath, are now generally preferred on account of their more regular character, though for small works they are often less convenient than the brick earths found above them.

The surface brick earths near Rochford and Southend are particularly advantageous for the manufacture of hand-made bricks, so far as their composition is concerned, being homogeneous and sandy.

The glacial drift (pp. 106 and 140) in many parts of the country is a useful brick earth, and in Suffolk¹ the neighbourhood of Woolpit has been famous since the time of Queen Elizabeth for its "white bricks." In central Suffolk this drift is usually a bluish-grey clay with many varieties of stones. Only certain portions of it can be used, the best being below the more readily distinguishable boulder clay.

The chief earths used for brickmaking in Norfolk and Suffolk are all of a superficial character, the solid beds of clay lying below being practically untouched.

The Geological Survey Maps of Kent and Surrey convey the impression that these counties are largely composed of chalk, but whilst this is true, the superficial loams which are often many feet in depth must not be overlooked. These loams are very similar to the Thanet sands (from which they have been derived), though they also resemble the mottled plastic clays of the Woolwich and Reading beds. These loams, which are specially abundant north of Paddlesworth, near Folkestone, and west of Waltham, vary greatly in character in different localities, even in the same district, and are apt to produce irregularly coloured bricks, though, with care, excellent rods and stock bricks can be made. The clay containing flints, which is associated with these loams on the North Downs, is a stiff, highly plastic clay of good quality when the flints have been removed and sufficient chalk added to reduce its shrinkage to within convenient limits. Brick earths with chalky gravel form the low ground west of Brighton (Worthing), and conceal a tract of Reading beds, London clay, and Bagshot beds, which occupy a syncline at Chichester (Sussex).

At Ashford and Wye the brick earths, though formed in a similar manner to the loams just mentioned, are very different in character, owing to the great variation in the proportion of the sand they contain, but they are good for the manufacture of red bricks, etc., and have been used for this purpose for many years.

The superficial clays in East Kent are much used for the manufacture of hand-made bricks, but their value for this purpose is often small, though in North Kent (Canterbury) they are of unusually good quality. The presence of pebbles and the necessity of washing prevent these clays being used where bricks made of other material are available.

North of Shepperton is another useful area of superficial brick earth about two miles square, with three others on the eastern side

¹ The whiteness of Suffolk bricks is due to their high content of calcium carbonate.

of the Colne Valley (Langley Marsh, Colnbrook, and Slough), and a small circular patch at Burnham.

At Upper Edmonton, Edmonton, Enfield, Highway, Forty Hill, and Bull's Cross, Broxbourne, and generally in the Lower Lea Valley, there are patches of very good superficial brick earth (loam) which are extensively used.

Further west and immediately south of Amersham the superficial deposits are of little value, except on the tops of some of the hills, which are good for high-class bricks, though they require washing to free them from gravel.

Near Windsor the superficial brick earths are covered thinly with gravel, and the Reading beds are therefore used, though near Burnham a ten-foot bed of light brown loam is used for making bricks.

The alluvium running due north and south on the east of Aldershot is a stiff clay of a marly nature and of uncertain value, but to the west, a little north of Crondall, it joins the Reading beds and makes a good brick material of so uniform a nature as to require very little mixing.

In Berkshire, a few miles north-west of Maidenhead, are three important outliers of brick earth near Bisham. Two of these are in use, but the one to the north-east, unlike one of the others, is free from a cap of gravel.

To the south and south-west of Maidenhead these clays are extensive and clear of gravel except near the river. Near Hedgerly the alluvium stretches some miles to the south in the valley, whilst the London clay abounds on the higher ground. There is, in fact, an ample choice of brick earths in Berkshire, though none of the beds are thick except the London clay. There is also an excellent brick loam at Banstead Heath and in several other parts of Surrey, but the superficial deposits of clay with flints so common in this county must be washed, and so are of little value. The washed clay is excellent, being a product of the Reading beds.

At Pevensey Level, in Sussex, the more sandy portion of the alluvium makes excellent bricks. The flats around Portsmouth Harbour towards Fareham, and on and near Hayling Island, could likewise be used in the manufacture of good "stocks."

Extending generally over the western end of the London basin a shelly loam occurs above the Reading plastic clays. This loam is very variable in composition, and in some districts is not readily separable from the plastic clays. It is frequently mixed indiscriminately with the latter, to their great detriment. This loam usually contains many pebbles and much grit, and is worth-

less, except in the immediate vicinity of Reading, where, being purer, it makes excellent bricks. In other localities it is a nuisance, as it breaks down very readily after rain and washes down into the Reading beds and spoils them. This difficulty can be obviated to some extent by drainage, but this is seldom attempted. Usually a large part of the top loam is taken away and the rest is left to chance. Using the term in its wider sense of any material suitable for brickmaking, most brick earths consist of an irregular mixture of pure clay with sand and other minerals.

Pure clays, especially when highly plastic, are not suitable for brickmaking unless mixed with appropriate non-plastic material.

No definite composition can be stated as truly representative of brick clays, as the amount of shrinkage on drying and burning is often more important than the chemical composition of the earth. Any plastic earth in which the total shrinkage does not exceed 10 per cent. is worth investigation as to its suitability for brickmaking, and particularly so if its composition approximates to silica three-fifths, alumina one-fifth, iron, lime, magnesia, manganese, soda, potash, and "loss on ignition," one-fifth. Such a composition corresponds to 50 per cent. "true clay" (hydrogen alumino-silicate), and this should form the chief constituent of brick earths. An excess of silica present in clay in the form of sand renders the bricks made from the earth weak and soft. Rubbers owe their special characteristic to the presence of sand in the clay from which they are made. The sand, or free silica, which is present in or must be added to the clay, prevents cracking, shrinking, and warping. Within certain limits, the larger the proportion of sand present, the more uniform in shape and equable in texture will be the brick; but, on the other hand, as already stated, an excess of sand in the clay will cause the bricks to be too weak and brittle.

The red colour of many bricks is due to the presence of 2 to 6 per cent. of iron oxide in the clay.

Yellow bricks may be relatively free from iron compounds, or, if they contain it, the red colour is destroyed by the simultaneous presence of chalk or other lime compounds.

Lime compounds, if in a very finely divided state (as chalk), are not injurious to clays used for brickmaking, but coarser particles must be avoided, as they cause disintegration later. Marls (which are rich in lime compounds) are much used for brick-making, but boulder clay (in which the limestone is in a coarse state) is less satisfactory, as the limestone cannot be ground sufficiently fine to be uninjurious.

A large proportion of carbonaceous or organic matter in an open brick earth is an advantage, as it reduces the amount of fuel required to burn the bricks, but in a dense clay it is difficult to burn out and so may prove objectionable.

Alkalies (potash and soda), when existing in clay to any great extent, are detrimental to its use as a material for brickmaking, as they act as a flux and thus cause the clay to melt and to become shapeless.

A good brick earth should contain, in itself, sufficient flux to fuse some of its constituents at the temperature attainable in the kiln, but not so much as to make the bricks run together and become vitrified.

It frequently happens that a clay, as found in nature, is unfit for brickmaking purposes; it will probably be found that it is deficient in some necessary quality, and this has to be supplied by mixing it with other clays, or by adding the constituent lacking, such as sand, lime, or burned clay. The amount of this addition must be found by actual trial.

Occasionally the different beds in a clay-pit vary so much that it requires a mixture of two or three different beds before an earth suitable for brickmaking is obtainable.

Further information on the effect of "impurities" in brick earths will be found in Chaps. VIII. and IX.

Brown clays usually owe their colour to manganese or to carbonaceous (peaty) matter. For common articles the colour, before burning, is unimportant, but "brown ball clay" is unsatisfactory for general pottery purposes even when it burns to a good white body. Such a clay is not sufficiently resistant to heat.

Clays which are brown after firing can only be employed for coloured articles. They are sometimes valued for use as engobes or slips, particularly in Germany.

Buff-burning clays are of two kinds: (a) those containing a large quantity of lime which destroys the red colour which the iron compounds present would otherwise produce (see *Marls*), and (b) clays comparatively free from iron compounds, such as the fireclays. The former cannot withstand high temperatures, but the latter are usually more refractory.

Some buff-burning clays, nearly free from iron, form a partially vitrified mass, and are then valuable for paving bricks and tiles.

Apart from the marls and fireclays (which are described under their respective headings), the chief sources of buff-burning clays are the Tertiary deposits of Devon and Dorset and the clay pockets in the Mountain-limestone hills of Derbyshire, East Staffordshire, and North Wales.

To obtain satisfactory results, great care must be exercised in the selection of these clays, especially as regards the proportion of silica, the fineness, regularity, and of freedom from iron, "pin," humus, and all pyritic nodules.

The mild Dorset clays of this kind may be written upon easily with an ordinary lead-pencil when dry, and in this way may be distinguished from ivory ball clays which often occur with them. The better qualities of such clays are largely used for deep cream-coloured and light buff-glazing tiles.

The clays found in pockets in Mountain-limestone are usually irregular and of coarser grain than the Tertiary clays of Devon and Dorset.

Burned clay or "grog" is much used abroad as the chief constituent of refractory articles. In Great Britain its value has not, hitherto, been fully appreciated, partly on account of the abundance of fireclays of specially good quality. As these become exhausted, the improvement in quality which may be effected by burning the greater part of the clay before use will become increasingly noticed.

Under the trade term of "chamotte," fireclays burned at 1100° C. are now obtainable, and form an excellent basis for all kinds of refractory articles. Equally good or even superior material may be made by most owners of fireclay mines, should the demand justify the erection of the necessary kilns (p. 152).

Burned clay or "grog" is one of the most universally obtainable remedies for preventing the cracking of goods made from highly plastic clays, though, in Great Britain, sand will often be found to be equally satisfactory and somewhat cheaper.

Grog is often obtained by grinding old fire-bricks, but the best qualities are made by burning a high-grade fireclay in a shaft kiln out of contact with fuel, grinding the product to a coarse powder, and removing the dust by screens with 12 or 16 holes per linear inch.

A use of burned clay which is rapidly extending in the United States is in the construction of country roads, particularly where large quantities of low-grade clay are available. For infrequent traffic it is cheaper and better than macadam and drier than beaten soil, and affords a better foothold. The bed of burned clay must be fairly thick in order to prevent any mud beneath it from oozing up through it. The material should be packed carefully, the larger pieces being laid first and the finest material being added last. Roads made by tipping a cartload of burned clay and roughly levelling it are unsatisfactory.

Burned clay was at one time much used as a means of improv-

ing heavy land agriculturally. The top soil was removed and the heavy clay beneath was piled in small heaps and roasted by means of small fires in their interiors, or by alternate layers of coal and clay. Overburning should be avoided, as it destroys some of the soluble inorganic matter which would otherwise serve as plant food. In addition to making the land more porous and absorbent, burning it in this manner appears to increase slightly the amount of inorganic material present in a form in which it can be used by plants.

Calcareous clays are those which contain sufficient lime to make this constituent important. Usually the term is restricted to clays containing more than 5 per cent. of lime.

Calcareous clays are of two chief kinds: (*a*) marls or clays containing chalk, and (*b*) clays containing limestone, such as boulder clay. The former are useful for many purposes, but the latter can seldom be used without previous removal of the lime, except for the manufacture of "puddle" for use in embankments, etc. (see *Marls* and *Limey Clays*).

Cement Clays.—For the manufacture of Portland cement, clays should be as free as possible from sand and gravel. They should not contain less than 55 per cent. of silica, and 60 to 70 per cent. is preferable. The alumina and iron oxide together should not amount to more than one-half the silica, and the best cement will usually be obtained if the sum of the alumina and iron oxide is exactly one-third of the total silica.

Magnesia and alkalies must not exceed 3 per cent., except under unusual conditions; but if, as is probable, the use of dolomite instead of pure limestones increases, this limit may be raised.

Any material, such as nodules of limestone, which increases the amount of power used in grinding, or which tends to make the clay irregular in composition, should be avoided, even though it may not be directly injurious. This precaution is necessary, because the composition of cement must be maintained within very narrow limits if it is to comply with the very rigid specifications now usually imposed.

The clays used in the manufacture of Portland cement are of two classes: (*a*) normal clays—usually high-class shales—to which limestone must be added to form the cement mixture, and (*b*) marls or limey clays in which a large proportion of lime in a suitable state of division is naturally present. The selection and value of a material belonging to either of these classes must depend chiefly on its accessibility and upon its composition being within the limits already mentioned.

The chalk formation on the banks of the Thames and Medway is quarried, and this material is mixed with the deposits of mud (alluvial clay) found in the estuaries and creeks. In Sussex the gault clay (p. 77), which is highly calcareous, is employed.

The chalk marls around Cambridge are also eminently suitable. The "marl" is a deposit of calcareous and argillaceous material found at the base of the local chalk, and, though the relative quantities of chalk may vary, it contains in the aggregate about the same proportion of calcareous and clayey material as is obtained artificially by mixing chalk with alluvial mud in the Medway Valley.

The cement-making districts of the Midlands and South Wales use Lias limestone and shale, though the preponderance of shale over limestone renders the cost of working heavy.

On the Tyne, Wear, and Tees, and in the North of England generally, Portland cement manufacturers import chalk from the Thames, Medway, or Sussex districts and mix it with a local clay.

The so-called **natural cement** is made by burning suitable calcareous clays, the material first used being the "septaria" or nodules of clayey chalk occurring in the London basin, or on those parts of the coast where they have been washed free from the smaller particles of material. Calcareous nodules from various other formations have also been extensively used in various localities; those from the Speeton, Kimeridge, Greensand, and Lias clays being the most important. To a large extent "natural cement" is now replaced by Portland cement, which is, in many respects, superior. As the composition of these septaria¹ varies greatly and does not necessarily correspond to that most suitable for the purpose, these natural cements are much weaker than true Portland cement and are only used for less important work. By carefully adding suitable materials so as to keep the composition uniform, a product so closely resembling Portland cement may be obtained that the one cannot be distinguished from the other.

Chamotte is a foreign term, sometimes used in this country, to signify burned fireclay of high quality. It is much used on the Continent as the basis of all the best qualities of refractory goods. Its British equivalent is "grog" (p. 193), though in Great Britain it is customary to use only sufficient burned clay to prevent the natural clay from cracking, etc.; whereas abroad exactly the

¹ Septaria are nodules of impure limestone which occur in some clays and derive their name from characteristic divisional lines (septæ). These lines appear to be shrinkage cracks which have become filled with crystallized calcium carbonate.

opposite method is employed, the burned fireclay (grog or chamotte) forming the chief constituent of the mass from which the goods are made.

China clays, porcelain clays, or kaolins are the purest form of clay known, and on analysis yield almost exclusively alumina, silica, and water. Mica in obvious proportions is an essential constituent of the kaolin used by the Chinese, and some of the differences between Chinese and European porcelains may be due to this material. Some samples of Chinese kaolin contain 20 to 30 per cent. of mica readily removable by washing, and are quite different from the much more carefully purified china clay used in this country. For this and other reasons previously stated, it is desirable to restrict the use of the word "kaolin" as much as possible, and to designate the corresponding English material as "china clay."

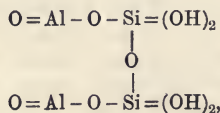
The term "china clay" is due to this material being the chief constituent used in China for the manufacture of porcelain and, in this country, for the manufacture of "china-ware."

The term "kaolin" is of Chinese origin and should, strictly, be reserved for the china-clay rock from which china clay proper is removed by washing. The term kaolin has, however, been so long in use in Europe and America as a designation for the purified china clay as well as for the relatively pure clays of low plasticity occurring apart from china-clay rock, that it is difficult, at times, to avoid confusion. China clays are less plastic than the common or "plastic" clays, and generally burn to a white porous mass; but even the less pure forms are greatly valued on account of their refractory nature, and under the name of "fire-clay" are in great demand for the production of ware intended to withstand high temperatures; *e.g.*, the lining of furnaces, etc. It is generally thought that they are produced by the action of the weather on feldspar (particularly that occurring in granite), but their origin is still unsettled. It is unusual in Britain to find china clay of good quality far removed from the rocks from which it has apparently been formed. When transported by water from its original site it generally becomes mingled with other materials, and in almost every case, when burned, it is found to be discoloured red or yellow by them, so as to be useless for its original purpose. On the Continent, however, there are clays of obviously Tertiary origin (especially in Thuringia) with all the characteristics of primary china clay, and Wheeler has advanced a theory (similar to that of Maw on ball clays) that some china clays are not of granitic origin, but are residues from the gradual solution of thick beds of clayey limestone. Although the com-

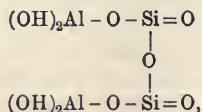
position of china clay is generally represented by the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$, corresponding to 46 per cent. silica, 40 per cent. alumina, and 14 per cent. of water, this is only true of most carefully washed and purified material, and even then takes no notice of the small percentages of lime, iron, and other bases which are invariably present and, even in the purest clays commercially obtainable, correspond to about 5 per cent. of impurities. Nor is it quite correct to express the hydrogen and part of the oxygen of china clay as though they were present in the form of water; they are more probably essential parts of the kaolin molecule and only form water on its decomposition. Some of the published analyses of china clay vary so much from one another as to render them useless for strict comparison. The figures just mentioned may be taken as typical of the best qualities of English china clay; other clays containing more silica being less valuable. In first-class china clays the sum of lime, magnesia, potash, soda (alkalies), iron, and titanium oxides should not exceed $2\frac{1}{2}$ per cent. and the total silica present should not exceed 50 per cent. Clays richer in bases or in silica are useful for other purposes, but are less valuable to users of china clay.

The constitution of the clay molecule has chiefly been studied in connection with china clay (*kaolin*) as representing the purest form of clay available; the crystalline *kaolinite* being assumed to be the true and essential mineral basis of clay. This remains to be proved, as some clays do not appear to contain kaolinite in either the crystalline or the amorphous form (*clayite*, p. 158) but to contain other alumino-silicates of similar composition.

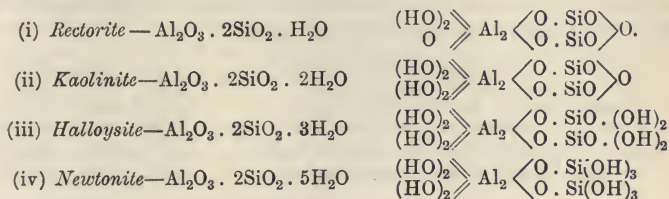
For the molecular constitution of the purest Cornish china clay and the approximately identical Continental kaolins a number of different formulæ have been proposed, but the subject is so difficult to investigate that these must be accepted with reserve. Mellor and Holdcroft have reviewed the chief literature on the subject to March 1909 (*Trans. Eng. Soc.*, ix. 94, 1911) and conclude that



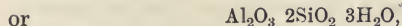
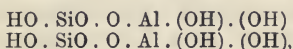
or Groth's formula,



best summarize the evidence, though no direct proof can be given that kaolinite contains its hydroxyl groups as shown in these formulæ. Nevertheless, this assumption appears to be justified. They conclude that kaolinite may be represented as one member of a series of aluminò-disilicic acids, viz. :—



Pukall has suggested a similar constitutional formula, but considers that kaolin and china clay are the anhydride of what he terms *Kaolinic acid*,



but which corresponds to what is ordinarily known as *Halloysite* (Chap. VII.), which acid he has prepared, though he has not been able to convert it into kaolin. This kaolinic acid is obtained by heating (1) quartz, aluminium hydroxide, sodium hydroxide and water, or (2) felspar, aluminium hydroxide, sodium hydroxide, and water to form the sodium salt ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), which is allowed to crystallize and is then washed until free from other salts. This sodium salt, or *zeolite* (Chap. VII.), dissolves readily in very dilute acids. On the addition of a slight excess of ammonia to an extremely weak solution a voluminous white precipitate of the kaolinic acid is obtained. When dried at 100° C. it is a white, amorphous material which is very refractory and not easily attacked by acids, though when freshly precipitated it dissolves readily. If boiled with acid it decomposes, liberating silica, and when fused with common salt it forms an easily crystallizable silicate. In this way it is readily distinguished from a mixture of silica and aluminium hydrate. If used to replace china clay in a mixture it forms a slightly plastic mass, and on burning at cone 12 a beautiful transparent white porcelain, whereas a mixture of silica and alumina will not do this. On heating to 350° C. it loses more than half its water, but a means of eliminating only one molecule and forming true clay has yet to be discovered.

Mellor and Holdcroft have pointed out that there are many

reasons for believing that alumina and silica form a special group of compounds different from the ordinary silicates and conveniently treated separately as aluminosilicates or aluminosilicic acids. In other words, kaolinite and clays are to be regarded as impure aluminosilicic acids and not as "hydrated aluminium silicates," the *zeolites* being the salts of these aluminosilicic acids. They have drawn up the following series:—

Alumino-monosilicic acid (allophanic type),	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$.
Alumino-disilicic acid (kaolinic type),	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$.
Alumino-trisilicic acid (natrolitic type),	$\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$.
Alumino-tetrasilicic acid (pyrophyllitic type),	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$.
Alumino-pentasilicic acid (chabazitic type),	$\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$.
Alumino-hexasilicic acid (felspathic type),	$\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

These aluminosilicic acids displace carbon dioxide from carbonates, sulphur trioxide from sulphates, chlorine from chlorides, and behave generally as acids, and their salts (the aluminosilicates) are decomposed by water and carbon dioxide, forming more or less colloidal aluminosilicic acids or clays.

On heating the purest china clay obtainable, Le Chatelier and, later, Mellor and Holdcroft, found that it shows an endothermal reaction at about 500°C . and an exothermal reaction at a temperature somewhat above 800°C ., but the decomposition appears to occur throughout a considerable range of temperature. In the neighbourhood of 500°C . the decomposition products appear to be free silica, free alumina, and water; the two former combine, in part, to form *sillimanite* ($\text{Al}_2\text{O}_3\text{SiO}_2$) when heated above 1200°C . The exothermal change at 800°C . appears to correspond with a physical change (polymerization) in the alumina, whereby it becomes denser and more inert.

The principal kinds of china clay found in commerce are the following:—

Pure china clays do not contain more than five or six per cent. of silica and two per cent. of fluxes. They are always obtained by washing less pure china clays. After firing, they form a body of milky whiteness. They are used in the manufacture of porcelain, fine faience, and paper.

Alkaline china clays only differ from the preceding ones in containing a higher proportion of alkalis (derived from felspar (?) and mica) which may reach five per cent. The proportion of iron oxide is sometimes two per cent.

These clays are used for earthenware and fine pottery and, if white enough, for weighting paper. They may be purified by very careful washing, which removes the greater part of the felspar and mica, and therefore the alkalis.

Siliceous china clays contain a considerable proportion of free silica (quartz) in the state of impalpable powder. The proportion present depends greatly on the care bestowed in the washing, but may reach 20 or even 25 per cent. These clays furnish a body of small plasticity, and are of a light granular texture; they are used in the manufacture of porcelain and certain kinds of faience, where a very plastic body is not required, and in making paper.

Alkaline-siliceous china clays partake of the properties and uses of the two preceding kinds, but are of less value.

Ferruginous primary clays contain so much iron oxide as to prevent them producing an entirely white body. The better qualities of these clays are used for the manufacture of porcelain and faience of inferior quality or of refractory products, if they do not contain too much alkali and iron.

Commercial china clay is white or creamy in colour, often with fine blue or brown markings running through it, caused by traces of organic matter, which are burned out in the kiln, leaving a perfectly white, dry, unvitrified mass with but little power of cohesion.

China clays are notable for their high melting-points, their whiteness when fired, their fineness, and their slight plasticity. Their plasticity is increased, when necessary, by the addition of plastic "blue" or "ball" clays. A fuller statement as to the causes of plasticity will be found later (Chap. IX.). It is generally understood that china clays are only slightly plastic because they are found near to their place of origin, and so have not undergone any treatment likely to make them plastic. Rohland, on the contrary, states that clays owe their plasticity to the colloidal hydroxides of alumina, iron, and silica, and attributes the low plasticity of china clays to these colloidal hydroxides having been washed out!

The quality of china clay may be ascertained from its chemical composition (especially its freedom from iron and alkalies), its colour before and after burning, its softening-point, its strength, and its appearance when freshly cut with a knife. For the paper trade it is sufficient if the colour before firing is a good white and the clay is moderately unctuous and quite free from grit—which last would scar the polished calender rolls. The tints are commonly due to staining by oxide of iron, but minute particles of other minerals, such as tourmaline or pale mica, impart faint tints to the less marketable products, which are consequently limited in their application.

In this connection it is interesting to note that Salamon and Grace have found that a warm solution of oxalic acid added to

the clay in the settling tanks will bleach it sufficiently to enable second grade clay to be sold as first grade to papermakers and others who do not require to heat their clay in the kilns. The excess of oxalic acid must be removed by washing.

China clay is soft to the touch and has a soapy feel, that from Cornwall being more unctuous than clays from other parts of Europe. If cut smooth and rubbed with a piece of smooth bone, it will take a beautiful polish. To the naked eye, china clay appears structureless, but under the microscope it is seen to consist of small flakes or scales, often so minute as to render the identification of their shape a matter of extreme difficulty. They have a very characteristic manner of occurring as groups which have a fan-like arrangement (*vermiculites*) and like a pile of coins (*rouleaux*). Even in the best china clays there are always small needles of blue tourmaline, scales of muscovite, and minute fragments of quartz, though they are much more common in the second grade clays and in the mica clays. A few clearly defined crystals of kaolinite (of the same composition as "clay"— $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) are usually found, but the bulk of china clay consists of very minute flakes which appear to be amorphous. It is very difficult to state satisfactorily what this mud is; Mellor terms it *clayite*. It appears to correspond to $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ in the purest clays, but is never obtained free from iron oxide or alkalis. There is no doubt, however, that in converting kaolin into ware these particles are more active than the minute kaolin crystals, and the proportion of amorphous mud-particles to crystals must be an important factor in determining the nature of the clay. Crystals of quartz and mica are also present in most commercial samples, but felspar is seldom found in commercial china clays of British origin.

Johnson and Blake found that most kaolins examined by them were composed of white pearly hexagonal flakes. J. M. Coon finds that, microscopically, those specimens which conform most closely to the chemical formula of the typically pure mineral consist of vermicular aggregates, or such aggregates broken down into sections and flakes. Many of these flakes are powder-like and almost amorphous, but high magnification shows them to be crystalline. Seen by reflected light, these vermicules have a slightly pearly lustre; mounted in Canada balsam they are scarcely visible by transmitted light. These flakes are quite invisible until the light is adjusted to show diffraction images of the edges; they are readily seen in water or cedarwood oil, which latter provides a very convenient mounting medium.

The flakes are so small and the traces of crystal faces or

cleavages so indefinite that the determination of their optical extinction is uncertain; in the vermicules it is parallel to the laminae and to the principal cleavage of the felspar of plane 010. J. M. Coon has not found these vermicular arkose forms in the overlying arkose or growan.

Kenngott also pointed out the crystalline nature of kaolin, and von Fritsch states that it belongs to the rhombic system of crystals and often appears in the form of twin leaves which are difficult to distinguish. Bischof independently reached a similar conclusion, but different observers are by no means agreed upon the precise shape of the clay particles.

On drying at 110° C. an ordinary commercial sample loses 10 to 12 per cent. of moisture, and on heating from 300° to 800° C. an additional 13 per cent., or about 23 per cent. or more in all. When burned at 1100° C. the best china clay is pure white, very hard, but not at all vitreous, close in texture, and does not readily absorb much water, though to the tongue it feels "porous."

China clay should not be affected by dilute hydrochloric acid, but it is decomposed by prolonged treatment with boiling concentrated sulphuric acid.

China clay is one of the most highly refractory materials known, and on heating it leaves an intensely white residue; but its contraction, whiteness, and porosity vary somewhat in different samples. It is almost infusible by itself, and does not readily dissolve in fused glass or glaze, but merely makes them opaque. If either lime or silica be added to pure china clay, in any proportion, the melting-point of the mixture is lowered.

China clays differ in tint of whiteness very perceptibly in their raw state, particularly if they are wetted; but these differences do not necessarily indicate what the colour will be when burned. This latter must be ascertained by special burning tests, trial pieces being fired along with other goods under the identical conditions they are intended to be used; different tints being obtained if samples of the same clay are burned at different temperatures and under different conditions.

In the manufacture of earthenware, the function of china clay is to make the body white and less liable to break under a heavy weight or sudden change of temperature.

In this it is superior to flint, the other whitening material, on account of the latter's lack of plasticity. China clay cannot be used exclusively in earthenware on account of its low plasticity, the proportions in which it is added to ball clay depending on the colour desired for the product and the amount of plasticity essential to the production of certain articles. China clay is the

chief clay, and usually the only one, used in the manufacture of porcelain. It is also much used as an engobe or covering for articles made of cheaper clay, such as glazed bricks, coarse white pottery, etc., but for this purpose it requires the addition of other materials to make it more adhesive and to adapt its contraction to that of the body on which it is used.

China clay is found in china-clay rock (p. 10), and also in pockets of relatively pure clay. In both cases it forms a yellowish-white mass, usually containing crystals of quartz and undecomposed granite, and numerous lamellar particles of mica. "China rock" seldom contains as much as half its weight of china clay. This heterogeneous mass occurs chiefly in South Devon and Cornwall, the principal localities being Leemoor, Cornwood, Bickleigh, St Austell, St Stephens, St Dennis, St Mewan, Roche, St Columb, St Burian, and Germo in Cornwall. It was discovered in Cornwall about 1755 by William Cookworthy, who in 1768 patented its use in the manufacture of porcelain.

According to J. M. Coon, as a general statement, the clays from the eastern parts of St Austell boss are better adapted for use in the arts as bleaching, filling, and facing materials, and those in the western parts for potting purposes.

The reported indications of china-clay rock in County Wicklow, Ireland, are not of sufficient importance to be used commercially.

The depth to which the larger bodies of china clay extend appears to be practically unlimited; the one at Caudledown being over 300 feet deep.

Fuller details of the occurrences of china clay will be found in the memoir accompanying the geological map (sheet 374) published by the Board of Agriculture and Fisheries, 1910, the memoir on *The Hensbarrow District*, by J. H. Collins, published in 1878, and *Memoir of the Geological Survey of Bodmin and St Austell*. See also under *Kaolin*.

In order to obtain china clay from the material in which it is found, the rocky mass is (a) broken up and washed; (b) the heavier impurities are allowed to settle; (c) the clay and water run off into various refining pits, and finally into drying tanks or hydro-extractors, wherein the greater part of the water is removed. The details of the method used vary according to local conditions; there is much room for improvement in some of the works.

A pit is first sunk and a convenient quantity of overburden removed. The exposed clay rock is dug out in steps, the more discoloured portion being discarded and the selected clay being wheeled away to the washer or "strake," where a stream of water is turned on to the clay rock as it lies exposed, and the

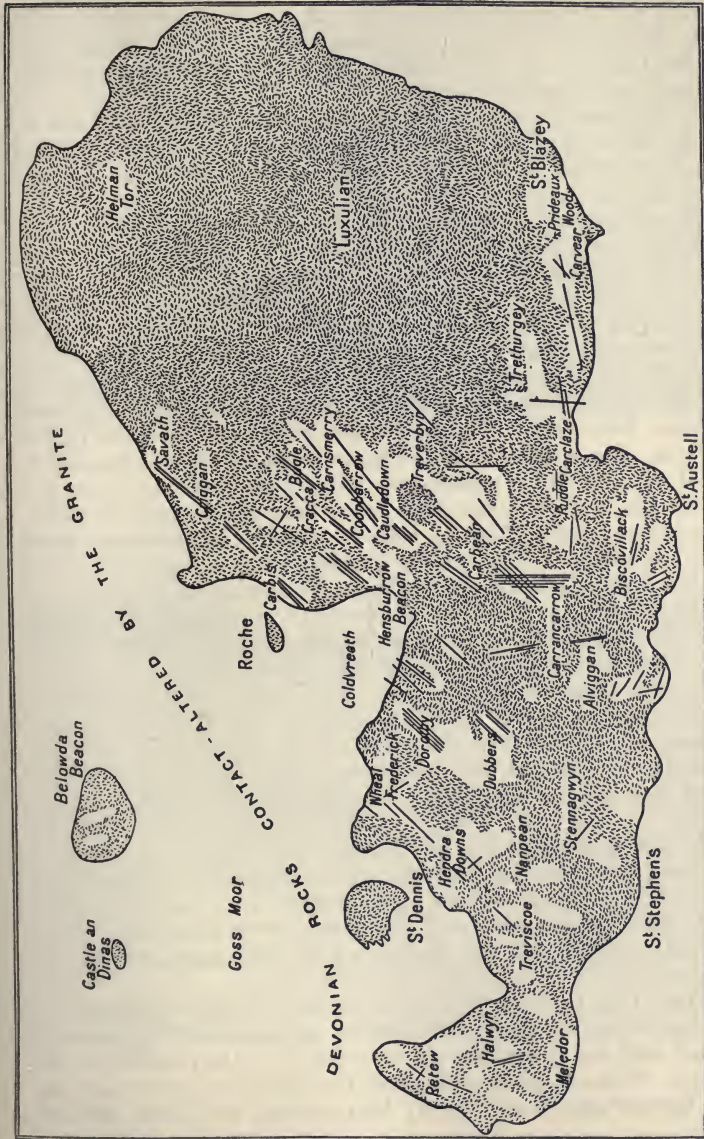


FIG. 11.—Map showing distribution of china clay in Cornwall. (After MacAlister, "Mem. Geolog. Survey," 347.)

clay is washed to the bottom of the pit, the workmen turning it over with spades. It is there passed into "boxes" (Plate VI.) where the bulk of the "sand" settles and the clay is carried forward to the pumping well.

When the clay forms a hill of convenient situation, the use of an adit or level tunnel driven into the material is often convenient. Open quarrying is practised where the nature of the deposit permits it.

A very common method consists in sinking a permanent shaft about 6 feet square and 30 yards or more deep, and from the bottom of this driving a horizontal adit leading to a second shaft in the centre of the clay deposit. The overburden, which varies from 6 feet to 4 feet in the neighbourhood of the second shaft, is then removed so as to form an open pit, and into this shaft or "rise" is fitted a wooden pipe or *launder*, which is about 9 inches square, the sides being perforated by a number of 4-inch holes about a foot apart. These holes are fitted with stoppers called *buttons*. The space around the base of this button-hole launder is filled up as closely as possible, so that all water passing out of the pit to the first or pump shaft must pass through this launder. The boxes shown in Plate VI. take the place of buttonhole launders in some works. The pumps employed are usually 10 or 20 inches in diameter and are fixed in the "permanent" shaft.

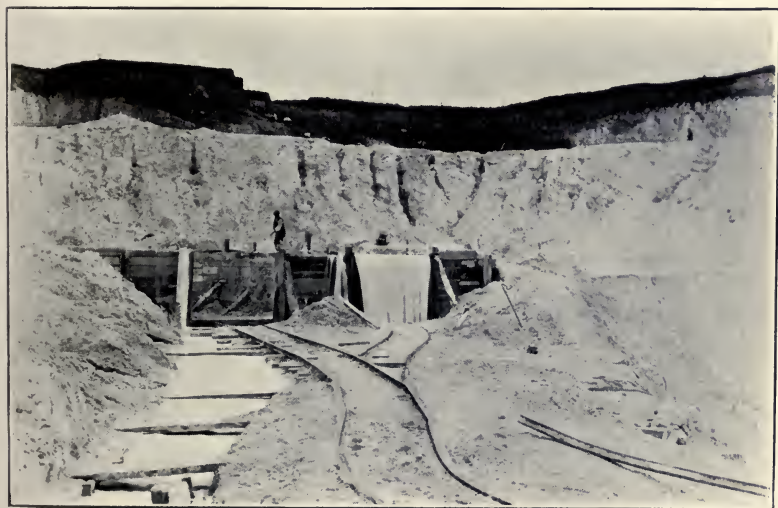
An ample supply of water is essential to the process of preparing the china clay. This water is played on the upper sides of the pit or "stopes," and in its descent it carries with it some of the clay, together with quartz and other rock particles—technically known as "sand"—and mica. It is collected in a pit where some of the "sand" settles to the bottom, but the other materials are carried with the water through one of the button-holes into the launder, along the adit, and are pumped up the shaft.

As the working of the pit deepens, other (lower) buttons are removed from the launder until, when the bottom of the rise is reached, the launder is no longer required, though the boxes may still be retained, and the stream runs along the bottom of the workings to the pump, and is then delivered to the "micas."

From time to time the "sand" is removed in waggons which are hauled up the sides of the pit, so as to prevent its becoming mixed with the clay as the pit is deepened by the removal of the latter. When no pumps are used, the stream of water carrying the impure clay flows directly into a trench and then into the pits.



Part of China-clay pit, showing the irregular structure.



Sand-intercepting boxes at bottom of slope.

(By courtesy of W. H. Patchell, Esq., North Cornwall China Clay Co., Ltd.)

[To face p. 162.]

The "micas," "pits," and "ponds" (Plate VII.) used for purifying the clay are built of rough stone, cemented by lime; the pits are 5 or 6 feet square and 4 feet deep, the ponds 20 feet by 12 feet by 4 feet, but larger ones are sometimes employed. The first pit receives the sand and coarser mica; the second and third the fine mica, and the fine clay settles in the last or passes on to the ponds, each pit being filled by the overflow of the previous one. When the ponds are full the clay is allowed to settle and some of the clear water is run off; the remaining contents are then transferred to shallow "pans" lined with granite, about 40 feet by 12 feet or more by 14 feet deep, where the clay settles out, fresh liquid being added as the clear water is run off. The material remains in these pans from four to eight months (often from September to the following May) or until it is stiff enough to cut up into square blocks, which are further dried by exposure or in fire-heated dryers. They are then scraped clean and stacked under cover ready for export; the scrapings are wheeled back to the strake and re-washed. If during rainy weather or from any other cause the clay does not settle, it is watered with a solution of alum from a common watering-pot, but this seriously contaminates it for some purposes.

The inferior clay and residue from the micas is sometimes made into fire-bricks.

Improved washing arrangements exist in some works, but the method just described is still used with but little alteration in many cases, though much might be saved by using more modern appliances and by more carefully sorting the material.

Much unnecessary washing may also be avoided by care in obtaining the raw material and the discarding of any veins of schorl or tin ore. This is done in some pits, the selected portions being taken to the first pit and played upon with a powerful jet of water, as much of the coarse material would be carried into the pits by the flowing water. Some firms use a preliminary trench about 10 feet by 4 feet by 4 feet, the exit end of which has an opening at the base, covered with a grid, through which the water with the finely suspended clay, etc., passes. Several of these troughs may be arranged abreast so that some may be used whilst the accumulated sand, etc., is being removed from the others.

If the works are properly arranged, it will be found much cheaper to move the liquid containing clay, mica, etc., than to transport the solid clay. Hence it is desirable that the refining plant should be placed so as to deliver the finished material as near to the railway or coast as possible.

This refining plant may consist of the simple pits already described, or these may be replaced by long troughs 20 feet by 12 inches by 8 inches, known as "mica drags" or "shell traps." These "drags" are arranged in groups consisting of a series of troughs side by side, each trough or channel having at the outlet an inverted sluice in sections which can be raised, little by little, as the deposit accumulates. Sometimes the troughs are provided with sieves. The clay stream is passed simultaneously over several drags abreast, so as to reduce its velocity and enlarge its area. The first group stops the coarsest mica, whilst succeeding ones retain the finer particles of micaceous clay and relatively coarse particles of the clay itself. It may be remarked, in passing, that there is a considerable demand for the pale mica separated in the preparation of the clay.

The speed of the stream must be regulated accurately, so that no unnecessary clay is retained and no coarse particles escape. When a set of drags is full of accumulated waste, the stream is diverted to another group of drags, and the first one is cleaned out. On emerging from the last set of mica drags the clay stream flows into pits, often 20 feet in diameter and 7 to 10 feet deep, and is allowed to rest for several weeks. As the clay settles, the upper water is run off by removing plugs from a special overflow in the side of the pit, and the thick, creamy clay-slurry is run into large shallow tanks, where it is allowed to settle until of the consistency of cream cheese. This semi-solid clay—containing about 60 per cent. of its weight of water—is then taken in hand-barrows, or by mechanical conveyors, to the drying floors, where it is dried by exposure to wind and sunshine or on large fireclay floors, heated underneath by steam or fuel. When stiff enough the clay is cut into cubical masses of 20 or 30 lbs. weight each, and when it has lost all but about 20 per cent. of moisture, these lumps are stacked in large open sheds called *linhays*, where the drying is completed by exposure to air.

China clay is considered ready for market when it contains about 10 to 12 per cent. of moisture; if much overdried, or if "burnt" upon the drying hearths, it is useless for some purposes.

Works which pride themselves on using the most modern methods, such as waggons, tramways, overhead hauling, pumps, etc., still use the crude method above indicated, the greatest improvement being the pumping of the clay in a liquid condition through long pipe-lines from the mines to drying works erected near to the seaport or railway station.

A method which has attracted some considerable amount of

attention, and is likely to effect still further economies in the refining of china clay, is known as the Gee process, after its inventor (W. J. Gee). It utilizes the effect of centrifugal force combined with gravitation in such a manner that if a clay slip is fed into the apparatus the water flows away quite clear, and the clay adhering to the sides of the apparatus is found to be graded according to the sizes of its particles.

Centrifugal separation is much more rapid than deposition by gravity, as by a sufficiently rapid rotation a separating effect upwards of one hundred times as great as gravity can easily be obtained. Thus, in place of a trough 400 feet in length a centrifugal machine of 4 feet produces the same complete separation coupled with grading.

The apparatus in which the Gee process is carried out is illustrated in fig. 12; a cylinder A, which is relatively long in proportion to its diameter, is mounted on a base B, to which is attached the axle or spindle C. The driving arrangements and bearing are not shown, as they do not affect the principle of the apparatus. The inlet end of the apparatus is fitted with a cap D, to which is attached the container, which is slid into the cylinder to receive the charge of solid matter. In the centre of the cap D is the hole E, and under this is placed a distributing disc F. In operation, the machine is first set rotating. When it has attained the required speed, the water containing solid matter to be separated (*i.e.* the slurry) is fed through the hole E upon the disc F, which throws it out to the periphery. The action of centrifugal force causes the liquid at all times to form a hollow cylinder within and passing through the apparatus, and so the liquid passes along the inner surface, depositing the solid matter on the way just as in an ordinary settling tank, the coarsest being found at G, and, with every intermediate degree of fineness intervening, the finest at H.

Within a few seconds a wall of liquid is formed in the machine to the thickness of the lip or false end at H, and when it reaches this thickness it overflows and is thrown out of the apparatus at J. The slip is continually fed into the apparatus until, as is easily found by experiment or calculation, a charge of solid matter of desirable thickness is obtained, when it is cut off and the machine stopped. The container, now charged with solid matter, is drawn out, an empty container inserted, and the operation repeated.

The lining of the apparatus is made in sections so as to be readily removed and replaceable, and the slabs of stiff clay may be taken out in a few seconds, and may be divided into three or four sections each of a different degree of fineness.

It will be seen that the operation of the machine is very simple. The correct rate at which the machine is to be fed is easily ascertained by watching the effluent liquid at J. If it is not clear, the feed is reduced so as to lessen the rate at which the

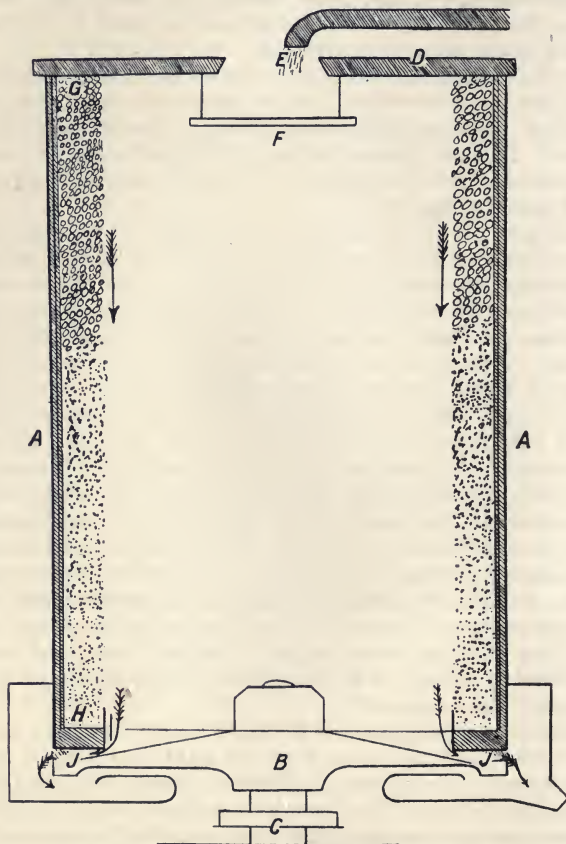


FIG. 12.—The Gee Centrifugal Separator.

liquid flows through the machine. If the feed is too slow, the effect will be that the charge of solid matter will not extend the whole length of the cylinder and so the capacity of the machine will be reduced. The feed once adjusted is, of course, adjusted permanently, as far as the particular substance is concerned.

It will be seen also, that once this adjustment is made, if the speed at which the machine rotates remains the same, the quality or grade of the solid matter deposited at any place in the machine will be the same at each successive operation, and in a battery of any number of machines operating simultaneously it will be the same for each. The apparatus is so simple in construction, and has so few working parts to get out of order, that wear and tear are reduced to a minimum.

For some purposes, before they can be used, china clays must be stored in cool cellars in air-tight bins to permit them to "mature." The changes which take place during this maturing are not well understood—though apparently even distribution of moisture and a slight fermentation are the chief results. Possibly some change in the colloid material—present in all clays—may also occur.

No definitely satisfactory method of determining the proportion of minerals other than clay in china clay has yet been published. That suggested by Seger, and largely adopted, of boiling the material for fifteen or eighteen hours with sulphuric acid ("rational analysis") never yields a pure product, the "clay" portion invariably containing iron oxide and other bases. For this reason the author has for several years preferred to follow Fresenius' suggestion and to regard all the bases other than alumina present in the material as in the form of mica, and to deduct from the ordinary results of analysis the figures corresponding to this assumption. Any remaining alumina is calculated to "true clay" (corresponding to the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), and any silica not required by this "true clay" and by the "mica" is set down as "free quartz."

Whilst this method is open to several objections it is much simpler and freer from defects than the "rational analysis" as ordinarily carried out. Even when the bulk of the foreign mineral does not consist of mica the results of this calculation are not seriously in error if a note is added to the analysis explaining that the term "mica" in this instance is used to include a variety of silicates other than clay and of somewhat indefinite composition.

The greatest difficulty arises in connection with the iron oxides present in the material. On treatment with boiling sulphuric acid practically the whole of the iron is dissolved and so is included in the figure for "clay substance." To do this is unsatisfactory, and to consider the iron as existing in the form of oxide is equally unsatisfactory, as silicates containing iron are so frequently found in clays.

At the present time the most direct way out of the difficulty—

though by no means theoretically satisfactory—is to add together all the bases except iron oxide and alumina and calculate them to mica¹ as above suggested, and to report the percentage of iron oxide separately.

Clay band or **clay ironstone** is not a true clay, but an impure iron carbonate containing uncertain proportions of clayey matter, the iron being contained in nodules or thin layers in association with shale—usually in coal formations. Its chief uses depend upon its iron-content, and not on the amount of clay it contains. For the ordinary purposes of clayworking it contains too much iron distributed in an irregular manner, and unless the proportion of iron present is sufficiently large to justify the smelting of the material the ore is practically worthless.

Claystone is, strictly, a rock composed chiefly of felspar, and now usually known as **felstone**, but the term is often (though undesirably) used for shales.

Clinker clay is a term used to signify clays which may be satisfactorily used for making vitrified bricks for paving purposes.

An enormous quantity of paving bricks of this kind is made from the Upper Estuarine clays extending from Little Bytham near Stafford to Oundle and Stamford from the Staffordshire “marls” and from various bastard fireclays (see *Vitrifiable Clays*).

Clunch is a term largely used to indicate any clay which is mined and not quarried, and particularly certain shales and fireclays found near coal seams. The “clunches” vary greatly in composition, and some of them are far too impure to be used for anything better than common bricks; others are good for firebricks and other refractory goods. The better qualities of clunch are identical with fireclays (*q.v.*), and can only be obtained by carefully selecting the material in the pit. Inferior qualities may be regarded as brickmaking shales. “Stone clunch” is another name for ganister.

Common clay includes a large variety of clays of widely different qualities, and accordingly it is known by a number of different names. Usually the term is restricted to surface clays, many of which are very impure; and as no accurate definition of “common clay” exists, the use of this term is to be deprecated rather than encouraged, and more accurate terms substituted when possible.

Conglomerate clays are those which form a kind of cement,

¹ A microscopical examination should be made, so as to ascertain the real nature of this “mica,” as felspar is common in some foreign kaolins, though seldom seen in commercial British china clays.

uniting the contained rounded stones into a firm mass. They are often extremely impure, and are seldom of any commercial value.

Crucible clays are selected fireclays, it being found that more than one clay must be used to obtain a body possessing the necessary strength, surface-density, refractoriness, and resistance to sudden changes in temperature required in crucibles. The clays most used for the manufacture of crucibles are the fireclays of Derbyshire and Stourbridge (see *Fireclays*), a cheaper local clay often being added, together with some burned clay or "grog." Plumbago is also added where the crucibles are to be used for melting easily oxidisable metals.

The value and suitability of a clay for the manufacture of crucibles depends upon its refractoriness under the conditions in which it will be used, so that the size of the particles and the method of preparation are often of more importance than the chemical composition of the clay.

Diluvial clays or **colluvial clays** are those collected by the action of powerful streams, floods, or other *unusual* action of water (p. 115). They may be of almost any composition, but usually contain considerable proportions of sand, chalk, limestone, gravel, or other impurities. Their value and use depend upon their chemical composition and physical nature, and when these are known they can usually be considered as belonging to a more definite class of clay than can be comprised under the term "diluvial." These clays must not be confused with those produced by the more *normal* action of water and termed *alluvial* deposits.

According to Phillips, the lower part of the alluvium in Yorkshire is of diluvial origin and is exposed in a number of places. Later observers appear to have regarded these exposures as of glacial drift.

Dinas rock is a highly siliceous material found in the Vale of Neath and used for making a certain kind of fire-bricks. It is not a "clay," though frequently so termed, but is more closely allied to the Millstone Grit. In order that it may be used, it must be mixed with lime-water so that, in the kilns, the lime and silica may combine to form a vitrified mass which cements the other particles in the bricks together. These bricks expand by heat, while bricks made of fireclay contract. Hence they are useful for the roofs of reverberatory furnaces, and for parts where a solid and compact lining is required. They must not be exposed to the action of slags rich in metallic oxides.

Many so-called "Dinas bricks" are made from siliceous rocks or pure sands, and only resemble the true Dinas bricks in their general composition (see p. 181).

Drift clays are the product of glacial action. See pages 31 and 115.

Earthenware clays and other white-burning clays are ball clays and china clays of various qualities, according to the kind of earthenware or other pottery required. The term is sometimes used for red-burning clays made into coarse pottery.

Eocene clays are described on p. 83. This geological subdivision contains many valuable clays.

The reader who wishes to gain a general view of the stratigraphical relationship of these numerous clays and sands to each other, can do so to the greatest advantage at Whitecliffe Bay on the east of the Isle of Wight, or at Alum Bay on the west of the island.

At both these places the Eocene beds have been displaced from their original horizontal position, viz. one above another, and are now side by side, forming the opposite extremities of an anticline. If visited on a bright, sunny day, shortly after heavy rain, the colour-effects of the different strata appear extremely beautiful, particularly at Alum Bay. The series at Whitecliffe is more complete, but the abundant vegetation and the past weathering of the cliff make it more difficult to examine some of the beds. To facilitate the identification of the various beds, the vertical sections given in the Geological Ordnance Sheet No. 25, or in Geological Memoir No. 10, should be used.

Owing to their peculiar anticlinal arrangement, these clays have but little industrial value in the Isle of Wight, though the less calcareous portions are used for bricks and roofing tiles in various parts of the island, notably at Newport, Ryde, Sandown, Shanklin, Ventnor, and Bembridge.

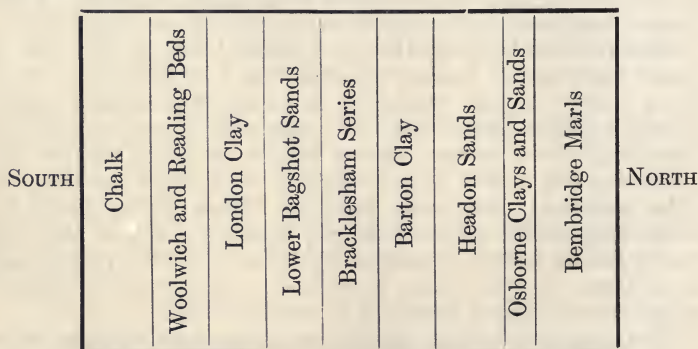


Diagram showing relative positions of the Eocene clays in Whitecliffe Bay, I.O.W.

Estuarine clays are those formed at the mouths of rivers (see p. 116). Those above the Oolite at Essendine and Little Bytham are used for brickmaking.

Fat clays are those possessing a high degree of plasticity, and are characteristically unctuous to the touch. They usually shrink on burning, and, unless carefully treated, are likely to crack and split. On adding sand and other non-plastic material, the "fatness" is reduced and a "leaner" clay formed. These lean clays shrink less and are more easily manipulated than are fat ones, though they are often less pure. By adding loam (which is lean) to a fat clay the shrinkage and the "loss in kiln" due to cracking may be greatly reduced. Ball clays and surface clays are usually fat; china clays and deep-mine clays are generally lean.

Ferruginous clays are, as their name implies, those rich in iron compounds. As these iron compounds may be introduced into clays of all kinds, the ferruginous clays possess an enormous variety of characteristics and composition. They form the bulk of the brick and terra-cotta clays (see these under separate headings), and are usually red when burned. If the iron compounds are reduced in the kilns, the ferruginous clays form dark grey or "blue" goods—the well-known "blue bricks" of Staffordshire being of this class. If much lime is present (as in marls) ferruginous clays burn to a cream or white colour.

The chief ferruginous clays are:—

1. Plastic ferruginous clays suitable for bricks, terra-cotta, flower-pots, and most red ware. They consist of a plastic clay with 4 per cent. or more of iron oxide.

2. Siliceous ferruginous clays or loams, similar to the foregoing, but less plastic and not so suitable for pottery manufacture.

3. Ferruginous calcareous clays, which burn almost white on account of the iron and lime compounds combining with each other. Many of the "white" bricks of the south and south-east of England are of this kind. They are moderately plastic and may be made into good bricks. Their most notable characteristic is the fact that in spite of the proportion of iron they contain they do not burn red for the reason just given.

4. Fusible ferruginous clays, suitable for vitrified ware, for roofing tiles and for specially strong bricks. They contain alkalis and some lime in addition to iron compounds, and usually form goods of a peculiar dark brown colour. They are chiefly used for making the lower grades of coarse stoneware and best (blue) engineering bricks (see *Vitrifiable Clays*).

Fireclays are lean clays so free from impurities that they can

withstand the action of intense heat. In Great Britain there is no standard temperature which such clays must be able to withstand, but on the Continent they must be at least as refractory as Seger cone 26 (see p. 189).

Fireclays—including *clunches* and *underclays*—occur chiefly in the Coal Measures, though other refractory clays are well known. The *china clays* (“kaolins”) and some *ball clays* and *pipeclays* are of this kind, but they are not usually spoken of as fireclays. If refractory clays are divided into two classes, (1) those in which the proportions of alumina and silica are nearly equal, and (2) those in which the silica largely predominates, the latter will include most ordinary fireclays, though a few of the most valuable will be included in the former class. Thus china clay may be taken as one limit and pure silica as the other, both these materials being highly refractory, and are, for some industrial purposes, included in the term “fireclay.”

Geologically, the term fireclay is sometimes used for any underclay, but this should be avoided and the use of the term “fireclay” confined to refractory clays.

Broadly speaking, the fireclays may be regarded as relatively hard, clean clays containing an indefinite proportion of free silica, and their value is largely, though by no means entirely, dependent on the proportion of true clay (hydrogen aluminosilicate) and of fluxes they contain.

Their refractoriness varies according to the proportion of impurities present, particularly as regards titanium oxide, iron oxide, lime, magnesia, potash, and soda. The last two are usually included under the term “alkalies.” Unless the proportion of these impurities is very small, the clay will not be refractory. Unless supported by other tests, an analysis will give but little indication of the behaviour of a clay when heated.

The fireclays are found in great abundance, and are used in large quantities in the manufacture of fire-bricks, retorts, crucibles, glazed bricks, and many sanitary appliances; they form one of the most valuable series of clays.

In the form of bricks, fireclays are used for the internal construction of air-furnaces, crucible-furnaces for brass-melting, etc. Similar furnaces for cast iron sometimes have the hearth formed of sand rammed on the top of the fire-brick. Fireclays are also used for the manufacture of clay crucibles for melting steel, etc. For bricks, crucibles, and other refractory goods a mixture of clays gives a better result than does any individual clay used alone.

The best known deposits of fireclay in England are the Upper and Middle Coal Measures—the Lower ones consisting of siliceous

rocks. They are worked in Staffordshire, Warwickshire, Shropshire, Yorkshire, Northumberland, Durham, Derbyshire, Leicestershire, and Wales, though fireclays occur beneath the coal seams in each of the other coalfields. The fireclays of the Teign Valley beds in Devonshire are of a different formation (p. 179). Fire-bricks of fair quality were formerly made at Hedgerley, near Windsor, from a sandy clay known as *Windsor loam*, and were much used in London. A refractory earth also occurs near Esher, Ewell, and Epsom, and is known as fireclay. It is much used locally, but its characteristics have not been fully examined. A fireclay from the Lower Oolite formation in Commondale, Yorkshire, and in a few other places, is made into fire-bricks and domestic fire-blocks.

Within the compass of a single volume it is impossible to give complete details of all the fireclay seams, owing to their sudden and serious variations within small areas.

Tables of strata are published in the various *Memoirs of the Geological Survey*, but with a few exceptions these afford little or no information as to the value of the fireclays tabulated, so that it is necessary to test each stratum thoroughly before its value can be known. Even then, the liability to sudden variations in composition necessitates the most constant vigilance and oversight, or the clay may be spoiled by admixture with a less refractory material.

The disastrous consequences resulting from the use of insufficiently refractory materials in large industrial furnaces make it imperative that the risks should be reduced as far as possible. Hence fire-bricks and other refractory goods are sold chiefly "by reputation." One result of this is to bring the fireclays of a small number of localities into great prominence, whilst those in other districts remain practically unknown outside the area where a local use is found for them. In addition to the well-known fireclay deposits mentioned above, the underclays of the Coal Measures in Gloucestershire, Somerset (p. 56), and Wales yield excellent fireclays, but so far they have not been well developed industrially. To some extent this is due to the better-known fireclays being so situated that their owners can deal adequately with all the ordinary demands of the market, and the profits of fire-brick manufacture are not sufficient to induce many colliery owners in other districts to cater for more than a local trade. Within the past few years there has been a considerable increase in the number of manufacturers of fireclay goods outside the districts mentioned above, particularly in Wales.

The **Welsh fireclays** (p. 56) are worked in Denbighshire and Flintshire, around Wrexham, Ruabon (p. 56), Mold, Ewloe, and

Buckley. The two last-mentioned districts are famous for goods with peculiarly high resistance to acids, as well as for the more refractory fireclays. In South Wales the fireclay works are largely confined to Glamorganshire, and are mainly found in the vicinity of Neath, Swansea, Llanelly, Merthyr-Tydfil, and Pontypridd. The siliceous rock is also made into fire-bricks at Kidwelly in Caermarthenshire.

The Welsh fireclays are very variable in character and are seldom above No. 2 grade (p. 189), though specially selected strata yield clays of the highest quality. With care in selection a much better average quality of fireclay could be used in this area, but hitherto—with the exception of those made near Ewloe and Buckley—the best fire-bricks have been sold locally, or the clays have been sent to the surface without selection, so that only medium quality bricks could be produced. This is due to the custom of regarding the Welsh fireclays as waste products from the collieries rather than as intrinsically valuable materials. In many respects the Welsh fireclays resemble those of the Midland counties (p. 178), but are somewhat more siliceous, especially in South Wales. Some of the fireclays in North Wales bear a close resemblance to the better qualities of those obtained from the Northumberland and Durham coalfields. The better qualities are well adapted for the manufacture of drain-pipes and brown sanitary ware, but not for glazed bricks and white ware.

The highly siliceous materials used for fire-bricks in and around the Vale of Neath are described as *Dinas rock* on p. 169.

Near Mold the fireclays occurring in pockets in the Mountain Limestone (p. 182) are worked.

In **Staffordshire** and **Warwickshire** (p. 206) the fireclays crop out, and are known (erroneously) as marls,¹ but the best qualities occur at a considerable depth. The “saggers” used in the Staffordshire potteries are chiefly made from these local fireclays, but the most famous fireclays are found in the Dudley coalfield in the neighbourhood of Stourbridge, where the material is largely used for the manufacture of retorts, fire-bricks, blocks, and other refractory goods.

The *Nuneaton fireclay* in the Warwickshire coalfield is exceptionally suitable for glazed brick manufacture.

Stourbridge fireclay varies somewhat largely in composition according to the particular stratum from which it is obtained, and much now being placed on the market is not superior to that from other districts. The best Stourbridge clay is character-

¹ The Staffordshire “marls” are not true marls, but are really low-grade fireclays occurring in the Coal Measures (see p. 56).

ized by its alumina, its plasticity, refractoriness, and low kiln shrinkage. This last is about half that of the Northumbrian, Yorkshire, and Scotch fireclays, and seldom exceeds 3 per cent. The strata near Stourbridge are much faulted, and the fireclay has been upheaved so as to be available in many places when only shallow shafts are used. These higher deposits are rapidly being worked out, and the lower portions of strata are coming more into use. Thus in the old mine seam of Stourbridge clay (fig. 13), the "mild" clay, rich in alumina, occurs chiefly at the top, and gradually changes to "strong" or siliceous clay at the bottom, with a "medium" clay in between. This "medium" stratum usually contains the well-known Stourbridge "Pot" clay. Under the microscope the "strong" clay consists of well-defined crystal-line particles, the "medium" clay has a few such crystals in a mass of amorphous material, and the "mild" clay appears to consist entirely of amorphous matter. The "mild" clays are more plastic, and are considered to make stronger and tougher bricks than the "strong" ones.

In **Shropshire** the fireclays are well developed in the Coalbrookdale district, particularly near Brosely, Jackfield, and Coalport. The most refractory clay lies immediately below the Ganie coal, in a stratum about 2 ft. thick. It contains nodules of ferrous carbonate, but after weathering burns to a pale cream colour.

In **Worcestershire** the best Bewdley fireclays from Wyre forest are used locally in the Worcester potteries. They resemble the fireclays of Stourbridge, but are richer in iron oxide and are somewhat less refractory.

Yorkshire fireclays (pp. 53 and 55) are of widely varying composition, the alumina-content ranging from about 2 per cent. to over 30 per cent. (see footnote on p. 181), chiefly found in what are known as the "Leeds" and "Halifax" beds, of the Lower Coal Measures, the fireclay industry in this county centring round Leeds, Halifax, and Huddersfield, and southwards to Sheffield, where the beds are more siliceous. The Halifax bed extends also into Lancashire, and several important fireclay works are situated on it in this latter county.

What is commonly known as the "Leeds bed" occurs near the town of that name, and covers an area of about thirty square miles. It is generally understood that the other fireclays in this district are suitable for refractory goods of medium quality, but not for making the most refractory articles, glazed bricks and other accurately shaped ware, for which the true "Leeds" clay is specially valuable on account of its freedom from organic matter and iron compounds. The "Leeds" clay occurs in two

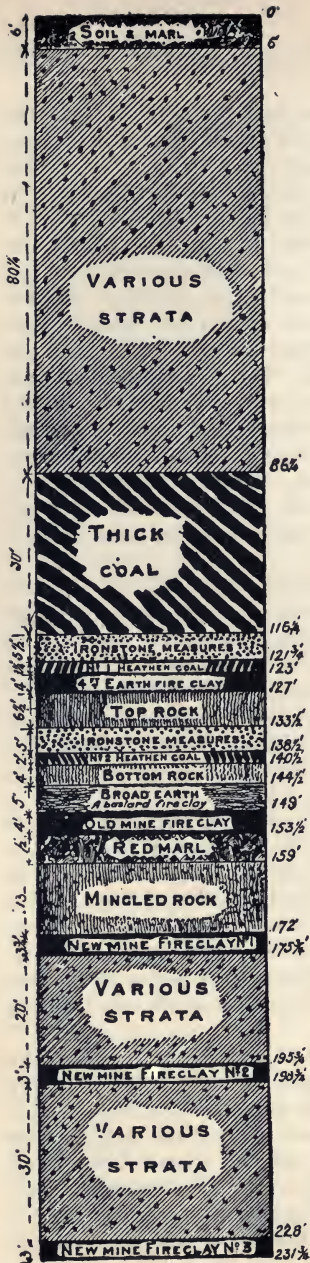


FIG. 13.—Section of Stourbridge Strata.



FIG. 13A.—Enlarged view of a fireclay seam in fig. 13.

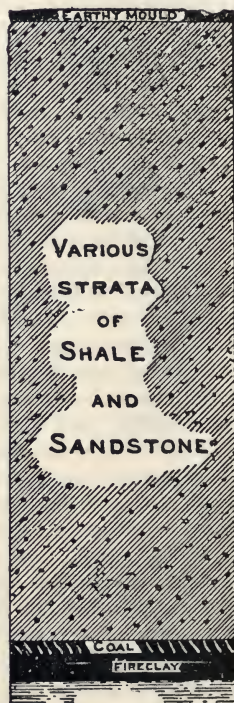


FIG. 14.—Section of South Yorkshire Fireclay Seams. (After F. J. Bywater.)

seams—one relatively near the surface, and the other nearly seventy fathoms below; the upper portion of the deep one is the most valuable part of the deposit. It occurs immediately beneath the “better-bed coal.” The clay found nearer the surface is usually tender, more plastic, and shrinks more than the deep-mine clay. This is objectionable for glazed goods and for large pieces of refractory ware, but less so for fire-bricks, particularly if ground burned fire-brick or “grog” be added. This “tender” clay is slightly richer in alumina than the strong clay found below it, and indicates a material somewhat richer in true clay.

Leeds fireclay is not rich in alumina, and corresponds in chemical composition to a mixture of equal parts of pure clay (hydrogen alumino-silicate) and free silica, with a tendency to contain rather more silica, but some seams are more aluminous.

The “Halifax bed” also consists of two or more series of seams and also extends over a large area. The upper series—known as the “Ganister” or “Hard-bed coal,” consists of hard coal underlain by ganister and fireclay—and below it, separated by a great thickness of sandstones and siliceous shales, is the “Soft coal” or “Low bed.” The ganister is made into silica bricks and furnace linings (p. 181), and the “hard coal bed fireclay,” immediately beneath it, is manufactured into similar articles to those made from the “Leeds bed” clays. Most of the works making refractory goods from the upper Halifax fireclay are situated at Elland and near Halifax, as further north and east it gradually alters and comes nearer to the surface, but is then very suitable for the manufacture of salt-glazed and engobed goods. To the south-east it is much used for drain-pipes and for a moderate quality of fire-brick, but is very liable to be contaminated with iron ore, which occurs as thin veins in it.

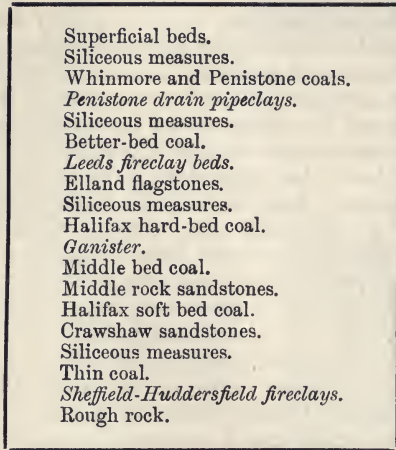
In composition the Halifax fireclay is somewhat siliceous, the best specimens corresponding to Stourbridge Deep Mine or to a mixture of true clay (hydrogen alumino-silicate) with rather more than an equal weight of free silica, but some portions of the bed are of distinctly inferior quality.

Around Sheffield and between there and Huddersfield the ganister (p. 181) is worked, as is also an excellent fireclay (fig. 14) obtained from immediately above the Rough Rock. This fireclay is at the base of the Coal Measures; the “Soft coal” is some distance above it and the Crawshaw sandstones are intermediately situated, except near the outcrops. This fireclay is largely used in the manufacture of crucibles for steel melting as well as for fire-bricks and other refractory goods.

Seams of so-called “fireclay” occur in Yorkshire in association

with almost every seam of coal, but except for those mentioned above, they are too thin to be worked profitably, or are so impure as to be insufficiently refractory. When abundant they are used, as at Penistone and Denby Dale, for making building bricks, tiles, and drain-pipes.

The relative positions of the various Yorkshire beds will be seen from the following diagram :—



The fireclays of **Northumberland** and **Durham** (p. 55) are chiefly concentrated around Newcastle and Sunderland, but these clays vary greatly in quality. The best specimens resemble those from the Stourbridge "Old Mines" as regards their alumina content, but the northern clays contain more alkalies and are not quite so refractory. Compared with the "deep-mine" clays of the Stourbridge district, the Newcastle clays are often richer in alumina and the better qualities are equally refractory.

In both Northumberland and Durham various seams of different characteristics and value are found. These are usually mixed together in suitable proportions.

Post clay is a local name for highly siliceous fireclay.

The "Corbridge fireclay" is less refractory than the ordinary Tyneside fireclays. It is valuable for the manufacture of drain-pipes and semi-vitrified goods.

The **Midland fireclays** are rather less refractory than those of Stourbridge or the North, but for the manufacture of sanitary goods this is an advantage, as the partially vitrified body is less

liable to absorb substances deleterious to health. They are often rich in alumina, but the presence of nearly 4 per cent. of lime, magnesia, and alkalis prevents them from being highly refractory. The term "clunch" (p. 168) is frequently used for all shales in the Midlands, and therefore includes these fireclays, though whether the clunch found at any particular site is sufficiently refractory to be made into fire-bricks depends on its chemical composition and physical characteristics, as the term "clunch" indicates almost any material of a shaly nature, and minerals to which it is applied are very varied in refractoriness.

On this account it is very desirable that the different strata should be kept separate from each other, though this is seldom done, the custom of most collieries being to regard the clunch as a waste material to be brought to the surface and tipped where it will be out of the way, without much regard being paid to its future uses. The result of this indiscriminate tipping is that many large heaps of material have been rendered worthless, and not a few brickmakers have been ruined.

The Derbyshire and Leicestershire fireclays are chiefly worked between Ashby-de-la-Zouch and Burton; Church Gresley and Swadlincote being important centres for sanitary goods, particularly sewer-pipes. The whole of the Trent district above the Midland coalfields may be regarded as a possible site for fireclay works, and the Nottinghamshire collieries are, in several cases, utilizing their fireclays advantageously for pipe-making and for No. 2 grade fire-bricks.

The highly siliceous fireclays found in the Derbyshire limestone are described on page 182.

The "Sida" clay obtained from beneath the ganister near Chesterfield is a well-known refractory clay, though richer in iron than the best fireclays.

The **Devonshire** fireclays are not associated with the Coal Measures, but are really inferior china and ball clays, some being deposited in pockets along with felspar, etc. The impurities contained in them prevent them from being highly refractory—though pockets of exceptionally refractory material are occasionally found. The more easily vitrifiable fireclays in this district are valuable for paving bricks, sewer pipes, and other articles where absence of porosity or unusual strength and toughness are required. The more refractory clays are used for fire-bricks, glazed bricks, and architectural work.

In **Cornwall** the refuse from the mica drags of the china clay-mines is sometimes made into high-grade fire-bricks.

The **Scotch** fireclays (p. 54) are chiefly worked near Glasgow,

the Glenboig Union Fireclay Co. claiming to be one of the largest firms of its kind in the world.

Fireclays of good quality occur in other parts of Scotland, but they are usually less refractory than those found in the neighbourhood of Kilmarnock, Gartcosh, Glasgow and Bonnybridge, Kirkcaldy and Alloa, and only serve the more local markets.

The best Scotch fireclays are unusually refractory, and as bricks and other articles made from them are burned at a much higher temperature than is usual in England, they have gained a great reputation for non-shrinkage when used in furnaces, though the shrinkage in the kiln is often very great.

At Glenboig (fig. 15) the chief seam crops out at Old Works, but is worked at a depth of 500 feet at Star Works, the dip being very rapid. The seam used is the lowest of several, the others being of less value. The proportion of iron is high (1.3 per cent.), but it is of such a nature that it does little or no harm.

In chemical composition the Scotch fireclays approach that of china clay more nearly than most English fireclays, but the best specimens obtainable from the "Old Mine" strata at Stourbridge resemble them, though the average percentage of iron is greater in the Scotch clays.

FIG. 15.—Fireclay seams at Glenboig. (After F. J. Bywater.)



are largely used in the manufacture of white glazed sanitary ware as well as for fire-bricks, etc.

The **Irish fireclays** are chiefly found in Co. Tyrone. They are of No. 2 and inferior grades (p. 189), but some are excellent for drain-pipes (see *Bastard Fireclays*, p. 184).

As already mentioned, the fireclays of the Coal Measures may be regarded as mixtures of true clay and free silica, their refractoriness depending partly on the proportion of these two materials and partly on the nature and proportion of lime, magnesia, iron, and alkalis present. These bases occur as minerals of various

kinds present in the original rocks from which the clay was formed or introduced at a later stage. They are very objectionable in fireclays intended to be used for refractory goods, as they lower the fusing-point of the clay as a whole (see *Refractoriness*).

Highly siliceous fireclays¹ differ somewhat from the ordinary fireclays, but are often equally refractory. These very siliceous clays contain from 75 to 95 per cent. of silica and correspond to silica which contains 10 per cent. or more of true clay, together with a small amount of impurities. The most important of these deposits are:—

(1) The ganister fireclays of South Yorkshire.

(2) The fireclay deposits in the limestone hills of Derbyshire, North Wales, North Staffordshire, etc., and various other "pocket clays."

(3) The more siliceous portions of the Coal Measure fireclays.

Their plasticity is naturally low and their texture usually somewhat granular; their use is confined to the manufacture of refractory goods of simple form such as fire-bricks, or they are moistened and rammed into position to form furnace-linings. The colour is generally grey, but is sometimes yellowish.

Ganister is a fine-grained siliceous grit occurring under the Coal Measures, chiefly in Derbyshire, Yorkshire, and Gartcosh (Scotland), and has probably been formed by the weathering of sandstone containing clay. It is much used as a refractory material for lining steel furnaces, and is also made into fire-bricks.

In composition and general behaviour it corresponds very closely to a pure silica mixed with about one-tenth of its weight of fireclay—sufficient, in fact, to bind the siliceous particles together.

Though commonly regarded as a "clay," it is not correctly so described, as it is most closely related to the sands and grit-stones. Bricks of the "Dinas" type (*q.v.*) resemble those made of ganister, but contain lime as a binding material in place of clay, and so are not quite so refractory. The composition of ganister should be within the following limits: Silica, 87 to 96; alumina, 4 to 5; ferric oxide, 0 to 1.5; lime and magnesia, 0.25 to 0.75; alkalis, 0 to 1.00 per cent.; otherwise it will not be sufficiently refractory. The greater part of the ganister deposits

¹ The term "fireclay" is used industrially to include Dinas rock, ganister and other siliceous rocks used in the manufacture of fire-bricks, etc., as well as true "fireclays." Some of the rocks are not, strictly speaking, clays at all, but are most closely allied to the sands and sandstones; others are true clays containing a considerable proportion of free silica.

are useless—except for road metal—because they contain too high a percentage of impurities. For use as a refractory material the ganister must, therefore, be selected with great care.

Best Yorkshire ganisters contain 95 per cent. silica.

After mining, the ganister is reduced to a coarse powder, without weathering, and in certain cases lime-cream is added during grinding. This addition is in all cases kept within low limits, and is only made when the material is deficient in binding qualities. In some works 25 to 30 per cent. of fireclay is added during the grinding. Ground ganister—mixed with a requisite quantity of water—can be used in any form of furnace construction which will permit of the material being rammed around a pattern or used in the form of a brick. It is largely used in iron-melting cupolas, Bessemer converters, and crucible-steel furnaces. Ganister is also an excellent material for patching and repairing worn places in kilns, etc. Ground ganister is also moulded into bricks or small blocks which on burning are commercially known as “silica bricks,” though this term is also used to include bricks made of any siliceous material. There are also a number of patent refractory bricks composed of silica rock or sand, to which 10 per cent. or more clay has been added in order to produce a material with a composition similar to that of the natural ganister, but higher in alumina, and therefore (theoretically) more refractory.

Puramachos is an artificial ganister of this type, and consists of powdered quartz with 10 per cent. of clay and a little water-glass, but this material appears to vary greatly in composition.

Owing to its lack of plasticity, ganister cannot be made into such large blocks as are produced from fireclays.

Pocket Fireclays.—These highly siliceous clays occur in the mountain limestone of Derbyshire, North Staffordshire, and more rarely in North Wales and Ireland¹; they consist of a mixture of fine white clay (coloured in parts) and clean sharp sand, often sharply separated, together with small amounts of other minerals derived from the limestone and the overlying Millstone Grit. Fig. 16 shows a typical cross-section of one of these pockets or “swallow-holes,” many of which are large and of considerable depth.

This clay has probably been carried to its present position by streams of water acting on the shales, sandstones, and grits on the higher ground. The bulk of this deposit in Derbyshire can only have been derived from Carboniferous limestone rocks, the

¹ At the present time the pocket fireclays in Ireland are entirely unworked.

calcareous portion of which has been removed by solution; the clays and sands left have since become mixed with debris from the overlying Millstone Grit. The presence of the quartzite pebbles (Bunter beds) can best be explained by assuming an extension of the Trias beyond Ashbourne, or that they were brought by glacial action (see p. 115).

The material in the pockets is a curiously irregular mass of sand, clay, and pebbles, and, unfortunately, the clay is often very impure and extremely variable in composition, though usually very plastic, and when fairly free from iron it is often valuable for architectural work and for sanitary ware. The average

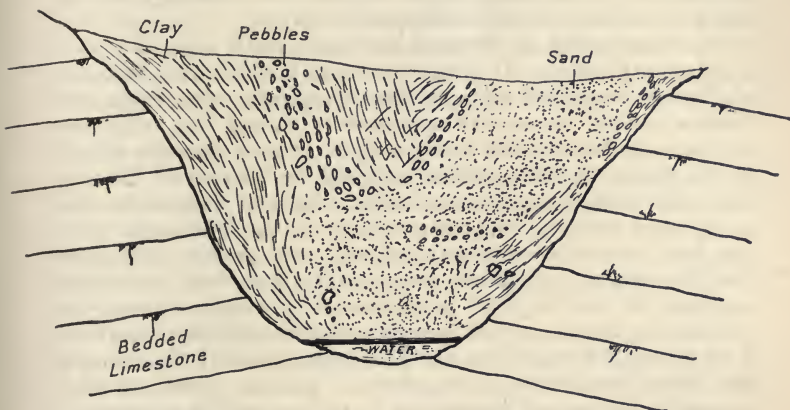


FIG. 16.—Typical Sand and Clay Hole in Mountain Limestone. (Harris.)

proportion of alumina in a large number of samples of this kind of clay is 10 to 14 per cent., but occasionally much richer clays are found. In some cases an abnormal whiteness in the clays is attributable to small flakes of white mica. The whiter clays and sands are usually blended, and the material is chiefly sent to Staffordshire to be made up into articles.

The principal pockets are found at Brassington and Newhaven, but odd ones are found scattered irregularly over parts of Derbyshire and North Staffordshire. Unfortunately they are somewhat difficult of access in spite of the railway. Similar deposits near Mold (North Wales) are much used for fire-bricks, but those near Llandudno are not, at present, being worked.

All bricks and blocks made of highly siliceous clays expand on heating, and should not therefore be laid too tightly or with too

fine a joint. It is necessary to heat and cool them very slowly, and they must be kept dry before and during use.

Bastard fireclays are the clays associated with coal seams (underclays) which prove not to be sufficiently refractory to be used for the manufacture of fire-bricks. Seams of such clays occur in almost every coalfield and beneath almost every seam of coal. The better qualities are largely used in the manufacture of salt-glazed ware, building and engineering bricks, sanitary ware, coarse pottery, and for all purposes where a high degree of refractoriness is not required. They are, in many cases, eminently suitable for the production of "stoneware," as they form a vitrified and impermeable ware without the tendency to twist and warp shown by more readily fusible clays.

The **composition of fireclays** varies so greatly that no general standard is possible. It is, however, essential that the proportion of fluxing materials, such as lime, magnesia, iron oxide, and alkalis, should be as low as possible, though the maximum amounts of these oxides which may be present depends greatly on the degree of refractoriness required by the user of the clay. The fact must never be overlooked that the composition and qualities of clays in contiguous beds in the same pit, and even of clay from the same horizontal bed, may vary greatly; and partly for this reason, and partly because clay from one bed seldom possesses all the required properties, it is usually necessary to mix the clays from several beds together in definite proportions. This is very different from the plan often adopted of mixing all the clays promiscuously together, a practice which is often extremely unwise and detrimental to the user of the material.

In judging the quality of a fireclay and its suitability for specific purposes a chemical analysis is of little value, and unless carried out with exceptional care it may even be misleading. Beyond indicating the total amount of bases forming the impurities which lower the refractoriness of the clay and affording a rough indication as to the amount of free silica in the material, a chemical analysis alone gives little information and should be supported by physical tests and observations on the refractoriness, colour, texture, cleavage, markings, and other special features or peculiarities of the material.

The chief impurities in fireclays are: *Silica* in the form of sand or quartz, or in a gelatinous hydrated form. In both cases it may be in such fine grains as to be incapable of complete mechanical separation from the true clay.

The whole of the silica present in a fireclay may be in one or more of three forms: (a) combined with alumina and water

to form clay; (*b*) as hydrated silica; and (*c*) as free silica ("sand").

Only the forms *b* and *c* can be regarded as impurities, and a certain proportion of silica in form *c* is often essential in the commercial usage of refractory clay, as it forms the bulk of the coarser particles which form a kind of skeleton and prevent cracking and excessive shrinkage. Hence the term "impurity," as applied to silica in a fireclay, does not necessarily indicate that the clay would be increased in commercial value if the free silica could be removed.

The hydrated silica mentioned above is of little commercial importance. It was at one time thought to be important in the manufacture of fire-bricks, in which lime is used as a cementing medium, but it has now been conclusively shown that so long as there is sufficient silica in an extremely fine powder present, there is little or no advantage in its being in a hydrated condition.

Titanium oxide, lime, magnesia, and alkalies are important impurities, as they all reduce the fusibility of the clay, though for some purposes they are valuable in effecting a partial vitrification of the material on firing, and so enable articles with greater mechanical strength to be produced. In a fireclay of the best quality the sum of the fluxes (other than iron compounds) should not usually exceed 3 per cent.

A clay which contains a large proportion of *mica*, easily discerned by its glistening appearance in the clay, is not likely to be very refractory, as mica contains potash, which on being heated rapidly fluxes the particles of silica and alumina, and so partially fuses the clay.

Vanadium, manganese, and various other rare metals and minerals are also frequently present in minute quantities. Their influence on the fusibility is unimportant, but they sometimes stain the fired goods containing them. The most important staining materials are, however, compounds of iron.

Iron compounds, particularly pyrite and marcasite (both sulphides), are extremely important impurities. The damage they do is not simply dependent on the proportion in which they are present, but upon their peculiar ability to form ugly blotches of grey or black slag even after being finely ground. These blotches not only detract from the appearance of fire-bricks and other refractory articles, but they may entirely ruin sinks, baths, lavatory basins, glazed bricks, and other sanitary articles, when the total percentage of iron present is extremely small. Hence every effort must be made to keep the proportion of iron com-

pounds as low as possible, and to remove whatever can be taken out previous to, or during, the grinding. This is, fortunately, not very difficult with most fireclays, as the greater part of the iron is present in the form of small nodules (pebbles or "kidneys") which are easily recognized. If the large lumps of clay received from the pit are broken carefully, with sharp, rapid blows of a hammer, the clay will split without breaking the nodules, and they can then be cut out of the clay so completely that the small amount of pyrites left can do little or no harm. It is, however, essential that the clay should be broken by hand into pieces not larger than a boy's fist, or some of the ironstone nodules will be overlooked. This work of sorting out the clay should be placed in the care of thoroughly conscientious men; if it is carelessly done the effect can never afterwards be removed, though certain additional precautions are possible which will, to some extent, tend to minimize the evil effect of any undetected pyrites. Thus the nodules are so hard that by stopping the grinding mill and cleaning it out twice daily, most of them may be thrown away with the material taken off during the cleaning. Care must, however, be taken not to run the mill too clean, or the pyrites will be ground and passed into the clay, and so make matters worse than if the "cleaning" had not been done. If the clay is very rich in pyrites, and the output of the mill is large, a greater quantity must be left on the mill when the latter is stopped, and then cleaned off. Thus a clay containing 2 per cent. of pyrites, ground in a mill with an output of 50 tons per day, must have about 5 cwts. left on the bed when the mill is stopped, so that this clay so left may be thrown away as being too rich in pyrites for ordinary use, and the mill should be cleaned at least three times daily. Even then at least a quarter of the total pyrites will be mixed with the clay, if it has not been previously picked out by hand before the clay was sent to the mill. If those nodules which cannot be picked out of the lumps of clay, or removed in any other manner, are ground very fine, but little harm will usually be done by them, unless the proportion of iron compounds originally present was excessive; but if the amount of these iron sulphides left in the clay after the most careful attempts at separation is sufficient to spoil the goods, this particular source of clay must be abandoned.

Another partially satisfactory process consists in grinding the material containing the nodules in a mill and adding water to make a slip, and then allowing the sludge to settle in catch pits, when the greater part of the iron pyrites will fall to the bottom, the upper part of the clay remaining comparatively free from

iron. This process of washing does not remove all the ironstone, and can seldom be made to pay financially.

Various efforts at electro- or magnetic separation of the iron sulphides present in fireclays have been made, but so far without much result, though there are indications that further experiments in these directions may be more satisfactory.

Owing to the peculiar manner in which it combines with the silica of the clay, it is not possible on a commercial scale to grind pyrites so fine that it does not appear as minute or larger blotches on the surface of the goods.

Good fireclays should not contain more than $1\frac{1}{2}$ per cent. of iron compounds. Iron sometimes occurs in clays in the form of oxide and is then comparatively harmless, as it does not form slag spots, but acts simply as a colouring agent and as a mild flux. This is the case with Glenboig fireclay, which contains an unusually large proportion of oxide with but little pyrites.

Organic matter—largely due to “coal-partings,” and to remains of plants occurring in the fireclay—is important in two directions: (1) if sufficiently extensive the porosity of the clay is increased and a little less fuel is required for burning the bricks, though this is seldom important in fireclays, and (2) the hollow spaces left when the organic material burns away may cause serious defects in the surface of glazed goods. Hence, for these, the amount of organic matter present should be very small or it should be in extremely minute particles. This organic matter has apparently played an important part in the formation of fireclays, especially in the production of iron sulphide (pyrites). Some of the larger pieces of coal and other organic matter may be picked out at the same time as the nodules of iron sulphide, but others, and a variety of other minerals, cannot be so removed. Fortunately there are many clays which are sufficiently pure to require no treatment beyond careful sorting. The cost of purifying the lower grades of fireclays is usually prohibitive.

Less suitable clays frequently occur amongst the better qualities and must be removed from the main bulk at the same time as the pyrites, etc., is removed, providing this has not been done at the pit. It is, however, far better if the miners set aside the superior qualities of clay and keep them separate from the rest, so that much sorting out of the different clays on the yard may be avoided.

Fireclays are not usually exposed much to the weather, though this would facilitate the grinding. The objection commonly urged against “weathering” these clays is that it tends to break them up into particles which are too small for the sudden

changes in temperature to be resisted or for large articles to be made from them.

In some districts, however, large heaps of fireclay which has undergone a considerable amount of weathering are much valued, as some of the iron pyrites in them is decomposed and is either washed out or accumulates into large reddish-brown masses which are easily removed by hand. Several years of exposure appear to be necessary to effect this change, and in some fireclays the chief effect of weathering is to distribute the iron compounds irregularly through the clay in a form in which it cannot be removed.

The **physical characteristics** of a fireclay must be such as to give it great refractoriness combined with some ability to withstand sudden changes in temperature, and a texture which will enable it to be glazed satisfactorily if the clay is to be used for the manufacture of sanitary or chemical ware.

The **colour** of fireclays, as mined, is usually grey or somewhat bluish, though some refractory shales are brown. The colour of the Coal Measure fireclays is due to minute particles of organic matter, disseminated throughout the clay by the action of the water; and to a less extent to other minerals. Imprints of vegetation—the knotted stems and branches of trees, or shells—are also frequently found in a very perfect condition. In some places the colour of the clay closely resembles that of freshly-cut Millstone Grit, and the fireclay is then usually coarse in texture, rich in free silica, and richer in iron oxide.

In other places fireclays are black, with bright cleavage surfaces; but are then inferior in quality, vitrifying at a lower heat, and too full of deleterious substances to be useful, though they are then usually plastic and of an oily nature.

In fireclays found near the surface the colour sometimes becomes almost white, with slight markings and traces of iron oxide, or a mottled grey and yellow colour with much strong red ochre-like matter in it.

The **texture** of a fireclay should be homogeneous, without laminations, except such as may be caused by the thin markings due to the fine veins of coal, and it should be free from any grains. A few of the secondary qualities and of the very siliceous fireclays are found in well-marked layers, and are both laminated and striated. It should be fine, apparently slightly greasy on a fresh-cut surface, and free from excessive grittiness.

The **density** of fireclays varies greatly. For refractory articles an open porous clay is usually best, but for sanitary ware and other glazed goods the closer and denser the clay the better

will be the glaze. For very large glazed articles, such as baths, a compromise must be effected so as to gain the smooth polish of a densely surfaced clay with the refractoriness of an open body.

Most fireclays are much less dense than the plastic ball clays, though no accurate comparisons have been published.

The refractoriness of fireclays has already been mentioned. For convenience, it is customary to recognize three grades of fireclay articles, No. 1 grade consisting of the most refractory goods; the clays concerned softening at a temperature equivalent to Seger cones 35 or 36; No. 2 grade softening at a temperature corresponding to Seger cones 30 to 35, and No. 3 grade corresponding to cones 26 to 30.¹ Further notes on refractoriness are given under *Refractory Clays* and under *Refractoriness* in Chapter IX.

Flaky clays are intermediate between fat clays and shales. When crushed, they form flakes which will not easily unite to form a uniform plastic mass unless this is made too soft to be convenient.

As the flakiness is a physical characteristic and is independent of the chemical composition of the clays, no classification of flaky clays is needed. They must be so treated that the flakes are destroyed, or the clays cannot be used. Many flaky clays become quite satisfactory if passed through a pair of crushing rolls in which one roll rotates faster than the other, the subsequent pugging into a paste with water being made more thorough than usual. Clays which form flakes when worked by the semi-dry process should be made into a plastic paste, instead of being used in the form of a damp powder.

Flint clays are usually refractory, but they derive their name from their intense stony (flint-like) hardness, their conchoidal fracture, and their general structure, which is not unlike that of flint. They appear to have been formed by the gradual accretion of sedimentary matter of a clayey, as distinct from a more purely siliceous nature, around a fossilized sponge or similar centre.

Flint clays are not plastic, though many become so after much grinding and mixing with water. They are not used directly for manufacturing goods, but when fairly pure are added to excessively plastic clays to reduce the plasticity of the latter, though

¹ The Institution of Gas Engineers' (1911) Standard Specification for fire-brick material recognizes only *two* grades, viz. :—

No. 1 grade showing no signs of fusion when angular pieces are heated to not less than Seger cone 30 (about 1670° C.).

No. 2 grade showing no signs of fusion when angular pieces are heated to not less than Seger cone 26 (about 1580° C.).

they are costly to grind. Many flint clays are very impure and are of little value. The term "flint clay" is sometimes applied to ordinary rock clays of unusual hardness, but this use of the term should be avoided, as it leads to confusion with the true flint clays.

Flower-pot clays are red-burning clays of moderate plasticity, which form a porous body when fired. They should be free from soluble salts—which would form a whitish scum—and should be capable of rapid and accurate manipulation on the thrower's wheel and of retaining their form during drying and burning. Most of the better and finer qualities of red-burning clay may be used for this purpose, but the manufacture of flower-pots is worked on so large a scale by a few firms that the industry is not a profitable one for others, except in very isolated districts or under unusual conditions.

Stony clays are quite unsuitable for this purpose, as are also very highly plastic ones with a heavy shrinkage in drying. Some of the best flower-pot clays are the "Midland Reds" (p. 219).

Fluviatile clays are those formed by the action of rivers. They are very irregular in composition, and are often unsatisfactory for use on a very large scale. Their chief characteristics have been described on p. 112.

Fuller's earth is a term used for any earthy material which will act as a grease-absorbent and may be employed for fulling wool. Fuller's earth is also used for decolourising oils, particularly cotton-seed oil, lard oil, castor and cocoanut oils, and in the manufacture of some soaps.

The term is usually applied to certain white marls and Oolite clays¹ (pp. 68 and 73), but some varieties of china clay are often used for this purpose. There is a considerable difference of opinion as to the true nature of fuller's earth, some evidence indicating that it is an impure primary clay, whilst other facts point to its being a decomposition product of impure siliceous rocks. Analyses by J. T. Porter suggest that it is mainly composed of montmorillonite, anauxite and chalk, with some hydrous silica and quartz. If this is the case, fuller's earth would be classed among the minerals analogous to clay (Chap. VII.), but not with true clays. Extensive beds of fuller's earth occur in the chalk-greensands (p. 74), where it occurs as a bluish, greenish-brown, grey or yellowish earth, easily cut with the finger-nail and leaving a shining streak.

¹ Much of what geologists term the Fuller's Earth or Fullonian series consists of limestone rocks or brown, blue, and yellow clays at the base of the Great Oolite. These are of insignificant industrial value and must not be confused with the true "fuller's earth."

It is chiefly worked at Nutfield and Bletchingley, Reigate, at Debtling near Maidstone, and near Woburn (Beds). It is also worked near Bath, where it is obtained beneath the Great Oolite. The natural fuller's earth is very fusible, and so is readily distinguished from white clays of greater commercial value.

Its chief characteristic is its ability, when made into a slip with water, to retain grease and oil, and upon this its value depends. When mixed with water it does not form a paste-like clay, but falls to powder, though this cannot always be relied upon as a distinctive characteristic. Its absorption of malachite green is extremely low. This is curious, in view of its power of retaining oil.

For a face powder it must be extremely fine, not too tenacious, and quite free from grit. For "fulling," or removing grease from cloth, a coarser quality may be used, though it must not be at all sandy. With the production of benzoline and other liquid grease-removers, the use of fuller's earth for its original purposes has declined. It is not now used so much in fulling or cleansing cloth as it is in papermaking, as a diluent for ultramarine, and as a filtering medium for oils. It is prepared by washing the crude earth, which is then thoroughly dried in ovens.

The complete recognition of true fuller's earth can only be effected by an expert, and its value and suitability are always appraised on the results of tests and analysis; but a clayworker who finds a bed of white non-plastic clay which fuses easily, is very porous, mixes well with water and absorbs oil, should investigate further in case he has discovered a valuable bed of fuller's earth.

Fusible clays vitrify and lose their shape at a relatively low temperature, such as that used in firing faience (1100° C.). They always contain a rather large proportion of silica and lime. Some are sufficiently plastic for making pottery, tiles, stoneware, etc., while others can only be used to make plain bricks. The chief flux present is lime, alkalies being usually in relatively small proportions. Amongst the numerous kinds of fusible clay the following are the most important:—

1. Plastic clays rich in iron and burning to a dark red or brown.

2. Plastic calcareous clays, burning yellow, brown, or even grey.

3. Siliceous ferruginous clays, burning red or brown.

4. Siliceous calcareous clays, burning to a yellow or grey tint.

The important characteristic of fusible clays is the production of a vitrified body on heating, but some fusible clays cannot be

used commercially, because they lose their shape as soon as they become sufficiently vitrified (see *Vitrifiable Clays*).

Fusible clays are added to refractory ones to bind the particles of the latter together (see *Binding Clays*, p. 138).

Gault is a term used to indicate the stiff blue chalky clays or marls occurring in the lower portion of the Chalk system (p. 75), immediately above the Greensand, or between the Upper and Lower Greensand. On weathering, it becomes deep grey or deep brown in colour, and usually becomes sticky. Its chief characteristics and geological formation have already been described.

Geodic clays occur in rounded nodules or balls with a hollow interior. They are of considerable geological and mineralogical interest, but of no value industrially. A description of the manner in which they have been formed is therefore beyond the scope of the present work.

Glacial clays are of Pleistocene origin (p. 115), and are chiefly represented by "boulder drift" or "Till" (p. 140). A more detailed description of their origin and characteristics is given under the headings just mentioned.

Glass-pot clay must be highly refractory, and must be sufficiently dense, when burned, to offer a reasonable amount of resistance to the molten glass. Owing to the high temperature used in glass manufacture and the changes in temperature to which the pots are subjected, they must be made of clays chosen with special care (see *Crucible Clays*, p. 169).

Gravelly clays are those containing much gravel, sand, or small stones. If the clay present in such a mixture is highly plastic, the whole material may sometimes be finely ground and made into bricks, but if the gravel contains much limestone serious difficulties will then arise, as the bricks, etc., made from such material will "blow" and disintegrate. The only effective means of removing the gravel is by washing—a process which is too costly, considering the number of much better clays obtainable in most parts of the country.

Green clay may be of any colour, the term "green" simply indicating that the material has not been dried or burned. Thus, bricks and pots which are being dried are said to be in a "green" state, and the clay of which they are made is correspondingly termed "green." The origin of the term is obscure, but is comparable to "green" and "dry" or "seasoned" wood.

Grey clays are of no importance as far as their colour is concerned, but they form a large and important class which is more conveniently described under the term *clunch* (p. 168), or *fireclay* (p. 170).

Grog is burned clay (p. 150). It is used to reduce the shrinkage of plastic clays with which it may be mixed, and to produce a more porous body than can be obtained from raw clay alone. In the manufacture of refractory goods grog is an important ingredient, as it enables them to withstand sudden changes in temperature, and has an advantage over sand and other forms of silica in that it does not swell when heated.

The use of a large quantity of grog in a clay mixture also reduces the proportion of alkalies present, as these are partially volatilized during the preparation of the grog. Hence this forms a convenient method of slightly raising the heat-resisting power of a clay.

For successful use it is important that the grog should be made from a suitable clay—the common practice of grinding up brickbats being by no means satisfactory—and on the Continent a number of firms specialize in the production of a particular quality of grog which they sell as “Chamotte” (p. 152).

This is made by carefully heating the best selected fireclay to a very high temperature so as to destroy all shrinkage, the lumps of burned material being then examined and seriously discoloured portions thrown away. For use the grog must be crushed to a coarse powder and carefully graded into the desired sizes by means of sieves. All “dust” should be removed, as the smallest particles should not be less than one-twentieth of an inch in diameter; the largest may be as large as big peas ($\frac{1}{4}$ -inch), and all intermediate sizes may be employed. In some firms it is customary to take all the grog that passes through a sieve of (say) 10 holes per inch, but this really is not satisfactory, and a more careful grading of the grog will usually result in more durable articles.

No definite sizes can be stated to be “best” for sagger production, as so much depends on the plasticity of the clay used and the nature of the goods to be fired in the sagers. As a general rule it is better to have the grog too coarse rather than too fine, but if only large pieces of grog are employed there is a tendency to lose strength owing to the reduced binding power. In most cases the grog particles should remain on a sieve with 25 holes per running inch, and pass through one having 5 holes per inch.¹

One well-known firm divides its grog as follows:—(A) Grog remaining on a 5-hole screen; (B) grog passing a 5-hole, but remaining on a 10-hole screen; (C) grog passing a 10-hole, but

¹ For gas retorts the Institution of Gas Engineers' Standard Specification states that none of the grog used shall pass through a sieve with 16 holes per linear inch. This is very coarse.

remaining on a 20-hole screen; (D) grog passing a 20-hole screen. This firm only uses the B and C portions, returns the A portion to the mill to be re-ground, and accumulates the D portion for other purposes. Since separating in this way the life of the saggars has been nearly doubled, owing to the greater exactness with which the proportion of materials of different sizes can be regulated.

In France a somewhat finer grog is used than in this country, and separation is made into three sizes: (a) passing a 5-hole sieve; (b) passing a 10-hole sieve; (c) passing a 35-hole sieve. This last size (though popular) is too fine for other than very small saggars.

The main disadvantage of using too large particles of grog is the brittleness produced in the goods, rendering them easily broken and very fragile under sudden changes of temperature. The size of the grog has little or no effect on the contraction of the mixture as a whole, but large grog produces goods which are weaker mechanically than those in which smaller particles are used.

The particles of grog should be sharp and angular, and should be produced by "crushing" rather than by "grinding," an edge-runner mill with fixed pan being generally preferred on the Continent.

It need scarcely be said that the material used for the manufacture of grog should be quite free from glaze, fluxes, or clinkered pieces of material.

Hartwell clay lies above the Kimeridge clay at Biert, Hartwell, and Haddenham (Bucks), and resembles the lower formations except in the nature of its fossils. It has no special commercial value, but is of some palæontological interest.

Indurated clay, or claystone, is clay which has become hard owing to its position, underlying other deposits, or by the action of other natural forces, some of which may be partially of a chemical nature. Indurated clay is not easily mixed into a slip with water, and requires to be crushed to powder before it can form a plastic paste. If the structure of the deposit is laminated, indurated clays are termed "shales."

Infusorial earth, or Kieselguhr, is a whitish powder consisting of the siliceous shells or frustules of microscopical plants (*diatoms*). It is sometimes used by potters, though it is not in any sense a "clay," and can be readily distinguished by means of a microscope. The separate particles of kieselguhr have a density of 2.2, but the powder as a whole is far lighter than this, and it is therefore valuable in the manufacture of light refractory articles.

In the Bann Valley, south of Lough Beg (County Antrim, Ireland), is a large deposit of diatomaceous earth in association with peat known as **Bann clay**. It contains 72 per cent. of silica, and is mixed with a stiff clay to make bricks, though alone it has no plasticity.

Similar deposits are known at Glen Shira in Argyllshire, also a little north of Loch Kinnord, and in the Isle of Skye.

Kaolin is a term applied to all slightly plastic clays of great purity and with a composition very similar to that of china clay (p. 153), which is the most important member of the series. Originally "Kao-lin" referred to the hill from which the ancient Chinese obtained their china clay, but at the present time the word is used generally for white-burning, slightly plastic clays found close to the rock from which they appear to have been formed. In France and Germany the term "china clay" is practically unknown, the word "kaolin" being exactly equivalent. Hence, in spite of many objections to the use of this word amongst British clayworkers, it is likely to continue to be employed abroad.

For all ordinary purposes kaolins may be regarded as identical with china clay (p. 153) in their properties; some of them have, probably, a somewhat different origin, though this is by no means clearly understood, and most authorities maintain that all kaolins are derived directly from the decomposition of felspar in spite of some evidence to the contrary, some kaolins (particularly in America) being distinctly of sedimentary origin. In Great Britain the larger deposits of kaolin are only represented by Cornish china clay, so that the composition and origin of deposits in other parts of the world is of minor commercial importance though of great technical interest.

There is a strong tendency amongst various writers on clay to employ the term kaolin to represent "true clay" or "clay substance." This is by no means a desirable use of the word, and should be avoided. The chief constituent of the purest clays is not "kaolin" (for this, strictly speaking, should refer to the "china-clay rock" or to the whole of the material as it is mined), but is variously described as "clayite," "true clay," and "clay substance." Kaolins are usually prepared from the crude material by careful washing (p. 162), but in some parts of the world they are found in a sufficient state of purity to be used direct. The chief characteristics of British kaolins are described in the sections on *China Clay*.

If the original rock from which the kaolin has been derived is rich in iron and other impurities, the "kaolin" may also be so

impure that it no longer burns white, but buff or red. Such a material is seldom termed "kaolin"; it is more suitably known as primary or residual clay. In Great Britain, however, such clays are rare.

It is extremely difficult to ascertain whether a given sample of kaolin is really pure. As much as 20 per cent. of white mica may sometimes be present without seriously affecting the analysis, and it is only when the investigation is exceptionally thorough that an accurate knowledge of the material can be obtained.

The view that kaolin is chiefly composed of crystalline matter (kaolinite) is held much less tenaciously now than formerly, the prevailing opinion at the present time being that the precise mineralogical composition of kaolin is unknown. This is not surprising when it is remembered that clay, like sand, is a product of the decomposition of many rocks, and may, therefore, contain many minerals of extremely similar chemical composition. With slight variations—probably due to the presence of mica even in the purest samples obtainable—kaolins have the composition assigned to pure clay, viz. silica 46 per cent., alumina 40 per cent., and water 14 per cent., corresponding to the formula¹ $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The correspondence is never exact, and unless exceptional care is taken in their purification, most kaolins will contain alkalis equivalent to at least 5 per cent. of mica. Pukall has recently suggested that kaolin is really an anhydride (p. 155).

Kaolinite is a crystalline mineral, occurring in many clays, but only in small proportions. These crystals have a composition corresponding very closely to that of "true clay" or to the purest china clays, and represented by the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.¹ The crystals are plates or scales with a hexagonal outline, or are occasionally pyramidal. Twin crystals resemble those of mica. Some varieties are monoclinic, others triclinic. They have an average density of 2.4 to 2.6, and vary in colour from white to reddish or green, usually with a pearly lustre.

The term "kaolinite" is due to Johnson and Blake (1867), who believed that true clay consisted entirely of pearly scales of kaolinite. The more modern view is that kaolinite is a minor constituent of clay, the major constituent being amorphous ("clayite"). The variations in the characters of the crystals in clays from various sources suggest that the word "kaolinite" may include a number of distinct minerals of similar ultimate chemical composition.

Although it is very generally understood that kaolinite is the

¹ See footnote on p. 126.



Working face of Oxford Clay near Peterborough.

(By courtesy of J. T. Turner, Esq.)



Mica drags at Stannon Works of North Cornwall China Clay Co., Ltd.

(By courtesy of W. H. Patchell, Esq.)

essential constituent of all clays, the evidence upon which this opinion is founded is extremely meagre. Clearly definable crystalline kaolinite does not occur in large quantities in any clay, and the nearest approach to it—being amorphous—is extremely difficult to identify. Many clays appear to be quite destitute of kaolinite.¹ Except for the absence of alkali, it is extremely difficult to distinguish between minute crystals of kaolinite and white mica.

The direct formation of kaolinite from numerous minerals (including mica) has been the subject of many positive statements, but is by no means proved.

Knotts clay is a local name for a variety of shale found in the neighbourhood of Peterborough, and of great value for brickmaking when properly worked. It is part of the great Oxford clay bed (p. 70), and is of marine origin. On account of the carbonaceous matter which they contain, the Knotts clays require but little fuel for burning, and as they can be most satisfactorily worked by the semi-plastic system, everything is in their favour for the production of bricks at the lowest possible price.

Lacustrine clays are those deposited in lakes, the water afterwards flowing away, leaving a material which, usually, has considerable plasticity and frequently a very uniform composition. The general characteristics of lacustrine clays have been described on p. 117. They are, as a rule, very suitable for the manufacture of bricks, terra-cotta, and pottery.

Laminated clays are those composed of layers or flakes of material. When sufficiently hard they form *shales*, but many clays show distinct laminations, whilst still remaining soft. Such clays must be very thoroughly mixed with water, and often require special treatment in order to crush them effectively. Attempts to work them without full cognisance of their nature are almost invariably futile, except when bricks of the lowest quality are required, but with skilled assistance and a proper mode of treatment they can be worked quite satisfactorily. The lamination is due to fortuitous circumstances attending their deposition, and it must be completely destroyed by efficient crushing and mixing with water before the clays can be used satisfactorily. The chief disadvantage of soft, laminated clays is the cost of manipulating them. When hard and shaly they offer few difficulties if converted into a plastic mass. Their separate classification would be unnecessary but for the fact that so many

¹ The relative scarcity of kaolinite crystals appears to be due to the general inertia of clay and to the conditions not being favourable for its crystallization.

people have attempted to work them in an improper manner (not realizing the effects of lamination), and have, in consequence, sustained serious financial losses.

Laterite clays¹ are those which are presumed to have been chiefly formed in tropical areas or under tropical conditions by a process of exposure or "weathering" which results in the production of a material containing free alumina as well as free silica. The manner in which this special form of weathering occurs and the agencies which effect it are not known, though it is understood that laterization is a kind of "continuation-effect" whereby ordinary clays under tropical conditions are partially decomposed into free alumina and silica, forming laterites.

The characteristic features of laterite clays are their peculiar red colour—though some grey ones are known—and the large percentage of free alumina they contain.

They were discovered by Schloesing, and have been investigated by Würth, Bauer, Van Bemmelen, and Tello. The last-named has stated that they are far more widely distributed than is commonly realized, and that they form almost half the clays of the Tropics, being found in formations of all ages.

In temperate climates their formation is not so noticeable, but it has been suggested that the bauxites of France, northern Ireland, etc., may really be clays in which the laterization is very complete.

In Great Britain they have not been investigated to any notable extent, though according to Van Bemmelen they may be readily identified by their ready solubility in hydrochloric acid and the large percentage of alumina brought into solution by this reagent. The ratio of alumina to silica in laterite clays is very variable, though seldom reaching 1 : 2. When so large a proportion of silica is present, the distinction between lateritic and kaolinic clays is based on the assumption that the alumina in the latter is quite insoluble in hydrochloric acid, whilst that in the former is completely dissolved.

Many clays examined by Van Bemmelen appear to be composed of mixtures of laterite and "kaolin." This may be due to the two kinds of clay becoming mixed during transportation by water or other natural agencies or to granites, gneisses, basalts, and other igneous rocks being capable of undergoing kaolinization followed by an incomplete laterization.

Just as the bulk of china clays is composed of an apparently amorphous substance (clayite) and a small proportion of a crystalline material of the same composition (kaolinite), so laterite clays are chiefly composed of amorphous laterite together with a small

¹ Cf. Ital. *Laterizio*, argillaceous, clayey.

proportion of *hydrargillite* ($\text{Al}_2\text{O}_3 \cdot 3 \cdot \text{H}_2\text{O}$) which crystallizes in monoclinic needles and plates, and in finely grained aggregates soluble with difficulty in strong acids.

Lean clays are those which are not strikingly unctuous to the touch, the term being used as the converse of "fat" (p. 171). Lean clays are particularly valuable where the articles to be made are moulded, but for "throwing" (working on a potter's wheel) or for modelling, fatter and more plastic clays are preferable. Lean clays usually contain a considerable proportion of free silica (see *Loams*) or chalk (see *Marls*), and consequently they shrink but slightly in drying and firing.

A fat clay may be made lean by the addition of any suitable non-plastic material, grog or fine sand usually being employed, though in some districts chalk is used on account of its accessibility.

When excessively lean, a clay is too weak to retain its shape if made into vases, etc., but for articles of simple form such as bricks and tiles the leaner the clay the better, for it may be dried more rapidly.

Lias clays and shales comprise stiff, blue clays, together with dark clayey limestones and bituminous and pyritic shales (see p. 65). The latter are often very impure, containing magnesium sulphate, sodium sulphate, common salt and other saline compounds, which produce a scummed surface when the clays are made into bricks and fired, but the better qualities of Lias clays have yielded excellent clay goods from time immemorial. Bricks, tiles, drain-pipes, flower-pots, and chimney-pots are the chief products. Most of the goods made are red, but if overheated they become yellowish on account of the iron and lime they contain, which combine together. At a still higher temperature this lime acts as a flux and first gives a greater toughness and uniformity, but, later, causes the goods to warp and lose their shape.

The lime is usually in a finely divided state, but in certain localities it is coarser and is termed "race," which causes the bricks to "blow" and disintegrate on exposure.

The shrinkage of Lias clays is much smaller than would be imagined from their plasticity, and if care is taken in their selection these clays are admirably suited to the production of the goods just named.

The shales of the Lias formation will repay careful attention, as many of them contain sufficient carbonaceous matter to render the fuel required to burn them very small in amount, but in others this combustible material is entirely absent. Owing to

the very slight indications of the nature of the subsoil, extensive digging operations are necessary before the prospector can gain a satisfactory idea of the nature of the Lias formation, as the clays in this frequently occur at a depth of seven or eight feet below the surface.

Selenite ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) frequently occurs in Lias clays; as it forms lime on burning, it is liable to make the bricks "blow."

When the clays are required for manufacturing into articles (as distinct from making cement), those portions should be selected which are free from fossils (*Ammonites*), some of which are very large in this formation. The chert-nodules and quartz crystals should, usually, be picked out, though, being very hard, some of them will be retained on the revolving pan of an edge-runner mill and may be removed if this is cleaned out daily.

Limey clays are those which contain limestones or other compounds of lime in relatively large particles, as distinct from "marls," which contain very finely divided chalk. The distinction is important, because the clays containing chalk often make very satisfactory bricks, whilst those containing coarse particles of limestone produce very unsatisfactory articles. The coarse particles form free lime when the clay is heated, and when exposed to air this lime hydrates and carbonates and, unless the clay is sufficiently strong, the article splits. In any case, the white spots of lime soon disfigure the articles, as they "blow" (p. 209) and form hollows of an unpleasant appearance.

The danger of destruction of bricks due to inclusions of limestone depends upon the size, location, composition and shape of the particles of stone, the strength of the burned clay, and the temperature and duration of the burning. A portion of the finer lime particles reacts with the clay to form easily fusible silicates which penetrate the pores of the brick, leaving space capable of accommodating the expansion due to the hydration of the free lime. The minimum limit for safety appears to correspond with a conversion of 30 per cent. of the lime present into silicate, this being effected by grinding the limestone to particles not exceeding $\frac{1}{12}$ -inch diameter, and heating the material for at least two hours at a temperature above 1020°C . (cone 04A) or for a longer period at 960°C . (cone 07A) until sufficient vitrification has occurred. Unfortunately many clays lose their shape during this last treatment.

No crushing plant has yet been devised which will reduce these limestone particles sufficiently, except at a prohibitive cost, so that the only way to remove this defect is to remove the lime, either by washing (which is expensive) or by the use of a "stone

separator.”¹ This machine is so constructed that moist clay and lime is compressed in a perforated metal cylinder or on to a slotted disc; the clay and small pieces pass through the perforations or slot, and may then be finely ground. The stones remaining behind are thrown away. This method is somewhat wasteful of clay, but is far cheaper than washing. It can, however, only be used when the lime is in large pieces, as stones less than one-twentieth of an inch cannot be removed effectively. Washing the clay is undoubtedly the surest and safest method of removing impurities, but it leads to other difficulties, such as the separation of the clay into layers of different qualities. This separated clay, when taken from the settling tanks, can never be so thoroughly re-mixed as if it had never become separated, and the washed clay, though easily worked in hand-moulds, is more difficult to work in presses, with the result that makers of machine-pressed bricks seldom find that it really pays to wash their clay before use. Dipping the fired goods in water undoubtedly works satisfactorily as far as preventing the lime from doing any harm is concerned, but it has the great disadvantage of soaking the goods with water, so that they require a considerable time before they become thoroughly dry, involving heavy transport charges and rendering them liable to fracture in winter when they are exposed to severe frosts.

When limey clays must be used, they should be thoroughly burned so as to combine the lime with some of the other ingredients of the clay and so form a glassy compound which increases the strength of the brick and is free from all the defects of uncombined lime.

In considering the best treatment for a limey clay, it is first necessary to have some idea of the sizes of the limestones. For this purpose it is wise to mix the material into a slip with water and to pass it through a series of sieves to separate out the coarser particles. Each “residue” may then be examined separately and a method of treatment devised according as the limestones are large, small, or as fine as sand. It not infrequently happens that the bulk of the lime is contained in stones larger than half an inch in diameter, and the removal of those by hand-picking or by a clay-cleaner¹ greatly simplifies the problem.

Hand-picking, though slow, is relatively cheap, and with reliable and conscientious men is very effective. As so much depends upon the thoroughness with which the pickers work, it is often desirable to award those who show special diligence by means of a bonus system, in which the percentage of material to

¹ Described on p. 61 of the author's *Clayworker's Handbook*.

be removed from the clay being known, the workmen engaged in picking it out are paid according to the proportion they remove. Thus one firm pays its pickers on a special piecework plan as follows :—

The clay contains on an average about 9 per cent. of removable limestone, and men are paid, not by the number of tons of clay they pick out, but by the number of tons of limestone they accumulate; 3s. 6d. a ton being the actual price paid in this instance, in addition to their standing weekly wage. As the place where the material is picked is difficult of access to men carrying loads, and the stones, when paid for, are removed safely out of reach of all the workmen, there is little likelihood of the men bringing stones from other sources and pretending that they had been taken out of the clay, and a further confirmation of the accuracy of the payments made is obtained by checking the number of tons of clay actually passed through the mills. This system of bonus has worked admirably in this particular instance, but it can obviously be only applied in the case of clays containing stones which are easily visible to the workmen engaged to remove them.

Much trouble may be avoided in some deposits if the clay diggers are carefully watched and all unsuitable beds of material are kept separate. This is particularly the case with "drift," "till," or boulder clay, which forms one of the chief sources of limey clay.

Loam is a term used to describe any soil which is neither distinctly sandy nor clayey in texture. It comprises the light, open soil produced by the decay of leaves and other vegetable matter, and also mixtures of sand and clay. Agriculturalists speak of light and heavy loams according to the proportion of clay present; also of sandy and calcareous loams according as sand or chalk is a predominating constituent. See also *Soil*, p. 237.

Some writers appear to confuse loams with *marls*. In loams there should not be sufficient limestone or chalk to make either of these substances characteristic of the material. Broadly, the distinction between them is that loams are sandy clays whilst marls are calcareous ones.

In the sense in which the word is used by brickmakers, loam is intermediate between the plastic clays, which shrink too much to be used alone, and the sands, which cannot be moulded into bricks without the aid of powerful machinery, but the value of a loam for this purpose cannot be stated unless its composition is known.

Many clays which contain sufficient sand to make them useful

for the manufacture of coarse pottery, tiles, and bricks are really loams, and as they may be dried and heated rapidly without cracking, they are, consequently, valuable.

Broadly speaking, any sandy clay may be termed a loam, but when the proportion of clay is small (say under 20 per cent.) the term "sandy loam" is preferable. These latter are, however, so loose in structure that they cannot be made into bricks without the addition of lime to flux and bind the particles together. For use in iron-foundries some of the sandy loams are invaluable. Loams rich in clay are sometimes distinguished as "loamy clays" (see below).

Earths which can be made into bricks and tiles by simple pugging and hand-moulding are somewhat rare. The stronger clays may be beaten up with water into a stiff paste and moulded with great ease into any shape; but they shrink and crack so much in drying and firing as to be almost useless.

The addition of any substance which will neither shrink nor dissolve in water may be used to overcome this defect without materially affecting the plasticity of the clay. For this reason the strong clays are mixed with milder earth or sand, but brick-makers naturally prefer to use materials, such as loams, which already contain sufficient non-plastic material.

When sand is scarce or too costly, other materials must be used, and brick earths in the neighbourhood of London are mixed with chalk and sifted cinders for the same purpose, and also to effect the fluxing of the earth.

In the Eastern counties a bed of marl or boulder clay is frequently found beneath the mild red earth or loam. A little of this marl may be mixed with the red loam during the washing, but in large proportions it will spoil the colour of the bricks, making them of a salmon or roan tint.

Some loams are so full of gravel that it is quite impossible to free them from stones except by washing, or by passing them through a clay cleaner.

Loam must not be confused with one meaning of the German word *Lehm*, which signifies a product of the action of the weather on glacial drift and other rocks forming marls or loess.

Loamy clays contain a considerable proportion of sand, which makes them much milder (leaner) and consequently more easy to work than highly plastic ones. The sand is due to the nature of the rock from which the clay is derived, and its mere presence gives no indication of the source or nature of the clay.

The loamy clays are among the best, if the manufacture of goods is to be made without any addition to the raw material,

though special care must be used in working the least plastic varieties (*i.e.* the *loams*). The quantity of sand contained in loamy clays makes them shrink less, and renders them less liable to warp than do stronger clays; but if present in excess it makes their texture so loose that an addition of chalk and a rather hard firing is necessary to bind them. These very sandy earths may be termed "loams," but should not be referred to as "loamy clays," this last being reserved for mild clays with a fair amount of plasticity but relatively low shrinkage. (See also *Soil*, p. 237.)

Loess is a German term, also used by American clayworkers, for a peculiar light yellow or yellowish-grey marly loam of fluvial origin. It also occurs as a quartz sand of a dirty yellowish-brown colour, mixed with a small quantity of clay and sometimes also containing chalk or limestone. Loess is not truly plastic. It contains numerous calcareous concretions, which sometimes take curious shapes and are known on the Continent as "loess-men." It also has a characteristic porous structure which renders it easy to recognize.

Loess, like boulder marl, is a diluvial material, but its origin is not definitely known. In some countries, *e.g.*, China, it appears to be of æolian formation (pp. 112 and 120).

The occurrence of loess in Great Britain has been denied; in any case it can only occur in insignificant quantities.

The most important European deposits of loess are in the neighbourhood of the Rhine, where it consists of 66 per cent. of clay, 16 per cent. of chalk, and 18 per cent. of sand, though its composition varies considerably.

London clay is one of the best known and, at the same time, one of the most treacherous clays in Great Britain. Its occurrence has already been described on p. 93.

It is, apparently, a highly plastic clay, though in some respects it is more sticky than truly plastic, and shrinks so greatly in drying and firing that much skill and time are required for its successful manipulation. It cannot, therefore, compete in the manufacture of common bricks with a material such as the Oxford clay used at Peterborough, except where buildings are being erected in the immediate neighbourhood of the brickyard. The absence of available sand in many parts prevents the clay being worked, though this difficulty is overcome by many London brickmakers, who add to their clay about one-third of cinder dust ("soil") obtained from kitchen dust-holes; so that the bricks shrink less in the fire, but they are less compact than the bricks made in the coal districts of England. Chalk is also added for the same purpose, and to produce a whiter brick. Incidentally,

the amount of cinder dust reduces the amount of fuel needed in the kilns.

The Reading bed (p. 219)—which forms the western end of the London clay basin—is admirably suited to the manufacture of facing bricks, roofing tiles, finials and modelled goods generally, but it must be properly treated or it will prove disappointing.

Malms are clays containing, in the natural state, a considerable proportion of chalk, and may often be made into bricks without any admixture, but as clays containing exactly the proper proportions of clay and chalk are somewhat scarce, it is usual to prepare artificial malms by adding chalk to clays otherwise suitable. The object of the chalk is threefold; in the first place it acts mechanically in diminishing the contraction of the clay during the drying and burning; secondly, it acts chemically as a flux during the burning, combining with the silica of the clay so that a much harder and more durable material is produced; and, thirdly, it produces bricks of a pleasant whitish or buff colour, due to the combination of the lime with any iron compounds in the clay. In many cases this last effect is not allowed to have full play, as the goods are not heated sufficiently for the lime to fulfil this purpose, so that the malm-brickmaker's object in adding chalk or similar material to his clay is usually to obtain, from an otherwise unsuitable material, bricks which are of a saleable tint.

The process of adding chalk to a clay is known as "malming," and before the advent of modern methods of brickmaking it was a very important means of enabling certain clays to be used. The mixture was effected by crushing the chalk in a wash-mill and running the "slurry" thus produced into a second wash-mill containing clay. In this second mill the chalk and clay are well mixed and the malm-slurry run off to "wash-backs," or on to a heap of unwashed clay and mixed in by spade labour. When a sufficient quantity of malm has been run off to the "backs," it is left to settle for a month or more, until it has become sufficiently consolidated to bear a man walking over it. As the solid portion of the malm settles, the water is drained off from time to time, and when the mass is sufficiently firm it is ready for use.

The term "malm" may thus mean three different materials¹: (1) a brick earth containing chalk, used direct without either washing or malming; (2) a brick earth which has been malmed, *i.e.* covered with an artificial mixture of chalk and clay; (3) bricks

¹ In Devonshire, Sussex, Hampshire, and Surrey a stone resembling the freestone of Reigate, and found in the Upper Greensand formation, is termed *malm* or *malm rock*. This must not be confused with the term "malm" used by clayworkers.

made entirely of artificial malm. The second process is the most common, as the expense of the third is very considerable, and, for the commoner sorts of bricks, all that is done is to mix in a sufficient quantity of malm to make the original earth suitable for brickmaking; the quantity of malm required for this purpose varies, of course, according to the quality of the earth. Malming is specially suitable when a clay burns to an irregular red colour, and on the addition of chalk is converted into a white- or buff-burning clay. For this purpose about twice as much chalk as there is iron oxide in the clay is usually needed, a clay containing 5 to 6 per cent. of iron oxide requiring 12 per cent. of chalk to produce a satisfactory buff or white brick or tile.

Marine clays are of two kinds: those now existing under the sea, and those deposited in sea-water in past ages, but which now are part of the ordinary "dry land." In composition they vary greatly in different parts of the country, but each different deposit is in itself comparatively uniform—far more so than fluvial or drift deposits. Many marine clay deposits are of enormous size and importance (see p. 118). The Oxford clay is one of the most used industrially.

Marls are natural mixtures of clay and chalk—the latter being in a finely divided condition—but the term "marl" is often used to describe a friable or crumbly earth in order to distinguish it from plastic clay, and from the harder shales. This use of the word "marl" is distinctly confusing, though very common, particularly in connection with the Staffordshire deposits used for making blue bricks. In the Portland cement industry the term "marl" is used to indicate fine-grained friable limestones which have been deposited in the basins of existing or extinct lakes and are practically pure limestones, though they differ physically from the hard, compact rocks to which the term limestone is more commonly applied, being granular, loose, non-coherent deposits. Agriculturally the term marl is sometimes employed for any rock that is valuable as a natural fertilizer, with the exception of the phosphate rocks and such well-defined minerals as gypsum. Any definition of marl wide enough to include all present uses of the word is unsatisfactory by reason of its comprehensiveness, and, in the author's opinion, its use is best limited to mixtures of clay and calcium carbonate (whether as limestone or chalk) containing at least 10 per cent. of each of these materials. Other fertilizer rocks may then be referred to under specific names; the impure limestones containing less than 10 per cent. of clay being known as limestones; the clays containing 5 to 10 per cent. of calcium carbonate as "marly clays";

and other rocks according to their nature. If such a limitation of meaning were adopted it would meet the needs of all users of the word "marl," and would prevent the present unsatisfactory employment of it being continued.

Owing to the multiple uses of the word "marl" several widely different substances are classed together. Thus the marls occurring as the lower part of the Old Red Sandstone formation in the Wye and Severn valleys, and in Hertfordshire generally, are red with irregular bands of cornstone; the Permian system usually contains two or more series of red and white marls in close vicinity to the magnesian limestone; the Triassic marls (Keuper marls) are very abundant, and are very variegated in colour and irregular in composition, being often interstratified with whitish sandstones. The chalk marls (sometimes spoken of as the "true marls") are equally abundant, and are much used for brickmaking, particularly in the south-east of England.

Unless distinguished by some adjective the term "marl" may be understood as referring to a clay made impure with chalk or extremely fine limestone, which often has a greenish or yellowish-brown tint, owing to the presence of iron oxide. If bituminous matter is present the material is dark in colour. When exposed to the air it breaks up and falls to a mass of irregular pieces, or even to powder.

Marls are chiefly the product of limestone, sandstone, and other sedimentary formations, the chalk or limestone having become mixed with the clay during its transportation. In fact, marls are formed wherever clay and chalky slimes become mixed; this occurs chiefly in rivers, lakes, and seas, and by streams carrying calcium carbonate in solution flowing into lakes containing vegetable and animal life. They are probably simple mixtures of the material forming them, but considerable differences of opinion exist as to the exact causes of the formation of marl deposits, and Le Chatelier and Vogt declare that the argillaceous material in marls is not clay, but corresponds in reality with the formula $Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$. When compressed and laminated they form marl-shales.

After limestone and sandstone, marls form the most important of the sedimentary deposits.

Boulder marls, on the other hand, result from the erosion caused by glaciers crushing igneous and sedimentary rocks, which are mixed with unbroken pieces of material. The boulder marls show no stratified structure, whereas marls deposited by lakes, seas, and rivers are invariably stratified.

Marls are classified according to the percentage of lime and

clay as (1) chalk marls and (2) clay marls, but no definite figures have yet been agreed upon as to the limit of composition for each class. Normally, a marl containing more chalk than clay is placed in the first class, but when very sandy marls are under consideration classification is more difficult, though calcareous marls containing from 20 to 40 per cent. of hydro-silicates of alumina (clay) are distinguished from "clayey marls," in which this proportion reaches 70 to 90 per cent. The term "marl" is not used for clays containing less than 10 per cent. of chalk, *i.e.* for those which do not effervesce violently on the addition of hydrochloric acid.

In addition to calcium carbonate (limestone or chalk), many marls contain small amounts of calcium sulphate and magnesium sulphate. Both of these are objectionable to brick, tile, and pottery manufacturers, as they cause a "scum" on the surface of the goods if present in notable quantities. Magnesium carbonate is also present in some marls and has a slight bleaching action, but more than 3 or 4 per cent. is rarely present.

Seger found that if the proportion of lime in a clay is one and a half times that of iron oxide the clay will burn yellow (cream colour) instead of red, the colour becoming paler as the proportion of lime increases.

Loeser has found that many marls contain calcium silicate and magnesium silicate, and do not consist exclusively of chalk or of limestone and clay. Marls nearly always contain oxide of iron, frequently 7 or 8 per cent. Mica and quartz particles are also usually present. The poorer a marl is in lime the worse it is adapted for agricultural purposes and the better for the brick manufacturer, being less liable to fuse in the kiln.

Marl sludge when freshly dredged may contain as high as 50 per cent. of water, and even dry marl beds often contain 15 to 25 per cent. of moisture. Marl is white when pure, but most samples have a greyish or yellowish tint, and some are a dark grey colour on account of the organic matter present. This burns out in the kiln, and may therefore be regarded as a harmless impurity by the brickmaker, but to the maker of cement it is very objectionable, as it retains moisture with great avidity, making it almost impossible to dry a marl containing much organic matter. Roots, branches, twigs, etc., should be taken out before the marl is used. Most marls contain but little sand or grit, though the larger shells and limestone particles make them feel gritty.

The *uses of marls* are (1) for agricultural purposes, (2) for the manufacture of Portland cement, and (3) for brickmaking.

As a fertilizer, marl is valuable for the phosphoric acid, potash, and soluble silica it contains. It also improves soil to which it is added by making it lighter, by increasing its content of plant-food, by neutralizing the acids in the soil, and in breaking up the constituents. If the soil is light the addition of marl will enable it to retain more moisture. It should be exposed to frost before being ploughed into the land, so as to facilitate its disintegration and spreading. Calcined or burned marl is occasionally used where a caustic lime is required.

For cement manufacture the composition of the marl must be accurately known, so that the proportion of the other materials to be used in the cement mixture may be adjusted. A fine, highly calcareous marl free from organic matter is best for this purpose, pure chalk being even better than marl.

For brickmaking the composition is also important. When the chalk and clay are in the correct proportion for making bricks the material may be used without further additions; but as such mixtures which are naturally correct ("malms") seldom occur in Nature, and then only in limited amounts, most manufacturers using marly clays make their own mixtures by the addition of either clay or chalk in the desired proportions (see *Malms*, p. 205).

It is very important that the chalk or limestone should be in a sufficiently fine state of division, as the presence of pieces far smaller in size than a pea will sometimes cause a brick to fall to pieces, as the quicklime (calcium oxide) formed in the kiln gradually absorbs carbonic acid from the air, and, in the presence of moisture, expands so much that at the first sharp frost the brick is unable to withstand the strain and is disintegrated.

With some lean clays, pieces of limestone as small as $\frac{1}{25}$ inch are capable of cracking articles in which they have occurred. More plastic clays may contain much larger lime-particles without breaking, particularly if the articles are "quenched" in water after firing.

"Blowing" and similar defects do not occur when the heat has been sufficient to effect a combination of the lime and silica, but as this amount of heating would often produce goods of an unsaleable colour, many bricks are never heated sufficiently (p. 200).

The proportion of lime compounds which can be present in a clay varies greatly according to its uses and to the methods of manufacture of the articles made from it. Some marls contain as much as 60 per cent. of calcium carbonate (equivalent to over 30 per cent. of free lime), but these are difficult to burn and are of little practical use unless mixed with other clays. For ordinary

malm bricks as much as 25 per cent. of chalk may be present in a clay, but for bricks and tiles intended to resist the action of the weather 12 per cent. is the most usually permissible, though much depends on the nature of the other ingredients.

Clays containing a large proportion of lime are always difficult to burn properly, as the difference between the temperature at which they vitrify and that at which they begin to lose their shape is inconveniently small.

Red bricks cannot be satisfactorily made from clays containing much lime, as, if heated sufficiently to make sound bricks, the lime combines with the iron and silica of the clay to form a whitish or buff product.

The plasticity of marls depends on the proportion of silica and alumina (clay), so that, generally speaking, clayey marls may be considered as plastic substances, but calcareous marls as lean and friable ones, without much coherence, though usually sticky when wet.

Marl is markedly lighter in weight than clay. The fineness of the particles of marl is very important to Portland cement manufacturers, as coarse materials increase the cost of grinding. Marls differ quite widely in this respect. The following varieties of marl are important, though the differences between them are not always clear:—

Blue marls, found in Staffordshire, are not true marls, as they are almost free from lime compounds (p. 206). The most important ones form part of the great "Etruria Marl series" (p. 212) of the Upper Coal Measures, and are in great demand for sagger-making and for the production of engineering bricks.

Boulder marls are to be distinguished from others, as they are not a product of flowing water, but are produced by the action of glaciers which partially grind the various stones to powder, though leaving a large proportion in the form of pebbles. Boulder marls form extensive deposits (see *Boulder Clay*, p. 140), and are readily identified by the pebbly materials they contain.

Buff or cane marls are really fireclays and not true marls, as the percentage of lime compounds is trifling (p. 206). Staffordshire cane marls are obtained by selection from the cleanest and most plastic of the grey fireclays of the Upper Coal Measures. The best belong to the Black Band series, particularly those from the Lower Bassy mine, the Littlerow and the Upper Peacock seams, each bed having its own peculiar characteristics. These "marls" are worked at Tunstall, Cobridge, Hanley, and Fenton in North Staffordshire, and in various parts of South Staffordshire, Derbyshire, Shropshire, and Yorkshire coalfields. Great care must be

exercised in selection, as certain portions in the deposits must be avoided, preference being given to the light grey material rather than to the dark ones. When these "marls" are to be made into decorative tiles they should be exposed to the weather for some months; be occasionally turned over, and any nodules or other foreign matter carefully removed. The marls should have a good and even colour when burned, be free from specks, cuts, or cracks, and of fine, smooth texture. The colour of the burned material cannot be predicted. It appears to be due more to the oxidizing and reducing conditions inside the kiln than to the proportion of iron compounds present. If white malm bricks are overheated they become brimstone colour and then fuse, particularly under the direct action of flame. An underburned marl brick is salmon or pink in colour.

Cement marls are those from which Portland cement and hydraulic mortars are manufactured (see *Cement Clays*, p. 151).

Chalk marls are true marls consisting of clay and chalk, with a preponderance of the latter ingredient. They are more useful for agricultural purposes and cement manufacture than for brick-making.

Clay marls are, as already noted, marls containing a large proportion of clay, *i.e.* they must contain more clay than lime compounds. They are intermediate in character between the true marls and the plastic clays.

Greensand marls are in no way related to the true marls, but consist largely of glauconite (an iron silicate) or greensand, with some clay and calcareous and phosphatic matter.

Keuper marls have already been noticed (p. 59). They usually contain a considerable quantity of sand, and if made into a slip with water some of them will yield a residue of 50 per cent. or more on a No. 100 sieve. Others contain only 5 or 6 per cent. of coarse material separable by this treatment.

Lias marls are characteristic deposits of the Lias formation, but do not require further description than that given on p. 66.

Permian marls are both red and white, and frequently contain considerable quantities of magnesia.

Red marls are those which have a red colour when fired.¹ Their colour when mined is sometimes red, yellow, or brown. Though the term should strictly be reserved for mixtures of clay and chalk or limestone which produce red bricks, etc., most of the "Red marls" are nearly free from lime compounds and are

¹ A "true marl" burns to a buff or whitish mass and never to a red colour, except at so low a temperature that the articles made from it are too weak to be of any value.

really low-grade fireclays or loams, the term "red marl" being used for many red-burning clays which are of a friable nature when dry (p. 206).

The colour is due to iron oxide, and depends on the amount and fineness of this material, and upon the temperature and other conditions of firing.

Below 900° C. the colour produced is a pale yellowish-red known as "salmon" or "roan," and the strongest colour is obtained at or near 1100° C. with most "red marls." Further heating to a higher temperature causes a reduction of some of the iron oxide and the formation of a "blue" silicate, followed by the partial or complete vitrification of the mass and loss of shape.

The most important of the red marls are those of the "Keuper" (p. 211) and "Etruria" series, the latter being much used for red and blue bricks and tiles. They run in an almost unbroken line from the north to the south of Staffordshire and generally west of the great coalfield, and are worked at Stourbridge, Tipton, Hanford, Basford, Tunstall, and other places.

The "Keele marls" do not appear to have been used to any great extent in Staffordshire, though precisely similar clays at Wrexham (N. Wales) are employed in large quantities for bricks and terra-cotta.

The "Etruria marls" (p. 55) are often interspersed with beds of gritstone shale and with nodules of "ironstone," "skerry" (limestone), and other injurious ingredients, so that they must be carefully selected before use. They are chiefly worked by quarrying at the various outcrops, the upper ones being chiefly made into red and blue bricks and coarse pottery. About ten different strata are known, and in practice it is necessary to make a selection from several of them so as to obtain a mixture of normal contraction on drying and burning.

The best known "Red marls" are those found at Madeley Heath, Bradwell Wood, Newcastle-under-Lyme, Hartshill, Penkull, Stoke-on-Trent, Fenton, Trent Vale, Hanford, Blurton, Cocknage, Cophurst, Wetley Moor, Thornyedge, Cellarhead, Frogghall, and Mow Cop, in North Staffordshire.

In Shropshire and North Wales the best deposits are near Broseley, Jackfield, Ironbridge, Madeley Wood, Sweeney Penybont, Hafod, Afongoch, Ruabon, and Wrexham. A valuable red marl lies immediately beneath the Lower Lias clay at the base of Dundon Hill, in Somerset, and for several miles around, but it should be mixed with some of the neighbouring plastic clays. Nearer to Shapwick it is much harder, more calcareous, and therefore less satisfactory.

Throughout the large area covered by Triassic clays in the centre of England (p. 58) the *Midland marls* are valued for the bricks, tiles, and terra-cotta producible from them. "Leicester red bricks" and "Ruabon terra-cotta" are specially well known in this respect.

At Nottingham and in its immediate vicinity a "red marl" overlying the Red Sandstone and the Coal Measures is much used. This material is really a loam rather than a marl, and contains many thin layers of "skerry" (impure limestone) and veins of gypsum. The latter are worked extensively near Newark for the manufacture of plaster of Paris. When carefully selected this Nottingham "marl" makes excellent bricks, tiles, flower-pots, and coarse pottery.

A similar marl is found around Radstock (Glos), but is softer than the Midland marls.

In Lancashire the Accrington shale may be regarded as similar to the above, and various other deposits are scattered throughout the country.

In several localities in North Yorkshire and East Durham, *e.g.*, Ripon, Stockton, Middlesbrough, Seaton, and West Hartlepool, the "red marls" are used for making red bricks, tiles, and pottery. In this area the material requires careful selection in order that it may be free from an excessive proportion of sulphates derived from the pyrites in the neighbouring deposits. (See *Red-burning Clays*, p. 219.)

Rock marl is shale or indurated chalk or limestone containing some clays and other minerals. On being crushed it forms one of the materials just named.

Sagger marls are really fireclays (p. 171) of second quality, but sufficiently refractory to be used in the production of saggars, bats, tile-boxes, quarries, etc., for potter's kilns. The term "sagger marl" is used almost exclusively for the fireclays of the Middle and Upper Coal Measures of Staffordshire, the similar materials in other parts of the country being termed "fireclay" or "bind" (p. 139). (See *Buff or Cane Marls*, p. 210.)

Shell marl is usually a "true marl" with a large proportion of calcium carbonate in the form of shells or fragments of shells, but the term is sometimes used for a calcareous shale in which no definite shell-forms can be seen. "Shell marl" is also regarded as the equivalent of "marl," and even of chalk containing little or no clay, but the term is preferably limited to true marls containing fragments of minute shells.

It was at one time extensively used for agricultural purposes in many of the ancient lake-sites of Great Britain, but chalk or

caustic lime is now substituted. Its value for brickmaking depends upon the proportion of clay it contains and on the smallness of the shell fragments, but apart from this it does not differ materially from the ordinary marls used in this industry.

Silurian and *Triassic marls* have been described on pp. 49 and 61.

Mild clays are those which possess a moderate degree of plasticity and shrink only slightly in drying and firing. They are identical with the "lean" clays (p. 199), but may be slightly more plastic than the latter. They are termed "mild" in contradistinction to the "strong" surface clays with high plasticity, great toughness, and excessive shrinkage.

Miocene clays (p. 81).

Modelling clays are clays suitable for use by artists, sculptors, and others. They must be very fine in texture, highly plastic, and yet must not shrink much on drying. It is extremely difficult to obtain natural clays which meet all the requirements of a modeller, and mixtures of waxes, oil, glycerine, and talc are usually preferred.⁶ These mixtures are sold as "modelling clays," or under special trade names as "Plasticine," "Plastilina," "Modello," etc.

Mottled clays are those with an irregular colour. This is usually due to organic matter unevenly distributed throughout the mass, or to the iron compounds which have been carried into the clay by percolation. The mottled clays are not, of themselves, either superior or inferior to any others, but in some cases their appearance is a valuable characteristic in recognizing them. The mottled clay of Reading, the mottled ball clays of Dorset, and the mottled "marls" of Staffordshire, are each readily identified by this means. The mottling disappears in the ordinary processes of manufacture, unless special precautions are taken to avoid this, as in making Lady Baker's "Dorset Marble."

Mud is the fine, almost impalpable material produced by erosion and formed by natural agencies into a stiff paste with water. It is of very variable composition, and often contains a considerable amount of vegetable matter.

According to the rocks from which it is derived, it may consist of limestone, sand or clay, or mixtures of these and other materials in any proportion. (See *Alluvial Clay*, p. 129.)

Mudstone is an earthy rock with no definite structure and apparently composed of compressed, dried mud. It bears a relation to mud similar to that of sandstone to sand.

Natural clays are those which are used without any preliminary purification. This term is used by some writers to distinguish

between "pure clays," such as china clays, which are obtained by washing, and "natural clays," such as ball clays, brick, terra-cotta, and pottery clays, which undergo no such treatment. "Natural clays" are, therefore, identical with "secondary" clays.

Ochre is a fine clay rich in iron compounds which give it a yellow or brown colour. In the best qualities the proportion of clay is very small, and these, therefore, consist almost entirely of hydrated ferric oxide of indefinite composition. It is chiefly obtained from the Upper Coal Measures or from thick beds lying above the Oolite. There is an exceptionally good quality found at Shotover Hill, Oxford, and less important beds at Winford (Somerset), and in Anglesea. Ochre is chiefly used as a pigment, the red varieties being produced from the yellow by careful heating.

Ochre is made artificially by mixing very fine ferric oxide or a ferruginous sand with ball clay or china clay, and a variety of "ochre" is also obtained as a residue from the washing of some ball clays.

A variety of ochre termed Bole or Lemnian earth is found at Sienna and elsewhere. It is usually burned slightly before use and then becomes the well-known brown pigment—*burnt sienna*.

Paper clays—so called because they are used in the manufacture of paper—must be white, moderately plastic, and free from grit. Washed china clays of varying qualities are chiefly used, a little mica not being objected to when cheap grades of paper are made. The clay fulfils several purposes, of which the two most important are the ease with which a smooth surface can be obtained and the greater relative weight and opacity of the paper when clay is mixed with the pulp.

Pipeclay was, originally, any clay suitable for making tobacco-pipes, but the term is now used to include all white-burning clays of considerable plasticity. Thus the ball clays form one end of a series, with pipeclay as the central member and china clay as the further end. It is, indeed, common to speak of some of the less pure ball clays as "pipeclays." The lightly burned material is very porous and of a good white colour, but when harder fired or glazed it becomes discoloured. The chief deposits are found at Bovey Tracey (Devonshire), in Dorsetshire, and in North Derbyshire, but small pockets are found in many parts of the country. The "extensive deposits of pipeclay" reported as occurring in Ireland require further confirmation, though there are numerous deposits of white-burning marl.

Various china clays, marls, and other white argillaceous materials are frequently sold as pipeclay, for cleaning and whiten-

ing leather goods, window-sills, etc., and a variety of pottery known as "pipeclay faience" is much used abroad, though no pipeclay enters into its composition.

Owing to its high plasticity and shrinkage pipeclay must be worked as stiffly as possible and dried with extreme care. When a clay containing much iron is used for the manufacture of tobacco pipes a little fine chalk is added so as to mask the colour of the iron.¹

The term "pipeclay" is sometimes used to denote a clay which is suitable for the manufacture of sewer pipes and drain-pipes (p. 215).

Plastic clay is distinguished from other clays solely by the amount of plasticity developed, for no raw clays are entirely devoid of plasticity. The term is generally used to differentiate between china clay and some of the other very lean clays and such materials as ball clay, terra-cotta clay, and surface clays. There are no well-defined limits between different clays in this respect, and loams and marls may be regarded as intermediate between the plastic or fat clays and the lean ones (see *Plasticity*).

Highly plastic clays are seldom used alone, as they shrink and crack too much in drying, no matter how carefully the operation is carried out, if articles of any size are made of them. To prevent this, various substances, which contract slightly or not at all, and do not combine with water to form a plastic mass, such as sand or grog, are mixed with the clay, and sometimes fluxes, such as felspar or Cornish stone, are added, in order that the material may be better bound together during the firing. The composition of these mixtures varies according to that of the particular plastic clay used and the purpose for which it is intended. It is in the successful production of such mixtures that much of the potter's skill lies.

It is a remarkable fact that highly plastic clays, in addition to having a limited power of absorbing water, are incapable of forming a uniform mixture with less plastic clays. According to Rohland, this is due to the fact that when the colloids in clay are coagulated

¹ Some of the earliest records of the manufacture of clay pipes date back to 1570—fifteen years before Raleigh's return from Virginia with tobacco—the chief centre of the industry being at Broseley, but it was not long before pipes were made elsewhere in England. Wherever a bed of pipeclay existed near a pottery tobacco pipes could be made. In 1619 pipemakers were numerous enough to be incorporated into a Guild. Ben Jonson praised the pipes made at Manchester. At a trial in Exeter, 1654, one Edward Trible, a local pipe-maker, gave evidence; a woman had bewitched his pipes, so that they would not fire properly. The kilns which baked the first Derby porcelain were pipe-kilns.

they form gels which cannot be brought into solution by the addition of more water, and which resist the absorption of water. They are also incapable of taking up anything from a second colloid. Hence if the colloids are coagulated, as in a very plastic clay, they will not absorb more than a certain amount of water, will not take up other plastic clays, and cannot be mixed homogeneously with them. Many objectionable qualities of a highly plastic clay may be obviated by saturating it with water and then adding a suitable quantity of non-plastic material. In this way also highly plastic clays gain the power to be mixed thoroughly with other plastic clays and with felspar, which also forms coagulable colloid solutions.

Plastic clays in which there is only a small proportion of colloids, and these not coagulated, may be uniformly mixed with other similar clays.

Porcelain clays are the nearest approach to china clay available in any given locality. Theoretically, porcelain is made of pure clay of the china clay type, felspar, and quartz, but in actual practice the materials used are never quite pure, and in this way many of the differences between porcelains of different countries, and even of different periods, are produced. It is sufficient for most purposes to consider porcelain clays as identical with china clay or kaolin.

Potter's clay is any clay suitable for the production of pots, but the term is usually restricted to clays which can be satisfactorily "thrown" on a potter's wheel. For this purpose plastic clays are required, the colour of the finished goods depending on the nature of the clay, and on the glaze, engobe, or enamel, if any of these are used. The best potter's clays are white-burning, but clays used for the production of coarse pottery are buff, red, or even "blue" when fired. Such clays are found irregularly distributed throughout Great Britain, but the best occur in the central portion of the Eocene formation (p. 83). The more highly plastic clays usually require the addition of sand or other non-plastic material to reduce their shrinkage; and to confer special qualities on the material a mixture of clays is sometimes used, together with Cornish stone or felspar as well as flint. The composition of these mixtures varies according to that of the particularly plastic clay used and the purpose for which it is intended, and it is in the successful production of such mixtures that much of the potter's skill lies. White-burning potter's clay must be free from more than the smallest traces of iron compounds (which would discolour), and must also be sufficiently low in silica and other non-plastic ingredients to be capable of easy manipula-

tion. The various clays used by potters in different localities will be found under their individual names (see also *Ball Clay*, *Plastic Clay*, *Red-burning Clay*, *Terra-cotta Clay*, etc.).

The so-called *pot clays* found at the outcrops of the Coal Measures are probably underclays from which the overlying strata have been denuded, or the clays may have been brought to the surface by earth movements resulting in faults. Others have been deposited from higher neighbouring lands from which they have been eroded.

The precise geological nature of some pot clays is extremely difficult to ascertain.

Primary clays are those which are found near the supposed place of origin. The term is also used to distinguish slightly plastic clays (china clay, etc.) from the more highly plastic ones ("secondary" clays). There is considerable difference of opinion as to whether any truly primary clays exist, the ones so called being considered by some authorities to be really of secondary origin. In primary clays the grains of pure clay are frequently less fine, less plastic, lighter, and less unctuous to the touch than those of secondary clays.

Cornish china clay, as it occurs in the rock and before purification, is a typical primary clay. Some of the kaolins of Germany, America, and elsewhere are primary; others are secondary clays. Hence it is erroneous to suppose—as is not infrequently done—that all lean clays are primary ones, and that all secondary clays are plastic.

Puddling clay or "puddle" is any clay or earth mixture of sufficient plasticity to be capable of forming a waterproof lining or backing to a reservoir or similar structure. The proportion of true clay in the mixture is unimportant, the chief requisite being that the material shall dry without cracking and that it shall be waterproof. Hence clays which are exclusively plastic must be "let down" with gravel, sand, or rock dust.

The operation of clay puddling, in which the mixing is done by the worker's feet, was at one time general, but is now only practised in connection with the manufacture of crucibles for steel-melting and in semi-civilized countries. In Great Britain "puddle" is made by mixing the materials in a pug-mill.

Pug, the material used as mortar in fireproof masonry, is usually furnished by the makers of fireproof goods. Theoretically this material has the same composition as the goods, but instead of being made into a paste it is dried and put in sacks, water only being added to it immediately before use.

As the material should not contain any coarse grains, only fine

sand or powdered grog can be used to reduce its shrinkage. Sufficient of this non-plastic material should be added to give the mixture only so much plasticity as is absolutely necessary for it to be used with a trowel.

Fireclay mortar or *pug* is also used for stopping cracks in masonry or in crucibles and retorts. All kinds of mortar containing clay shrink, thus causing them to break off the parts repaired and making this repairing only temporary. By taking advantage of the property of silica of swelling when heated and using ganister, this difficulty may be overcome. A material similar to ganister may be made by adding about 10 per cent. of clay to a crushed rock, which is chiefly composed of silica.

Pure clay does not occur in Nature in a free state. The purest clay obtainable is prepared by the most careful washing of the purest natural clays (see p. 214). Perfectly pure clay is therefore a theoretical substance consisting of "hydrated silicate of alumina" or aluminosilicic acid, corresponding to the formula $H_4Al_2Si_2O_9$, and composed of silica, alumina, and water, and *nothing else*, in the form of a single compound.

Reading Clay.—Some of the clays in the Reading bed are particularly suited for the manufacture of tiles, finials, and chimney-pots (see p. 205).

Red-burning clays are so called from the colour of the goods made from them. They usually contain upwards of 4 per cent. of iron oxide, but must otherwise be fairly pure, because the presence of relatively small quantities of lime compounds spoils the colour by combining with the iron to form whitish or buff compounds.

The percentage of iron oxide is not a reliable guide, as the colour is dependent upon the size of the particles quite as much as on the proportion present.

According to the origin of the clay and the amount of silica it contains, red-burning clay may be used direct, after purification or after admixture with other ingredients. Very stony clays seldom give a good red colour, but sandy loams are much used.

Clays which become a good colour on burning may in their native state be red, dull purple-red, red-brown, yellow, or grey. They are extensively used for making facing bricks, terra-cotta, and coarse pottery, and a limited number are also made into ornamental floor-tiles. The value of a red-burning clay must be judged by its texture, colour, density, and durability after firing, rather than by its geological formation or chemical composition. Hence it is necessary to burn a sufficient number of full-sized articles under commercial conditions before a correct opinion of the technical value of a red-burning clay can be given.

Some of the Welsh (Ruabon) clays are specially famous for the fine colour of the goods made from them, but excellent red-burning clays are known to exist almost all over the world, though in many places there is not sufficient depth of clay to pay for working.

The finest red-burning clays are used for the manufacture of coarse pottery and terra-cotta, and are frequently known as *terra-cotta clays* (*q.v.*). The so-called "red marls" of Staffordshire (p. 211) and the best red-burning clays of Shropshire and North Wales are much used for ornamental floor- and roofing-tiles and similar work.

Other red-burning clays occur generally in the Midlands (where they are much used for flower-pots, etc.), in Lancashire, and Peterborough, where they are made into bricks, and at Reading, Corfe Mullen, and Fareham, where they are used for tiles. The distribution of red-burning clay useful for brickmaking is, however, so general that no further details need be given here (pp. 143-150).

Many red clays are of little value because they are of too poor a colour when burned; others are too porous and weak; others, again, contain particles which produce black or white or cane-coloured specks when burned. A few red clays are excessively vitreous and plastic, and must be mixed with sand or loam. The indurated rock-like clays must be thoroughly weathered before use. Good red-burning clays when properly burned should develop a full red colour inclining toward a crimson shade, free from scum, specks, and blisters, and with the least possible twisting, buckling, cutting, or cracking of the goods.

Clays experimentally found to possess most but not all the required qualities may be mixed with other clays or red-burning sand.

Care must be taken not to reduce the vitrifiableness of the clays if they are to be used for the manufacture of floor-tiles. For terra-cotta making, clays may be let down with sand to a large extent, but this tends to make them mature in colour at so low a heat that the product is too porous and weak for tiles, and a further heating may ruin the colour.

Clays yielding a poor colour can seldom be much improved by the addition of any oxide or hydrated oxide of iron, as these artificially added materials are far too coarse to produce a satisfactory colour. Hence if the colour of a red-burning clay is unsatisfactory it can only be improved by dipping the articles in a slip made of a suitable clay, unless the poor colour is due to impurities in the clay. For instance, soluble salts in the clay will produce a whitish scum on the goods, which can often be

prevented by the addition of barium carbonate to the raw clay. Sometimes the presence of only 5 per cent. of lime or magnesia in the clay causes an irregular colour (see *Marl*, p. 206).

It must therefore be remembered that whilst the essential colouring agent is extremely finely divided iron oxide (Fe_2O_3), the full colour cannot be developed except in the absence of certain other oxides, particularly lime, magnesia, and alkalies. The last named, by causing a partial fusion of the material, usually darkens the colour and imparts to it an unpleasant sheen.

The colour produced depends also upon the firing of the goods in the kiln, the shade gradually becoming brighter and more intense as the temperature increases, until a point is reached about Seger cone 1 when further heating spoils the colour. The exact point varies with each clay.

The colour appears to be due to free iron oxide, as the addition of fluxes or any heat treatment which brings about a partial fusion of the mass and induces combination of the iron oxide and silica at once spoils the colour.

Hence the freer the clay is from other materials than naturally occurring iron oxide in an extremely fine state of division the better will be the colour of the product. For this reason, some potters and tile makers find it necessary to purify their clay by means of a careful washing. An under-burned red brick will crumble under the action of weather and is only fit for inside work.

Reddle or Raddle is a highly ferruginous clay of small value.

Refractory clays are those which possess a high degree of resistance to heat. There is no generally recognized standard of heat resistance in this country, but on the Continent no clay is considered refractory if, when made into a small three-sided pyramid whose height is at least four times as great as one side of its base, it cannot stand the same steady heating as Seger cone 26, corresponding to a steady rise of temperature to 1580°C. , before the test piece bends over (see p. 189).

The most refractory clays will not bend, except at such a temperature as will bend Seger cone 36 (1790°C.), but in practical use other influences must be taken into consideration, such as the cutting action of flue gases, the influence of slags, and of sudden changes in temperature. Hence whilst the word refractory, as applied to clay, refers simply to its resistance to a steadily increasing temperature, in practice a clay is only considered refractory if it is heat-resisting under commercial conditions, though these latter are seldom defined in detail. It frequently happens, therefore, that a clay is condemned as not being sufficiently refractory when the true defect is its weakness to abrasion or

accidental blows, or its inability to withstand rapid cooling. In such a case a clay of lower absolute refractoriness (*i.e.* with a lower softening temperature) may prove more durable than one of the purer clays. Thus china clay is one of the most refractory substances known, but bricks made of it are by no means satisfactory in many furnaces, as they cannot stand the repeated heating and cooling, whereas a fireclay with a lower fusing-point serves admirably.

In the broad sense in which the word "refractory" is used amongst users of furnaces a clay must, when made into bricks, blocks, or other articles, be capable of (1) resisting temperature to which it is likely to be exposed in use; (2) resisting any pressure¹ likely to be put upon it by adjacent masonry or by material in the furnace; (3) resisting the cutting and abrasive action of the flame, flue-dust and any other material with which it may come in contact, including accidental blows from a poker or clinking iron; (4) resisting such sudden changes of temperature as are unavoidable in ordinary work; (5) uniform expansion or contraction within conveniently narrow limits.

Few refractory clays can fulfil all these requirements under very severe conditions, and the user must therefore decide to what extent he will forgo some of the (to him) less important requirements. Thus by using a brick with a moderate degree of absolute refractoriness he may be able to get a material much more resistant to slag, flue-gases, or other influences of importance in his case. To a very large extent this method of "compromise" depends upon local circumstances for success, and without full details no satisfactory guidance can be given. It must also be remembered that skilled construction is often equally as important as suitable materials in the construction of furnaces, as badly laid masonry will be unsatisfactory even if made of the most refractory clays.

¹ Bleining and Brown have found that fireclays with a high content of bases and of silica soften seriously when heated to a temperature of 1300° C. under a load of 50 lbs. per square inch, and they advise that fireclays containing more fluxes than corresponds to 0.22 R.O. $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ should be mixed with a clean sand or sandstone, so as to reduce the fluxes to below this amount. Otherwise, if the clay is subjected to pressure when at a high temperature it may easily become so soft as to lose its shape. This may, to some extent, be avoided by using a clay which is of a coarse texture, whereby the interaction of the various constituents is hindered. This tendency to soften under pressure may also be reduced by firing the material at a sufficiently high temperature in the course of manufacture. The extent to which a clay is burned cannot, of course, affect its true refractoriness, but it may make a noticeable difference in its ability to withstand the combined action of heat and pressure, and is therefore of great practical importance.

Refractory clays are of two main kinds: (1) those containing nearly as much alumina as silica; and (2) those in which the silica largely predominates. The first class includes the china clays (p. 153), kaolins (p. 195), some ball clays (p. 131), and a few Coal Measure fireclays (p. 171); though the two former are not used for refractory purposes so much in Great Britain as in Germany. The second class includes most of the Coal Measure fireclays (p. 171), the clays from pockets in Mountain Limestone (p. 182), various highly siliceous fireclays (p. 181), ganister (p. 181), and Dinas and other siliceous rocks from which firebricks or furnace linings can be made.

It will thus be seen that many clays are refractory, though this term is usually confined (in this country) to certain fireclays.

In selecting a refractory clay for a particular purpose it is necessary to know whether it will come into contact with acid or basic materials, as if this is the case a clay of the same nature must be used. For this reason refractory materials are divided into three groups: (i) basic; (ii) neutral; (iii) acid.

The **basic** refractory materials are not composed of clay, and so are outside the scope of the present work.

The **neutral** refractory clays are those containing but little free silica, and are useful for most purposes.

The **acid** refractory clays contain a large proportion of free silica, and may in some cases contain so small a percentage of clay as to be more properly termed siliceous rocks. Ganister, Dinas rock, and silica bricks are of this extreme character; the ordinary fireclays of the Coal Measures represent a moderately acid material owing to the free silica present in them.

For many purposes a mixture of several clays is preferable to the use of a single one, and the bulk of these should, usually, be of the nature of fireclay (p. 171). In Germany it is customary to use a burned clay as the basis, and preference is given to one which does not soften sooner than Seger cone 35, but in Great Britain raw fireclays softening at cone 30 are more frequently employed. Even when a clay is not required to withstand high temperatures in use, refractory clays must sometimes be used. Thus, in order that a sufficiently durable glaze may be fired on bricks or sanitary goods it is necessary to fire them at a high temperature (1300° C.). For other purposes the clay mixture requires heating to a high temperature if it is to gain its maximum durability and strength, so that whilst the refractoriness of the raw materials is in such cases only a secondary consideration, it must not be overlooked. In order to withstand rapid changes of

temperature, clay used for baths, hot tanks, etc., must be sufficiently porous.

Pure silica is nearly but not quite as refractory as pure clay, and sometimes mixtures of clay and silica are quite refractory so long as they are pure. Directly a small percentage of lime, magnesia, iron, or alkali enters into the composition of the mixture, however, the refractoriness is seriously diminished. The relative amount of such fluxes is often very small, so that chemical analysis alone is seldom sufficient to determine the refractoriness of a clay, though with the better qualities much assistance may be obtained from the use of a Ludwig chart (fig. 34). The only reliable measure of the refractoriness of a clay is a determination of its softening point.

A discussion of the cause of refractoriness in clay must be deferred to Chap. XIII.; it may, however, be briefly stated as due to the proportion of true clay in the material, to the size of the particles, and to the absence of any fluxing ingredients.

Residual clays are variously defined as those which have (*a*) been left behind at the place where they were originally formed by the decomposition of rock; (*b*) those which have been left when a mixture of various materials, such as clay and limestone, has been subjected to the action of water containing carbonic acid whereby the limestone has been dissolved out and carried away; and (*c*) those which have been collected by glacial agency.

They vary greatly in composition and contain coarse fragments of foreign rocks, such as quartz, chert, flint, and limestone pebbles as well as softer materials like chalk; apart from their irregularity in composition they call for no special notice.

The purest of those in class *a* (sometimes known as "primary clays"), form the chief source of china clay and the kaolins.

The most refractory of those in class *b* are used for fire-bricks (p. 171).

Those of class *c* are usually of little value—see *Boulder Clay* (pp. 104 and 140)—though some of them may be used in the manufacture of bricks and tiles.

Retort clays are used for making gas-retorts and other refractory articles. They are specially selected portions of the ordinary fireclay deposits of the Coal Measures. On the Continent, gas retorts are chiefly made of chamotte or grog (p. 193), the particles of which are bound together by ball clays.

Rock clays or compressed clays are formed by the pressure of neighbouring strata, and constitute an important class of which the shales, slates, knotts, and fireclays are the most important members. The water present in such clays before their com-

pression escapes very slowly, thereby tending to re-crystallize some of the amorphous matter in the form of a cement binding the remaining particles together.

The lost plasticity of such compressed clays may be partly restored by grinding the materials sufficiently fine and working them up with water so that the particles are again separated and the material thus obtained in its original condition, though it is never quite so plastic as before its compression.

Roofing-tile clays are similar in character to those used for making the better qualities of hand-made bricks, and must possess a good red colour when burned. They must be sufficiently plastic to be used for the manufacture of thin slabs or sheets, and yet must not shrink sufficiently to cause a warping and cracking in the kilns.

The chief requirements and characteristics of a clay for roofing-tile manufacture are that it shall be highly plastic without being "sticky"; it must be sufficiently refractory to give a tile having great durability, yet should contain enough vitrifiable matter to produce tiles having a good "ring" without being too dense. In addition to these properties the clay should burn to a pleasant colour—preferably to a good "red," with a tendency to maroon rather than to yellow.

Many clays possess some, but not all, these characteristics, and the skill of the tile-manufacturer largely shows itself in the adding of other materials or in the treatment of the clays so as to produce saleable articles at a reasonable price.

Mild red clay or loam is found near the surface in almost all parts of the country, but it is not worth working if in layers less than a yard deep, and then when only readily accessible.

The older clays, such as are found near Reading, the Bagshot beds lying near those of the London basin, certain Staffordshire and Shropshire clays, some of the brick earths of the southern counties, the alluvial clays of Somerset, and selected portions of the Lias and Trias clays extending throughout the Midlands and into Cheshire, are the best for roofing-tile manufacture, though to a small extent shales and buff-burning clays with or without a covering of red clay are sometimes used. Further particulars of all these clays may be found on reference to the index under the names of the clays or of the localities mentioned.

The Reading clays are not so rich in iron oxide as are those from some other districts, and consequently they are somewhat light coloured and require a considerable exposure before the tiles become well "aged" and attractive to architects. This defect is often overcome by partially covering them with a staining material.

The clays from the Bagshot bed are of a much better colour, whilst those from Staffordshire and Shropshire—and particularly the Broseley clays from the latter county—are much prized on account of their variegated colouring in which the bright red tones are relieved by shades of blue and purple, due to the action of reducing gases in the kiln on the iron compounds contained in the clay.

There are a large number of other red-burning clays which are worked to a small extent in various parts of the country; thus in the Nostel district in Central Yorkshire tiles are produced in considerable quantities from a clay so rich in fluxes that the tiles are almost entirely free from porosity. This clay is found above the Coal Measures, and when burned has an interesting chocolate colour quite distinct from that of the tiles of other districts.

There are many varieties of clay in this country which are admirably adapted for tile-making, but they require a considerable amount of study and no small amount of experimental skill before most of them can be utilised at a profit.

Rubber clays are very sandy clays or loams rich in iron and practically free from lime compounds, which when fired at a low temperature have but little binding power, owing to the absence of any fluxing material. Bricks made from such clays are convenient for many purposes, as they can be rapidly shaped by rubbing either against each other or on a harder stone. Except for their lack of plasticity, rubber clays are not difficult to work and have little or no tendency to shrink greatly, crack, or warp in the kiln. They must be carefully fired to obtain a good colour.

Sagger marls are really fireclays, but the term "marl" is used in Staffordshire for a number of clays almost free from lime (p. 213). Saggings are the cases used to protect the goods whilst in the kiln, and may be made of any suitable refractory clay. Thus in France the clays used for sagger-making are of an entirely different character to those employed in this country, being more of the nature of the Devon and Hampshire clays (tertiary clays) than of the Coal Measure series. This difference is chiefly due to the scarcity of the Coal Measure clays in France, and not to any special characteristics in the clay they use. In America there is no clay at present in use which is precisely the same as that used in Staffordshire.

It is an interesting sign of the amount of empiricism existing in sagger manufacture that although the clays used in the Staffordshire potteries are all from a very small number of sources, yet in order to please and satisfy the varied demands of different potters, special parts of each marl hole are reserved for different firms.

Occasionally a potter gets clay from a different portion of the pit (though of practically identical composition), but he does not usually notice any difference unless a slight variation in the colour makes him suspicious. It is a fact that more than one firm of marl dealers sell the same material under a large variety of names to different firms, as these would not purchase the same material under a different title.

The chief characteristics required in a sagger clay are that it shall be reasonably plastic, whilst not excessively so, that it shall produce a material of great strength when fired at a relatively low temperature, and yet shall not lose its shape when fired to the highest heat in the oven. It should mix readily with water so as to render the preparation of the paste as easy a matter as possible, and must not shrink too much on either drying or firing.

These qualities are not easily found in a single clay, and mixtures of several clays are frequently employed. Some grog (burned clay) must also be added, and the characteristics of this are important. Thus S. T. Wilson has found experimentally that the size of grog does not alter the contraction during drying but is influential in other ways, as coarse grog will make saggars which will stand repeated firings, but will not stand the weight of goods in them; whereas fine grog with a greater percentage of porosity will not stand changes in temperature, but the saggars will stand the weight of the goods very well. A mixture of both coarse and fine (not dust) grog gives the best results. If insufficient air is used in firing the oven, the iron oxide will probably be reduced and a fusible ferrous silicate formed which weakens the saggars and causes them to collapse.

Sandy clays are natural mixtures of clay and sand; they are technically known as "loams" (p. 202).

Secondary clays are those which have been carried away by water from the place where they were originally formed and have been re-deposited. They are usually highly plastic and often far more impure than the "primary" clays from which they are derived. Most plastic clays are of a secondary nature.

Sedimentary clays are identical with secondary clays, and owe their name to the fact of their first being suspended in water and then allowed to settle, forming sediments. They are sometimes termed "transported" clays.

A sedimentary clay having been transported by water for great distances has usually lost much of its coarser material and is a fine-grained and more homogeneous product than a primary clay. With the possible exception of china clay all British clays are sedimentary.

Sewer-pipe clays are those used for the manufacture of sanitary appliances. Fireclays with sufficient silica to take a good salt glaze are largely used, but preference is now usually given to those which become partially vitrified on burning. This enables them to become impervious to water even when the glazed surface is imperfect. Low-grade fireclays which are somewhat rich in lime are usually selected for the manufacture of sewer-pipes. Their general properties are described under *Vitrifiable Clays*.

Shale is the general name given to any clayey rock which can be split into thin layers, so that under this term is included a large number of rocks of diverse origin and whose composition is seriously affected by the presence of other minerals (such as pyrites) which are usually present. The term "shale" is by no means confined to clays, though some of the most useful brick-making materials are clay-shales. The bulk of the Silurian shales, for example, is almost free from clay.

Although it is generally agreed that shales are formed by subjecting clays and sands to enormous pressures in the presence of water, exactly what occurs in their production is unknown, and the result of pressure alone does not explain numerous cases. These may be better understood if water is assumed to have been present during the compression and to have formed (with salts it carried in solution) a kind of cement which binds the clay particles together.

The presence of decaying animal or vegetable matter also appears to exercise a strong influence on the formation of shale, and it has been suggested that this is due to the colloid materials formed during the decomposition of the animals or plants. Some authorities consider that the smaller proportion of combined water in shales than in some clays is due to dehydration and the formation of such minerals as andalusite, kyanite, and sillimanite, which also consist entirely of alumina and silica.

Clay-shales are not entirely amorphous, but contain a notable amount of crystalline material, frequently of a micaceous character. They are found in the Coal Measure, Permian, Jurassic and Wealden formations; mottled shales also occur in the Red Sandstones (see Chap. IV.). Some of the best known clay-shales are the fireclay shales of the Coal Measures and, when partially metamorphosed, the slates.

They are moderately hard, but this property varies with the pressure to which the material has been subjected. Hence the shales from great depths are usually harder than those found nearer the surface. The colour may be light grey, red or brown to black, and is usually due to organic impurity which burns out

on heating, and to iron compounds, which are all largely converted into ferric oxide on burning.

Clay-shales show many variations in composition and are usually defined as (1) calcareous, (2) sandy, and (3) bituminous. They pass on the one hand into clays, on the other into flagstones and sandstones; or through calcareous graduations into limestone; or through ferruginous varieties into clay ironstone and through bituminous kinds into coal. Some shales can be cut quite easily with a knife without any grit being observable, but others resemble a soft sandstone. In chemical composition shales of the same strata tend to be fairly uniform, but on exposure to air the unoxidised iron compounds (which cause so much trouble when unweathered shales are used) become converted into higher oxides (which are almost harmless). Hence the colour of the shale on the exposed portion of a heap is usually lighter than that which is freshly brought to the surface. A high percentage of iron in a shale is not objectionable for many purposes, provided that it be fully oxidised before the goods enter the kilns; but if attempts are made to burn goods containing more than 2 per cent. of ferrous oxide (the lower oxide of iron) or 3 per cent. of pyrites or of siderite, serious difficulties will have to be overcome by the fireman.

Where shales are used to manufacture refractory goods or glazed articles, the proportion of iron compounds must be as low as possible and should not exceed $1\frac{1}{2}$ per cent.

Most shales are rich in pyrites and are liable to produce unsatisfactory goods unless this is removed before grinding. It cannot be ground sufficiently fine to have no effect on the appearance of the fired goods, as it always shows itself in the form of slag-like masses of varying size from a pin's head to half inch or more in diameter.

Many shales contain considerable amounts of carbon which imparts to them a black colour. This carbon—derived from bituminous matter deposited along with the clay—is liable to cause trouble in the burning unless sufficient caution is observed when the goods are in the kilns, as it acts precisely as though a quantity of fine coal had been mixed with the clay, and can easily "set the kiln on fire" and melt all the contents to a useless clinkered mass. Shales containing 4 per cent. of carbon are frequently used for brickmaking in this country. They are, however, difficult to work, not only on account of the carbon, but also because of the iron in a very low state of oxidation, which renders it difficult to obtain a satisfactory colour.

Some shales, notably of the Oxford clay, Lias, Wealden, and the

Coal Measures (pp. 52 and 172), have gained a great reputation as materials for brickmaking.

According to the nature of the impurities they may burn either buff or red, the colour depending largely on the amount of iron oxide present in them.

Shales require to be crushed by powerful machinery, and many of them produce good clays of moderate plasticity which can be used for the manufacture of bricks, tiles, and many varieties of moulded goods. They can seldom be made into a paste sufficiently plastic to be "thrown" on a potter's wheel, except for crudely shaped articles.

The purer fireclay shales are much used in the production of glazed sanitary articles such as lavatory basins, and of refractory goods (see p. 221), though the unstratified underclays are usually superior.

Calcareous shales, particularly those of the Lias formation, are used in the manufacture of Portland cement and hydraulic mortar; otherwise they are of small value to clayworkers.

Sandy shales, if sufficiently refractory and capable of being made into a plastic paste, may be used for sanitary ware, fire-bricks, etc.

Bituminous shales seldom contain true bitumen, but have received this title from the combustible material in them. Some of these shales are so rich in organic matter as to resemble a low-grade coal; others contain yellow resinous substances. Most so-called bituminous shales yield oil on distillation; hence the term "oil shales."

Oil shales occur at Portobello, Leith, West Calder, in the Lower Carboniferous rocks at Kirkcaldy, and in the Linlithgow Coal Measures in Scotland, and in some of the Kimeridge beds in England (p. 69). They contain so much carbonaceous matter (20 to 25 per cent.) that they are capable of yielding a crude oil (shale tar) on slow distillation at a low red heat. It is a true shale, though highly impregnated with bituminous (?) matter and intermediate between common shale and cannel coal. Many shales yield small proportions of oil, but only the richer qualities are commercially valuable. Some of these richer varieties yield 30 to 40 gallons of crude oil, 60 gallons of ammonia water, and 2000 cubic feet of illuminating gas per ton of shale; they may be distinguished from the poor shales by slicing them with a knife, when the cut paring curls up in front of the knife and shows a characteristic brown lustrous streak.

The composition of this crude oil is highly complex, the chief commercial products obtained from it being naphtha, burning oil,

lubricating oil, and "scale" or crude paraffin wax. For further information on the shale oil industry the reader is referred to Redwood's *Treatise on Petroleum*.

Alum shales occur in the Upper Lias near Whitby, and were at one time largely used in the manufacture of alum (see *Alumine Clay*, p. 131).

At Boulby—where the chief works were situated—the main bed of alum shale is over 200 feet thick, and a second, lower bed, 100 feet thick, runs down to the coast. These beds are no longer used.

Alum shale is also fairly common in the Silurian formation of Scotland. Some of the shales of the Coal Measures are equally rich in pyrites and form alum on exposure or on roasting and subsequent treatment.

They may be recognized by an efflorescence of aluminium sulphate, tinged red with iron oxide, which forms on them after exposure; by their high content of carbon—whence they are included in the bituminous or oil shales—and by the sulphurous odour emitted when they are burnt.

Alum shales are usually grey in colour; they are soft, sectile, and contain a considerable proportion of organic matter.

The chief characteristic of alum shales is due to their large content of pyrites. On exposure or roasting with an ample supply of air, ferrous sulphate and sulphuric acid are formed. The latter attacks the clay, forming aluminium sulphate. The mixture of sulphates is treated with water and the solution is decanted, and then evaporated until almost strong enough to crystallize. Much of the ferrous sulphate crystallizes out on cooling, and the clear liquid having been run off to another vessel, potassium or ammonium sulphate is added and the alum then crystallizes out.

Some alum shales—particularly the bituminous shales of the Coal Measures of the south-west of Scotland, and the Lias shales near Whitby—have been exposed to the air for so long a period that no roasting is necessary, all that is required being alternately to extract the salts with water and to expose the shale repeatedly to the air until all the pyrites has been oxidised.

With improved appliances, alum is now largely manufactured from the much purer ball clays of Dorset and Devonshire. There are various methods in use; one employed by several large works consists in mixing the clay with potassium sulphate and forming it into balls. These balls are calcined in an ordinary potter's kiln and, when cold, are treated with hot, strong sulphuric acid. The potassium and aluminium sulphates are dissolved out by extract-

ing with water, and the alum is recovered by evaporating the solution until it is strong enough to crystallize. An alternative method consists in calcining the clay at a dull red heat, dissolving out the alumina by sulphuric acid; alum is then produced by adding a solution of potassium or ammonium sulphate and evaporating the liquid until it begins to crystallize.

Short clays are those which have only a moderate degree of plasticity, the term "short" being the converse of "plastic" or "fat" and synonymous with "lean." In some cases, however, clay pastes are known as "short," which break off very suddenly when pulled asunder, without the usual tapering extension shown by highly plastic clays. Such clays are not exactly "lean," and the term "short" or "short working" appears to express their characteristic more accurately. Clays of moderate plasticity (as fireclays) to which coarse grog has been added are usually very "short," though capable of being moulded or "thrown."

Siliceous clays are, as the name implies, rich in free silica. This term is not, however, applied to loams (p. 202) but almost exclusively to the siliceous fireclays (p. 181) which contain 50 per cent. or more total silica, to the rocks containing much silica and little clay, as ganister (p. 181), and to the so-called fireclays of Ewell, Epsom, and Dinas, which are really sands and contain but little clay.

They are extremely abundant, and unless containing too much fluxing material (lime, magnesia, and alkalis) are well adapted for the manufacture of most articles of a refractory nature. The more highly siliceous clays are, however, incapable of withstanding sudden changes of temperature (see *Fireclays*, p. 171).

Silt is a river-, lake-, or glacier-deposited material composed of fine rock dust and often containing much clay and fine sand. It has been defined by Seger as the portion which may be washed out of a natural clay at such a speed (0·7 millimetres per second) as to consist of particles between 0·01 mm. and 0·025 mm. diameter. This definition excludes the presence of clay, the particles of which are much finer, except when in the form of small fragments of shale or rock-clay. Seger's definition is commonly used in reports on the mechanical analysis (washing) of clays and earths.

Silt which is not purified by washing, as just mentioned, usually contains sufficient clay to make it somewhat plastic, though its chief ingredient is non-plastic rock-dust of a calcareous or siliceous nature. It may occur as veins or pockets in clay beds (particularly in those of glacial formation), and is exceedingly difficult to distinguish from short or lean clay, though it contracts less on

drying and has but little cohesion. It is sometimes known as *dump* or *duff*. Under favourable conditions it is a serviceable brickmaking material, but it is usually deficient in plasticity and cohesion. The silt from the Humber is successfully used for this purpose. When freshly dug it is dark blue in colour, but turns brown on exposure.

When fairly free from lime, magnesia, and alkalis, good fire-bricks may be made from silt, though they seldom withstand sudden changes of temperature without fracture on account of the fineness of the material.

Warp is a special kind of silt described at the end of the present chapter.

Slates are hard clayey rocks, often coloured dark with carbonaceous matter, which may conveniently be regarded as shales which have undergone more than the usual compression and have, at the same time, been subjected to the influence of a considerable amount of heat.

Their origin is somewhat uncertain, but is usually attributed to the waste from pre-Cambrian rocks deposited very slowly in deep water, and later compressed, indurated, and partially metamorphosed by heat.

They are practically non-absorbent, have a high resistance to crushing (6 to 14 tons per square inch), and a transverse strength greater than that of other stone. Being much harder than most shales, they are not readily broken up into a smooth slurry, and frequently show a marked crystalline structure. Various sandstones and limestones which are used for roofing purposes are also known locally as "slates" or "tile-stones," but they split along the lines of deposition, which true slates do not. Such stones are also more absorbent than true slates, and are much thicker and heavier, necessitating more timbering in the roof.

Slates are in fact characterized by their capability of being split into thin leaves in a different direction from that of the original deposit, thus giving them a fissility quite independent of the primary lamination.

Slates are chiefly used for roofing, for slabs, for sanitary and scientific purposes, and to a small extent for writing materials. Their quality is judged by their freedom from spots and flaws, evenness of colour and thinness, the sound when struck, and their absorption. A good slate partially immersed in water in a vertical position should not become wet above the water-line in twenty-four hours.

The chief British slates are of Cambrian, Silurian, and Devonian formations, and are extensively worked. The largest and most

valuable quarries in North Wales are of Cambrian (at Llanberis and Penrhyn) and Lower Silurian (at Festiniog) origin, and other important quarries are worked in Cumberland (Lower Silurian), Westmorland, and Lancashire (Upper Silurian), and in Devon and Cornwall (Devonian and Carboniferous). The Westmorland slates appear to have been derived from volcanic ash rather than from clay. The slates of Argyllshire, Dumbartonshire, and Perthshire (Lower Silurian and Cambrian) are also valuable. In Ireland the Lower Silurian, Devonian, and Carboniferous slates are worked in the counties of Wicklow, Tipperary, Cork, and Kerry, those from Valencia Island being highly prized. The Scotch slates are chiefly blue in colour, whilst those of North England are green, and those of Wales chiefly purple.

Slates are usually rich in iron, lime, magnesia, and alkalies, and vitrify at 1000° C. or thereabouts. On account of their great hardness and low plasticity, waste slate (chippings) is not suitable for brickmaking, but some beds may be made into common bricks by the semi-dry process. Notwithstanding much published opinion to the contrary, the best slates are not the most suitable for brick-making but rather the reverse, as the qualities prized by the builder are positively disadvantageous to the brickmaker.

Enamelled slate is used principally for chimney-pieces. The enamel is a kind of japan, and is "fixed" by heating the painted slate to 130° C. The background is usually black, but various colours are used above this to represent marble and other stones.

Flint-slate is a particularly hard shale which breaks with a conchoidal fracture. Like many shales, it is frequently termed a slate, though devoid of the chief characteristic of true slates.

Clay-slates or *Killas* of various formations occur in several areas. They are intermediate between clays and slates, and whilst they could be used for brickmaking, they are not so employed on account of the existence of more convenient clays.

The term "clay-slate" is very misleading, as a true slate devoid of any micro-crystalline aggregate is almost unknown.

Mica-slate is composed almost entirely of microscopic plates of mica and chlorite, quartz and felspar particles; these occur along with clay and dust-like fragments of older rocks. The fact that mica-slate occurs chiefly in the oldest formations, the shales in later ones and the clays in the most recent, simply shows that the older a material is the more likely is it to undergo metamorphic changes as the result of physical and mechanical influences.

A list of the chief British slates, compiled by G. A. T. Middleton, is given on the following two pages.

TABLE XI.
ENGLISH SLATES.

Quarry.	Nearest Station.	Nearest Port.	Colour.	Remarks.
Delabole, Old	Delabole	Wadebridge	Blue-grey	The slate is noted for its lightness, durability, and strength.
East Cornwall	Doublebois	Par	Blue	Slate very durable.
Elterwater .	Coniston, or	Barrow-in-	Finest light	Rough in texture, but of a durable character.
Honister .	Windermere	Furness	green	
	Keswick	Maryport or	Light sea-green,	
		Workington	deep olive-green, dark sea-green	
Kirkstone .	Windermere	Barrow	Green	Very strong and durable,
Launceston .	South	..	Blue	
Okehampton	Petherwin	Watchet	Blue and variegated	Slate slabs, damp courses, etc.
Parrook End	Wiveliscombe	Barrow-in-	Light sea-green,	
	Coniston	Furness	deep olive-green, dark sea-green	
Tilberthwaite	Tilberthwaite	..	Green	
Tracebridge	Burlescombe	..	Dark blue	Mostly used for slabs, pump troughs, cisterns, hearths, flooring, chimney tops, garden edging, etc.
Torver . .	Barrow-in-	Barrow.	Blue	
Treborough .	Furness	Watchet	Blue	Roofing slates, and slate slabs for all purposes.
Yeolmoridge	Washford.	Plymouth	Blue veined, grey, hard	Chimney-pieces, water-tanks, sills, steps, paving, etc.

SCOTCH SLATES

Aberfoyle .	Aberfoyle	Bowling	Blue and green	Only roofing slates. This slate is blue in colour, with small iron pyrites.
Balvicar .	Oban	Glasgow	Blue	
Belnahua .	Oban	Belnahua	Blue	
Breadalbane	Oban	Luing and	Blue	
Craiglea .	Methven	Talevonoehy	Blue, green	
Cullipool .	Oban	Perth and	and grey	
		Dundee	Blue	
		Cullipool		

WELSH SLATES.

Quarry.	Nearest Station.	Nearest Port.	Colour.	Remarks.	
Aberllefenny Alexandra . Bettws - y Coed	Aberllefenny Dinas Junction Bettws-y-Coed	Aberdovey Carnarvon Deganwy	Dark blue Purple Dark blue	Carnarvon large vein; producing slabs for mantel - pieces and slates of all sizes.	
Cefn . . . Cilgwin . . . Dinorwic . . .	Kilgerran Nantlle Port Dinorwic	Cardigan Carnarvon Port Dinorwic	Blue Blue, purple Grey, blue, red and green Blue		
Diphwys Casson Dorothea . . .	Blaenau- Festiniog Nantlle	Portmadoc Carnarvon	Blue Blue and purple		
Glynrhonwy	Llanberis	Carnarvon	Blue and purple		
Llechwedd . . .	Blaenau-Fes- tiniog	Portmadoc	Dark blue		
Moelferna . . .	Glyndyfrdwy	Saltney	Blue-black, blue Blue		Roofing slates; slabs for brewery tanks.
Okeley . . .	Blaenau-Fes- tiniog	Portmadoc	Blue		
Penrhyn . . . Rhiwbach . . .	Bethesda Blaenau Fes- tiniog	.. Portmadoc and Deganwy	Purple Blue		One of the oldest quar- ries producing Port- madoc slate; worked since 1812.
Votty and Bowydd Wrysgan . . .	Blaenau-Fes- tiniog Tan-y-Grisiau	Portmadoc Portmadoc	Blue Blue		Genuine Portmadoc or Festiniog slates.

IRISH SLATES.

Fourcoil . . .	Skibbereen and Clonakilty	Leaf Quay, Glurdere Harbour Limerick	Dark blue	Billiard-table beds.
Garrybeg . . .	Nenagh and Killaloe	Limerick	Grey	
Madrana . . .	Skibbereen	Leap, 2½ miles	Very dark grey	
Ormonde Slate	Carrick-on- Suir	Carrick-on- Suir, 6 miles	Blue	
Valencia	Valencia Island, Kerry	..	

Numerous other varieties of slate exist, but they are of comparatively small importance.

Readers wishing for more detailed information on the geology and use of slates in building, for enamelling, etc., should consult special treatises on the subject. Howe's *Geology of Building Stones* will be found useful in this connection.

Slip clays are those which are used for covering articles made of an inferior clay in order to improve their appearance. Thus bricks and terra-cotta goods may be made of a clay which has an unsatisfactory colour when burned alone, but if the goods are first covered with a red-burning clay, ware of excellent colour may be obtained. The slip clay is so called because it is made into a fluid ("slip") with water and the articles are immersed in or otherwise covered with it.

For successful application, the slip clay must contract to exactly the same extent as the clay on which it is fired.

Some firms apply the term "slip-clay" to one which is so fusible that it forms a natural glaze on the goods, but this is an exceptional use of the term.

Soil is that portion of the uppermost layer of the earth's surface which is in a sufficient loose state or division to be suitable for the growth of plants. It consists of the finer mineral particles produced by the action of the weather on rocks together with decayed animal and vegetable matter, and is exceedingly varied in character. In Great Britain the soil forms a layer a few inches to more than a foot thick, and below it lies the rock with an intermediate material—the subsoil—between them. There is frequently a strong resemblance between a soil and the rocks on which it lies, but great differences between the soil and the rocks below it exist so frequently that it is impossible to lay down any definite rule for their comparison.

Most soils are derived from the adjacent subsoil, but in some places they have been washed down from higher ground and may then be quite different from the underlying strata.

The action of the various natural agencies at work in the disintegration and weathering of rocks has already been described (Chap. II.).

Soils are termed "sedentary" when they have been formed by the simple disintegration of the rocks on which they rest, and "transported" when they have been carried to other places by water, ice, or wind.

Soils are divided into four chief groups according to their chief constituent:—

Chief Constituent.	Nature of Soil.
(a) Clay	Argillaceous.
(b) Sand	Arenaceous.
(c) Limestone or chalk	Calcareous or marly.
(d) Organic matter	Humic or peaty.

There are also many soils of intermediate composition, the

names of which are usually adopted from Schuebler's classification as follows:—

1. Argillaceous, above 50 per cent. clay; under 5 per cent. carbonate of lime.

2. Loamy, 30 to 50 per cent. clay; under 5 per cent. carbonate of lime; 20 to 60 per cent. sand.

3. Sandy loams, 20 to 30 per cent. clay; under 5 per cent. carbonate of lime; 60 to 70 per cent. sand.

4. Loamy sands, 10 to 20 per cent. clay; under 5 per cent. carbonate of lime; 80 to 90 per cent. sand.

5. Sandy, under 10 per cent. clay; under 5 per cent. carbonate of lime; over 80 per cent. sand.

6. Marly, 10 to 50 per cent. clay; 5 to 20 per cent. carbonate of lime.

7. Calcareous, above 20 per cent. carbonate of lime.

8. Humic, above 20 per cent. of humus.¹

It must, however, be understood that these figures are not to be taken too literally, and a comparison of the terms just mentioned with other definitions of them given in the present volume will indicate the wide variations permissible.

For agricultural purposes the size of the soil particles is more significant than their actual composition. The finer particles of soil regulate the water supply available for the plant, and profoundly influence the tillage operations; unless a sufficient proportion is present, the soil could not be cultivated, but is left as waste, agriculturally speaking, though it might be valuable for building purposes. On the other hand, too great a proportion of fine particles is detrimental, because it increases the difficulty of tillage. The coarser particles determine the openness and "lightness" of the soil. A number of crops have very special soil requirements, and are only found in any quantity on a particular type of soil. It is possible to define these types over a given area by means of mechanical analysis. At the same time, there is no simple solution to the question—What is the cause of the fertility of soil? There is no single cause; a number of factors, any one of which might at a given time become a limiting one, really determines the growth of particular plants. All that science can do as yet is to ascertain the existence of these factors one by one and bring them successively under control, but though it has been possible to increase production in various directions, experimental agriculturalists are not yet able to disentangle all the interacting forces whose resultant is represented by the crop.

¹ Humus is decayed vegetable matter of indeterminate composition, usually colloidal and somewhat acid.

Light soils are those which are porous, friable, and very open in texture, consisting chiefly of non-plastic materials, such as sand, chalk, limestone, or humus. They are also termed *dry* and *warm* soils, and *barley* and *turnip* soils.

Heavy soils are those which are stiff and impervious, sticky or plastic or close in texture, the labour of cultivation being consequently much greater. All heavy soils contain much clay. They retain moisture well, and are termed *wet* and *cold*, and *wheat* or *bean* soils.

It is important that soils should be able to absorb sufficient moisture from the air; clay and humic soils are best in this respect, and sandy soils are worst.

The ability of a soil to raise water from below by capillary attraction is also important. In this respect clay is the most powerful, humus second, and sand the least.

The presence of large stones on the surface affects the soil by preventing evaporation and radiation of heat. If they are removed the soil may become cooler, drier, and of less value.

The fertility of a soil determines whether it is *rich* or *poor*.

Some soils may be improved by adding other soils to them, as when marl, chalk, or quicklime is added to a heavy clay soil. Sometimes very lightly burned clay is mixed with the soil. This increases the amount of soluble matter (plant food) present, and by making the soil more porous it increases its absorptive power. Fully-burned clay (bricks, etc.) is useless for this purpose.

The productiveness of a soil depends chiefly, however, on the soluble salts present in it and upon the climate.

Stoneware clays when burned form an opaque impermeable (vitrified) ware, usually of a greyish, yellowish, or bluish shade. The chief characteristic is the impermeability of the ware. If stoneware is underfired so that it is not vitrified, it is simply terracotta or earthenware, according as it is plain or covered with a glaze. It is frequently necessary to mix a vitrifiable clay with a refractory one in order to obtain a satisfactory stoneware, but for coarse stoneware some natural clays may be used.

The chief requisite in a stoneware clay is that it shall not lose its shape when fired to a state of impermeability, the colour of the fired clay being of secondary importance. Hence for the best stoneware it is usually necessary to produce an artificial stoneware body from a mixture of various clays and fluxes. If the proportion of very fine clay in the material is too large, sufficient vitrification may be accompanied by so much shrinkage as to be unsatisfactory.

In making clay mixtures for stoneware it is necessary to remember that a fusible clay mixed with coarse grog will produce

a brittle ware which is liable to crack in the kiln. The grog should be fine enough to pass completely through a No. 75 sieve, but should leave a considerable residue on a No. 200 sieve. Quartz, sand, or flint are less suitable than grog, as they expand on heating. The composition and preparation of such bodies is, however, beyond the scope of the present work, but see *Vitrifiable Clays*.

The best stoneware clays are the upper ball clays of Dorset and South Devonshire, and some of the Coal Measure Clays of Buckley and Ewloe, near Chester.

Strong clays are usually free from stones and sand, and are highly plastic or sticky. Bricks made from them usually warp and crack in the drying and burning, owing to the large contraction such clays undergo. It is therefore advisable to mix them with mild clay, sand, flint, chalk, vegetable mould, crushed stone, ashes, or even with burnt ballast, so as to reduce the shrinkage, whilst still leaving the mass sufficiently plastic to be worked easily. The choice of this added material depends largely on what is available, as it is seldom found near to the clay. Attempts are frequently made to use strong clays without admixture with non-plastic materials, but these must usually end in failure, as the effect of heat on highly plastic clays with heavy shrinkage inevitably tends to make them warp and crack. With the addition of suitable material, on the other hand, such clays form a valuable material for almost all the requirements of the clayworking industry, as they are then converted into lean clays, or, if sand be the material added, into loams. Unless some suitable sandy material can be readily obtained, strong clays should be avoided.

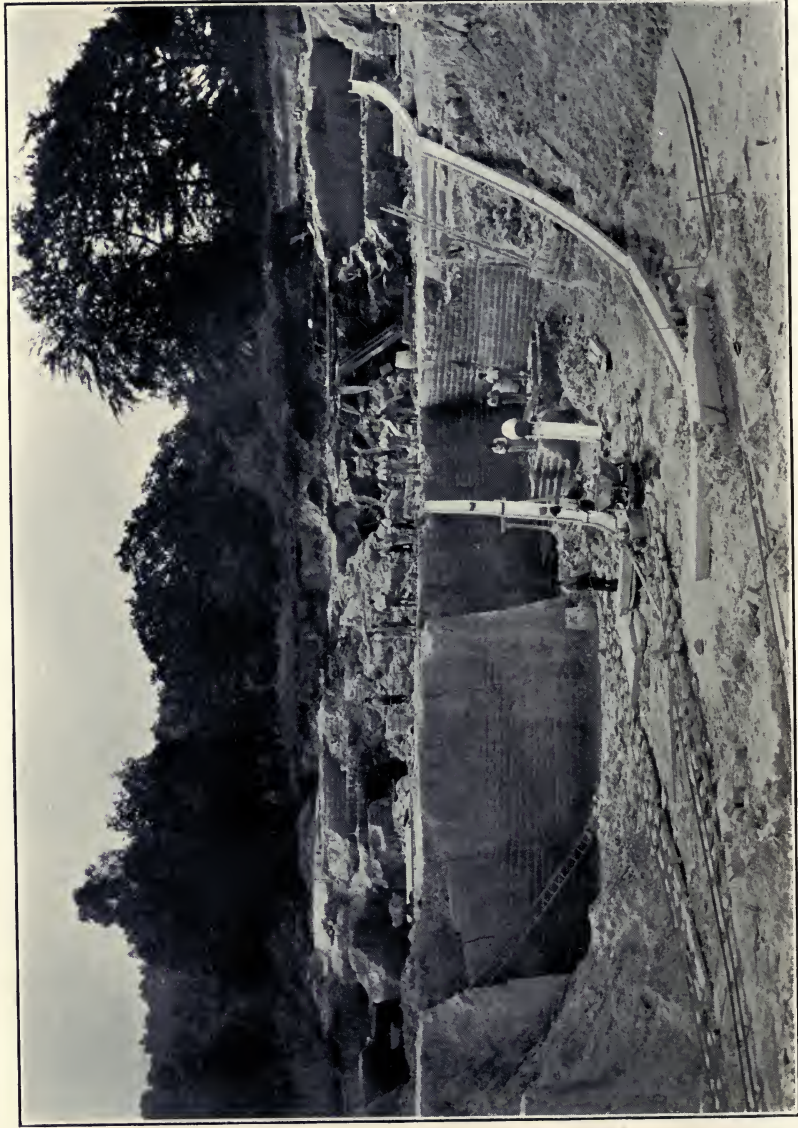
Subsoil is, strictly speaking, the geological formation below the soil, but the term is used loosely (see *Soil*).

Surface clays are those which are found on the surface of the land or immediately below the soil. They are usually strong and plastic, but vary greatly in their composition (see *Soil*).

Where the material extends to a considerable depth it is preferably termed a subsoil or "solid bed" clay; the term surface clay being confined to clays found above the solid beds. Boulder clay and the brick earths of the south of England are typical surface clays.

The ordinary British brickmaker means a red-burning clay (p. 219) when he speaks of a surface clay, but this limitation is by no means correct, as many buff-burning clays and shales are also found as outcrops on the surface.

The sandy, red surface clays burn usually to a good red colour, varying from salmon to a dark Indian red, according to intensity



Cutting Stoneware Clays, Decoy Quarry, Newton Abbot.

of burning. Bricks of red earth become black if more strongly heated, and shrink considerably from partial vitrification.

Surface clays are the most convenient to quarry, and so are much sought after; but as any kind of clay may be found on the surface, such deposits must always be examined carefully before their value can be ascertained. Thus a white clay may be a ball clay or a kaolin of great purity, refractoriness, and value, or it may be a pipeclay and worth comparatively little.

The fact that a clay occurs on or near the surface is therefore chiefly of interest as regards the cost of obtaining it, and gives little or no indication of its nature.

Owing to the adventitious action of wind and water, true surface clays are often very impure, and are frequently very shallow. It is seldom profitable to work a deposit which is less than 3 feet deep, unless it is of unusual value.

A mixture of clay and other materials on the surface of the ground which cannot be used by the clayworker is known according to the locality as **overburden** or **calow**. This must usually be removed before any excavations for useful clay can be carried out.

Teignmouth clay is a ball clay obtained from Bovey Tracey in Devonshire (p. 131). It owes its name to the port of shipment.

Tender clays are those which require specially careful treatment, particularly during drying. The "strongest" clays are, curiously enough, the most "tender" and require the slowest drying, as their close texture and heavy shrinkage sets up internal strains and causes them to crack.

Bleining has found that the tenderness of many clays may be removed by heating them in rotary kilns to about 250° C. This heating reduces the plasticity without destroying it, and makes the clays sufficiently porous for them to be ground without inconvenience.

Tender clays may also be improved by the addition of sand or any suitable non-plastic material, and by pugging with hot water instead of cold.

When, for commercial or other reasons, tender clays cannot be treated by any of the methods just mentioned, the drying must be carried out in closed chambers and with extreme slowness, and is a tedious and often costly process, so that unless the tenderness of a clay can be destroyed such clay is not adapted to profitable manufacture.

Terra-cotta clay is a variety of red-burning clay, with a very fine texture and surface, but modern clayworkers use the term "terra-cotta" for all large unglazed objects made of clay without

much regard to their colour. The use of the term in this wider sense may be justified by the literal meaning of *terra-cotta*, baked earth.

Terra-cotta is largely used in buildings for decorative purposes, as it is practically indestructible by weather so long as it retains its natural surface. It can be used in large blocks, and is capable of reproducing the finest carving.

In addition to possessing a fine texture, *terra-cotta* clays must be sufficiently plastic to enable the workman to carry out the required modelling, of good binding-power, and must burn to a uniform colour throughout. They should be somewhat porous when burned, so that large pieces of ware may be made from them. A pleasing colour when burned is essential, and the best qualities have a thin natural glaze when fired, due to slight vitrification on the surface. The best *terra-cotta* clays have been deposited at a great distance from their original sources, from bodies of water having a slow but uniform current. As such clays are scarce, most manufacturers of *terra-cotta* ware use mixtures of various clays, so as to give the required colour and other characteristics. The better grades of fireclay are used for "buff" *terra-cotta*, but they are quite different in texture from the true red-burning *terra-cotta* clays of Tamworth, Ruabon, and elsewhere (see *Red-burning Clays*, p. 219). They require to be carefully dried and burned so as to avoid twisting and warping or discoloration, as large designs are frequently made up from a number of pieces fitted together, and *terra-cotta* cannot be chipped to shape without seriously reducing its durability.

Till clay is a term used as synonymous with "Glacial Drift," but, strictly, it is the most plastic constituent of the lower "boulder clay" (see pp. 140 and 192).

Transported clays (see *Sedimentary Clays*, p. 227 ; *Soil*, p. 237).

Ultramarine clays are extremely fine china clays. The material used in the manufacture of ultramarine must be specially selected so that only the most minute particles are present. These are required to act as a nucleus for the colouring material. A somewhat coarser grade of china clay is often used as a diluent. The clay used must be perfectly white, as any yellowish tinge diminishes the value of the ultramarine.

Underclays are those which lie immediately beneath an important seam of mineral. In Great Britain the term is confined to the clays beneath the Coal Measures (p. 52), so that underclays may be regarded as one of the chief sources of fireclays (p. 171). It is, however, erroneous to term all underclays "fireclays" as do some geologists, for whilst it is true that some of the most

important fireclays are underclays, only a comparatively small proportion of the whole mass of underclays are refractory enough to be termed "fireclays."

Underclays derive their name from the fact that they occur beneath practically every coal seam, though in some areas they are found apart from any association with coal, and occasionally the coal is beneath instead of above them. They differ from the shales in being unlamated.

Underclays consist mainly of clay, but some of them contain so large a proportion of free silica as to be more accurately termed clayey sandstones, so that out of the enormous quantity of such clays in existence only a small proportion is actually used.

Some underclays are so impure as to be quite worthless, others are only fit for making common bricks; others are well suited for the manufacture of salt-glazed goods of a coarse type, such as drain-pipes, and a few are highly refractory fireclays. The underclays of Denbigh and Flintshire (particularly near Ewloe and Buckley) are specially valuable for the manufacture of acid-resisting ware used in the production of strong acids and other chemicals (see *Stoneware*).

Experience shows that by careful and skilled selection refractory clays may be found in every coalfield in the United Kingdom, but the cost of obtaining them and the small quantities available in some areas are so great that the underclays are only worked extensively in a few districts, such as those mentioned under *Fireclays* (p. 171).

Vitrifiable clays are those in which some of the constituents melt at a relatively low temperature and fill the pores of the clay during the firing to such an extent that a tough, impervious mass is produced containing sufficient refractory or unfused material to prevent the goods from losing their shape. All clays will vitrify if heated sufficiently, but the term vitrifiable clay is best confined to those which become impervious under commercial conditions, *i.e.* at temperatures under 1400° C., and without loss of shape. They contain a higher proportion of fluxes than refractory clays, the chief being lime, magnesia, and alkalis. These last are undesirable and should not exceed 5 per cent., as they tend to diminish the difference between the vitrifying point and the temperature at which loss of shape occurs. Really good vitrifiable clays are rare, and most manufacturers requiring them have to add lime or other flux. Lime in excess is very injurious, as it changes to caustic lime in burning, and afterwards moisture will cause it to slake and the articles to disintegrate. Lime compounds also resemble the alkalis in effecting loss of shape very soon after

vitrication has started. A small amount of magnesia, on the other hand, aids in producing vitrication without loss of shape, while alumina gives elasticity and renders the material hard and tough.

Analysis alone will not show reliably whether a clay will prove satisfactory for vitrified ware or not, though it will give valuable information. According to Kerl, clays containing 68 to 70 per cent. of silica, 22 to 24 per cent. of alumina, and 6 to 8 per cent. of lime and alkalies, make the best vitrifiable clays.

In order to prevent the ware from losing its shape as soon as vitrication sets in, the clay must contain so much refractory material that the temperature of vitrication (*i.e.* at which the pores begin to fill with molten matter) and that at which the whole mass begins to soften and "squat," are about 300° C. apart.

When a flux is to be added to make a clay more vitrifiable, magnesia is excellent, because it permits a wide range of temperature between the commencement of vitrication and loss of shape. With limestone and chalk the range is much shorter, and with alkalies it is too short to be recognizable.

This "range of vitrication" can be increased by substituting coarser materials (particularly silica), but this may necessitate an alteration of the firing temperature, and it also creates other difficulties.

The preparation of special mixtures of clays which shall possess all the advantages of the best stoneware clays (p. 239) is a matter requiring much skill. These mixtures are too costly for most purposes for which vitrifiable clays are used, and natural clays are therefore used, with such little admixture as may be necessary. These natural stoneware clays are usually ball clays for the fine class of stoneware, but for coarser ware some of the Coal Measure clays are used. Artificial stoneware clays are best composed of a very vitrifiable clay (such as a marl), to which a fireclay is added until the necessary stability in the kilns is obtained. The addition of chemical fluxes, such as whiting, to refractory clays is seldom satisfactory. Seger found that the use of china clay or highly aluminous fireclay is unsatisfactory, and considered ball clay or other plastic clay to be essential. The best known beds of vitrifiable clays in Great Britain are:—near Newton Abbot, Wareham, Newcastle-on-Tyne, Longport (Staffs), South Yorkshire, Derbyshire, Ewloe, Buckley, and in the chief coalfields, particularly in the Midlands. They all depend upon the presence of lime and alkalies, though the iron oxide present in some cases also acts as a slight flux. Their colour is generally bluish, inclining to violet or grey: and on firing they give a body of which the

tint varies from a bluish-white to a deep pearly grey, or from yellowish-white to brown. They are much used in the manufacture of stoneware and chemical ware, and the coarser varieties are used for buff paving bricks. What are known as vitrifiable ferruginous clays can also be employed for the manufacture of sanitary stoneware, but are chiefly used for the making of paving tiles and vitrified bricks. They are of a yellow, red, or brown colour, and produce a fired body of which the tint varies from reddish-brown to black. Of these, the buff-burning clinker brick clays of the Midlands and the famous blue-brick clay of Staffordshire are among the best known species. With such an abundant supply of suitable materials there is no necessity for British clay-workers to adopt the Continental methods of preparing special mixtures for the manufacture of paving bricks, floor tiles, and similar articles of vitrifiable clay.

Warp clay is a laminated clay with sand, worked for bricks and tiles near York. It requires special care in drying and burning, in spite of its loamy nature.

The term is applied locally in several parts of Yorkshire to fine silts and alluvial clay, and is also used for a laminated clay occurring in thin seams just beneath the boulder clay.

The most characteristic deposit of warp is in the form of a fine sediment or silt in the tidal waters of the Humber and its tributaries. It is of a light chocolate colour, and is very soft and silky to the touch. Apparently it is composed of the disintegrated boulder clay brought by the sea from Holderness, and carried up the river by the flowing tide. It is quite different from the fluvial deposits of the rivers feeding the Humber, and is richer in clay and mica.

It has been suggested that the land west of the present mouth of the river Hull is a dried-up delta formed largely of warp.

Yellow clays are usually strong, surface clays, but the colour before burning gives little or no indication of their nature. They are seldom of much value, on account of their shrinkage, unless sand is available (p. 254). Clays which are yellow ("buff") after burning are much used. If refractory, they are described under *Fireclays* (p. 171); if vitrifiable, under *Vitrifiable Clays* (p. 243) and *Stoneware Clays* (p. 239). Other yellow-burning clays are made into bricks and terra-cotta, and have the usual characteristics of clays used for these purposes.

CHAPTER VII.

MATERIALS SIMILAR TO CLAY.

THE essential constituent of some clays appears to be one or more alumino-silicates similar to, but not identical with, kaolinite or with the amorphous material of the same ultimate composition found in china and ball clays. These materials possess some plasticity, which they lose when heated, and they behave in many respects in exactly the same manner as certain clays.

Some chemists and geologists incline to the belief that these substances, which are analogous to clays, are really distinct minerals, but there are excellent reasons for supposing that some of them are not independent silicates but consist of true clay mixed with hydrated silica and alumina. Le Chatelier, who has investigated this subject very fully, found that when relatively pure clays are heated they suffer a drop in temperature at the moment they give up certain proportions of their "combined water." From careful measurement he concluded that this was due to the presence of definite minerals in the clay, and he accordingly divided clays into five groups: (1) Halloysite; (2) Allophane; (3) Kaolin; (4) Pyrophyllite; and (5) Montmorillonite.

It should be understood that these minerals are only present in small quantities in most clays and that Le Chatelier's observations merely indicate the manner in which the water is given off and not the presence of important quantities of the minerals named. Unfortunately the difficulties in the way of investigating precisely the structure of these substances are very great, and the matter is therefore of scientific rather than of immediate practical interest. The subject has, however, an important bearing on the behaviour of clays from different sources. Some information on the constitution of the kaolin molecule is given on p. 154.

The following are the most important of the substances analogous to clay:—

Halloysite is said to occur in Glenboig fireclay, in much smaller quantities in other fireclays and china clays, and to a limited extent as a natural earth, though seldom, if at all, in Great Britain. Its composition is very variable, but usually contains 39 to 45 per cent. silica, 20 to 40 per cent. alumina, and 10 to 26 per cent. water. When heated at 150° C. a variable proportion (3 to 12 per cent.) of water evaporates, and, according to Zirkel, at 250° C. kaolinite is formed, but Mellor states that free alumina, silica, and water are produced. The crystals are soft, somewhat soapy in appearance, generally opaque but transparent at the edges, and become more transparent when in water. Their colour varies from bluish-white to green or gray. According to Ries, halloysite is never crystalline, the crystalline form being **Pholerite**. It is often associated with zinc silicate in Derbyshire limestone, in well-developed crystals of the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, but it is most frequently found as rough nodules with a conchoidal fracture, harder than talc but softer than gypsum, and with a specific gravity of 1.9 to 2.1. It is moderately plastic. Fuller's earth may be an impure variety. **Lenzenite** is a similar substance.

Collyrite is found in rather hard nodules, which are very brittle and have a specific gravity of 2.1. The freshly broken surface is as soft as talc. The powdered material is dirty white with a dull surface, and is slightly unctuous and plastic. In water the particles become transparent and dissolve completely in hydrochloric acid. According to Le Chatelier the composition corresponds to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 9\text{H}_2\text{O}$, but Zirkel gives twice as much alumina, viz. 48 per cent.

Allophane in many respects resembles collyrite, but is harder and usually blue or bluish-green in colour, owing to the presence of copper and, occasionally, of iron. It has a conchoidal fracture; is brittle, pellucid, and vitreous. Its composition corresponds to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$.

Kaolinite—presumed to be a crystalline form of kaolin—has been described on p. 196.

Nacrite is a white, finely flaked and rather dense aggregate, with a slight pearly sheen. It is of the same composition as kaolin, but is decomposed by hydrochloric acid. According to Des Cloizeaux, it sometimes crystallizes in the rhombic system.

Steinmark or **Lithomarge** is sometimes regarded as "a variety of china clay." It is a white or cream-coloured material, somewhat dense and coherent, but not very plastic, which is converted by hydrochloric acid into a white glistening mass. According to Wöhler it is really composed of minute rhombic plates. Its composition appears to vary greatly, but this may be due to miners

termining any white material which bears a close resemblance to china clay, lithomarge or steinmark. An average composition for this material appears to be 47 per cent. of silica, 39 per cent. of alumina, and 14 per cent. of water, but Bischof has found some samples with as high a proportion of alumina as 41.48 per cent., and classes it with the bauxites rather than with the clays. Its unctuous feel, slight though distinct plasticity, and its general physical nature, suggest, however, that it is closely allied to clays.

Its origin is uncertain, though the best specimens are found in association with the Bunter sandstones, particularly in Germany. It is, however, impossible to allocate it to any single geological period. Indeed, the term lithomarge is applied to so wide a range of materials that it is almost as indefinite in meaning as the geological terms "pipeclay" or "fuller's earth."

Myelite is regarded as a white, conchoidal variety of lithomarge, and *Carnalite* as a pink and more compact form. *Tuesite* is a bluish variety found at the mouth of the Tweed.

Argillite is not strictly a mineral, but is a term sometimes used for argillaceous schists or clay slates (*q.v.*).

Hydrargillite and **Laterite** possess many properties of clays, but are deficient in silica as compared with ball and china clays. They are believed to contain a considerable proportion of free alumina and occur chiefly in tropical regions, but have been found in temperate climates and in all but the earliest geological formations (see *Laterite Clays*, p. 198).

Nontronite ($\text{Fe}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) corresponds to kaolinite in which the alumina has been replaced by iron oxide. It occurs in minute monoclinic plates, resembling kaolinite in appearance, and is characteristically "fat" to the touch. It is usually found in compact nodules, which often appear to have been split after formation. Its colour is yellow to pale green. On heating to dull redness it is decomposed into ferric oxide, silica, and water. Its chief interest lies in its many close analogies to kaolinite and the light it throws on the constitution of the latter.

Pyrophyllite forms radiating groups of rhombic crystals, corresponding to $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

Montmorillonite corresponds to the formula $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. It is a soft, coherent material, usually of a pinkish tinge, and non-plastic.

Nepheline occurs in the more recent lavas, is glassy or granular, and is only found in this country in a decomposed form, though on the Continent it forms an important source of brick earths in many localities. It contains silica 44 per cent., alumina 33 per cent., soda 15 per cent., potash 8 per cent.; but its com-

position is not yet settled. It forms hexagonal crystals which react alkaline and are soluble in hydrochloric acid, but on heating the solution silica is precipitated. It is as hard as felspar, has a specific gravity of 2.6, and is usually white, though occasionally tinted green or brown. (See p. 18.)

Cancrinite, closely allied with nepheline, crystallizes in the hexagonal system. It is composed of 39 per cent. of silica, 29 per cent. alumina, 40 per cent. lime, 18 per cent. soda, 4 per cent. water, and 6 per cent. carbon dioxide. It fuses readily, effervesces with hydrochloric acid, and forms a jelly on heating. It is chiefly found in connection with igneous rocks containing nepheline, soda, and felspar.

Andalusite ($\text{Al}_2\text{O}_3\text{SiO}_2$) forms colourless or pale brown rhombic crystals and radiating masses, which are usually opaque. It is exceptionally resistant, and is scarcely attacked even by hydrofluoric acid. It is widely distributed in igneous rocks and clays, but is chiefly of interest as one of the products formed when clays are heated to partial fusion and then cooled very slowly, particularly in the presence of fluxes, as is the case with some porcelains; but, according to Vernadsky, it is converted into sillimanite at 1350°C .

Sillimanite ($\text{Al}_2\text{O}_3\text{SiO}_2$) forms characteristic rhombic crystals which are usually massed together into a network of thin needles. Being but slightly attacked by hydrofluoric acid, it may, to some extent, be separated by dissolving out the other constituents of a clay with this acid. Like andalusite, with which it is isometric, it is sometimes formed where clays are heated to partial fusion, but the size of the crystals produced in this manner is seldom sufficiently large to admit of complete identification.

Kyanite or **Disthene** has the same composition as sillimanite, and is, according to Vernadsky, converted into the latter at 1350°C . The crystals of kyanite are, however, triclinic instead of rhombic, though those occurring in clay—either naturally or produced by heating in the presence of a flux—are usually too small to distinguish their shape accurately. Larger crystals of kyanite are pale blue in colour, but small ones appear to be colourless.

Steatite or **Talc** is sometimes used in the manufacture of tips for gas-burners and for other refractory articles under the name of "soapy clay." It is not really a clay, but a hydrated magnesian silicate, which is only slightly plastic; when mixed with sufficient clay to give it sufficient plasticity it forms a valuable refractory material.

Sericite is closely related to mica, and is sometimes regarded

as an aggregated form of muscovite. When present in small quantities it may easily be mistaken for kaolin, which it greatly resembles in appearance, though the presence in it of about 11 per cent. of alkali should enable the confusion to be avoided.

Zeolites (p. 155) may be regarded as the salts of the aluminosilicic acids and, in a sense, as salts of some "clays." There are a large number of zeolites, some of which bear no distinctive names, and many others are of small importance. *Natrolite* ($\text{Na}_2\text{OAl}_2\text{O}_3\cdot 3\text{SiO}_2$), *Analcime* ($\text{NaAlSi}_2\text{O}_6 + \text{H}_2\text{O}$), and *Chabasite* ($\text{CaNa}_2\text{Al}_2\text{Si}_4\text{O}_{12} + 6\text{H}_2\text{O}$), with an alumina-silica ratio varying, according to Zirkel, between 1 : 3 and 1 : 5, are among the best known.

Many of the zeolites crystallize readily on cooling their aqueous solutions, or they may be prepared by "mixing the contained acids and bases in the proper proportions with water and cooling the boiled mixture." Zeolites, on account of their closely analogous composition and the ease with which they can be prepared, have been studied to a large extent with a view to elucidating the constitution of the clay molecule, without, at present, any very definite result.

CHAPTER VIII.

MINERAL AND OTHER CONSTITUENTS OF CLAYS.

IMPURITIES IN CLAYS.

ASSUMING that "pure clay" is composed of alumina, silica, and water in the proportions in which these occur in kaolinite or in the purest china clays,¹ viz. silica 46·51 per cent., alumina 39·54 per cent., water 13·95 per cent., an excess of any one or more of these ingredients and of any other materials present may be regarded as "impurities," though these may be necessary for the production of certain goods or in order that the "clay" may have certain properties. Thus iron oxide is an essential constituent of red-burning clays, and felspar or other fluxes are equally necessary in clays which it is desired to vitrify. Nevertheless, this assumption is convenient in so many ways, since the errors involved in employing it may usually be neglected, and all "clays" may, for most purposes, be regarded as composed of a hypothetical "true clay" and "impurities."

In this sense the chief "impurities" in clays are silica and alumina compounds other than "clay"; iron compounds; lime, magnesia, soda and potash (usually termed "alkalies"), and compounds of all these oxides, water, carbonaceous matter, and various minerals which may be conveniently classified together without regard to their composition.

¹ This is not the same as stating that "kaolinite is the basis of all clays and that they are therefore to be regarded as a mixture of kaolinite with other minerals," for kaolinite is found in quantities far too small to justify so sweeping an assertion. All British clays when subjected to a mechanical analysis show, in the finest particles so separated, a composition corresponding to a mixture of minerals having the common formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, with free silica and mica, felspar, and variable proportions of other substances.

That the assumption made in the text has several objections is fully recognized, but as a working hypothesis it is the most convenient which has yet been published.

Silica (SiO_2) may be present in an uncombined state or as a constituent of one or more other minerals (silicates). The former is usually understood to include *hydrated silica*—a compound of silica and water which is very different in its behaviour to sand or quartz, and is often termed silicic acid on account of the manner in which it reacts with bases to form neutral silicates. The presence of hydrated silica in certain clays is not absolutely proved; it is usually found in very small proportions, has little or no influence on the plasticity, and decomposes to form amorphous silica at a temperature just above 100°C .

Silica occurs in what are termed “soluble” and “insoluble” forms, the first readily combining with caustic alkali or lime in aqueous solution, but the so-called “insoluble” form is attacked by these solutions if it is in a sufficiently finely powdered condition. Extremely finely divided silica will react with boiling water forming colloidal silicic acid (hydrated silica); a large proportion of colloidal silica reduces the refractoriness of a highly refractory clay and increases the shrinkage on drying of all clays which contain it.

The soluble form of silica is made insoluble on heating to 105°C ., at which temperature it is coagulated.

For the effect of silica on clay, see p. 255.

The most frequently occurring form of uncombined silica is **quartz**, which, with a certain amount of siliceous material, forms the sandy portion of many clays. It may be removed to a large extent by exposing the powdered clay to a very slow stream of water, or by stirring the material up with water and pouring off the supernatant liquid after it has been allowed to stand for a couple of minutes. Neither of these methods effect a complete separation of the silica, as the finest particles of it are carried away with the clay, as may be shown by an analysis.

Pure quartz has a hardness of 7 on Mohs' scale, and a specific gravity of 2.653. It melts at 1600°C ., but is so viscous at that temperature that its fusing point cannot be ascertained accurately.

When pure, quartz grains resemble small irregular fragments of glass; the edges are sometimes rounded by attrition. The fragments may be clear, but are often cloudy or even opaque on account of the impurities they contain. These grains are quite devoid of plasticity and act as a diluent of the clay, reducing its shrinkage on drying and heating, and making it “short” or “lean.” They are irregular in shape, but are frequently rounded on account of the trituration they have undergone since the time when they formed a part of the huge rocks from which they were originally derived, and from which they have been separated by the action of the weather and other natural forces.

In colour, quartz varies from the colourlessness of pure crystal to yellow, brown, purple, or even black.

Tridymite is another form of silica, with a sp. gr. of 2·318. It is produced when quartz is heated to above 800° C. It slowly changes back again into quartz.

Glassy silica has a still lower sp. gr. (2·215), and is formed when molten silica is cooled under conditions not favourable to crystallization.

Chalcedony is an apparently amorphous form of silica, but it really consists of a mass of minute crystals. Its colour depends on the impurities present when the silica was in a state of solution. Chalcedony is chiefly found as a magma or cement filling up hollows or interstices in other minerals.

Flint is another form of free silica which has been formed around an animal or vegetable nucleus. It seldom contains more than 95 per cent. of silica and, though somewhat rich in lime, is highly refractory. Flints may readily be recognized by their shape and conchoidal fracture. Owing to their excessive hardness they are preferably removed from clays in which they occur, the silica which they would supply being replaced, if necessary, by flints which have been heated to redness, quenched in water and ground separately, or by sand.

Quartzite is a sandstone rock composed of free silica which has apparently been derived from quartz or from the decomposition of complex silicates, but has lost some of its characteristics during the treatment it has undergone. It is usually amorphous (though some of the quartz grains may be fragments of crystals), or the whole mass be composed of such minute crystals as to appear amorphous. The quartz of which it is composed is usually somewhat impure, and is often coloured red or yellow by its impurities. Owing to the many varieties of rocks from which quartzite may be derived, its chemical composition and physical characters vary considerably. In the proportions in which it ordinarily occurs in clays, these variations are relatively unimportant, but where a highly siliceous material is used (as the so-called "clay" of Dinas, which is exclusively composed of quartzite and is almost free from true clay) its origin is important. For making refractory bricks a quartzite containing sufficient flux to cement the particles without reducing their fusing point too seriously should be used, care being taken to employ a material in which the grains interlock to a considerable extent.

Quartzite is characterized by the close fitting of the quartz grains without the presence of any apparent cementing medium, though such a material is sometimes present.

The chief colouring agent of quartzite is iron oxide or the corresponding minerals, such as limonite.

As quartz is converted into tridymite on heating above 800° C. and this change is accompanied by an increase in volume of about 20 per cent., it is important that articles made of highly siliceous materials should be burned for a sufficiently long time at a suitable temperature in order that the conversion into tridymite may be as complete as possible.

Sandstones and **grits** composed of grains of sand, consolidated by pressure and by interstitial cement, occur in large deposits and form important building materials.¹ They occur in varying proportions in clays, and may usually be regarded as sands.

Sandstones consist for the most part of grains of quartz (silica), cemented together by silica, carbonate of lime (chalk), carbonate of magnesia, and oxide of iron, in varying proportions, or by combinations of these substances. They vary in texture, colour, and durability to a very great degree, the nature of the cementing material being the chief element of strength or weakness.

Grits are composed of coarser and more angular grains than are sandstones, but are, otherwise, identical. (See also *Quartzite*, p. 48.)

Sand is a term used to indicate small grains of silica in the form of quartz or quartzite, or of other minerals of a highly siliceous character. It is valued according to the percentage of silica it contains, very small amounts of other ingredients greatly reducing its worth for glass-making and other manufacturing purposes. Sand is derived from a large variety of rocks, and may, in a broad sense, be regarded as naturally occurring powdered rock, of indefinite composition, produced by the action of weather, rivers, seas, etc. This term may thus be used to include numerous minerals in clay and other deposits, whose chief characteristics are their granular form, their hardness, and freedom from plasticity. These particles vary very greatly in size; when larger than one-twentieth of an inch in diameter they are usually termed **gravel** or small stones; if less than $\frac{1}{1000}$ inch in diameter, they are termed **silt**, though in some cases the minimum size of sand grains is taken as $\frac{1}{200}$ inch, anything smaller than this being termed **dust**.

Sand in Clays.—The proportion of extraneous silica (whether as quartz, quartzite, flint, sand, or as a constituent of another mineral) in clays is important, yet it varies enormously. The purer china clays are almost free from it, but some "clays" used for brickmaking contain as much as 95 per cent.

¹ For further information on the use of these materials for building purposes, the reader should consult J. A. Howe's *Geology of Building Stones*.

In studying the reports of the analysis of a clay the fact must not be overlooked that true clay contains rather more silica than alumina, and that in endeavouring to estimate the proximate composition of a given sample a deduction must be made from the "total silica" in the report, to account for that combined with the alumina and alkalies present. Thus a fireclay containing 25 per cent. of alumina and 65 per cent. of silica will probably not contain more than 30 per cent. of uncombined silica.

The effects of this uncombined silica on the chemical and physical characteristics of clays containing it are more fully described on p. 349.

Briefly, the chief effect of adding free silica to a plastic clay is to reduce its plasticity, shrinkage, tendency to warp and crack, the amount of water required to make it plastic and the tensile and crushing strength, and to increase its porosity after firing. If the clay is very impure, the addition of free silica may also increase its refractoriness, but the opposite effect is produced with a clay relatively free from fluxes, though the ability of the latter clay to withstand sudden changes in temperature may be increased. When much silica is present the amount of water required to convert the clay into a good modelling paste is reduced, and the drying of articles made from it is greatly facilitated. Silica is largely used for the prevention or reduction of shrinkage, and is added in the form of sand or crushed rock to bricks, tiles, and coarse pottery, and as ground flint to white ware.

The addition of silica to a clay will raise the fusing-point of a clay if the latter is rich in fluxes (lime, magnesia, and alkalies), but it may have no influence on, or may even spoil, a refractory clay.

In all its forms pure silica is a highly refractory material, being almost as infusible as the best fireclays when heated alone. If it contains lime or other bases, however, it melts much more easily. Thus felspathic and micaceous sands introduce alkalies (which act as fluxes) as well as silica. Grains of felspar are to be preferred to lamellar spangles of mica.

Some sands are composed of the siliceous remains of diatoms and other living creatures. These may be easily recognized under the microscope. They are described on p. 194, under *Infusorial Earths*.

Natural sands are distinguished by the size of their particles, their shape and colour; thus there are fine, medium, and coarse sands; silver, white, yellow, brown, grey, and black sands. The sizes and shapes of the grains have usually a pronounced effect on the characteristics of the clay containing sand. The colour is seldom a reliable index of the purity of a sand, though it may

give some indication of the amount of iron present as limonite, etc. For clayworking, however, the composition of the minerals composing the sand is often important, as some of these minerals may fuse easily, or may react with the clay and produce very noticeable results when the mixture is burned.

Sorby has classified sands into five groups which are convenient, but have no very clearly defined limits:—

1. Normal, angular, fresh-formed sand, such as has been derived almost directly from the breaking up of granitic or schistose rocks.

2. Well-worn sand in rounded grains, the original angles being completely lost, and the surfaces looking like fine ground-glass.

3. Sand mechanically broken into sharp angular chips, showing a glassy fracture.

4. Sand having the grains chemically corroded, so as to produce a peculiar texture of the surface, differing from that of worn grains or crystals.

5. Sand in which the grains have a perfectly crystalline outline, in some cases undoubtedly due to the deposition of quartz upon rounded or angular nuclei of ordinary sand.

A sand almost entirely composed of quartz grains is generally the most valuable except where a coloured one is needed, and large quantities containing as much as much as 98 per cent. of silica and less than 2 per cent. of impurities can be obtained without difficulty.

Glass-making sands occur in the Lower Greensand formation at Reigate, Godstone, Aylesford, Berstead, Hartwell, Headon Hill, Leighton Buzzard, King's Lynn, and Ballycastle (Antrim). They should not contain less than $98\frac{1}{2}$ per cent. of silica, and little or no iron compounds.

Less pure sands are found in many places, but are of relatively small commercial value, with the exception of the following:—

Brick-facing or brick-moulding sand is used to produce a good colour on the articles. For this purpose the best sand is the finest-grained portion of the Bagshot beds (p. 84) if a red-burning sand is desired, but for white bricks a purer estuarine sand is preferred. This is sometimes termed **shore sand**, but must not be confused with sand obtained from the sea coast (see *Sea Sand*).

A sand corresponding to No. 4 in Sorby's list (above) is usually the best for mixing with clay, as it possesses certain binding properties, but the usual type of sand met with in brickyards corresponds to Nos. 1 or 2. For facing bricks, on the contrary, a sharp sand is undesirable.

Moulding sand for foundry use is usually obtained from the red

Bunter formation or from the Thanet beds, the latter (p. 103) being considered superior to the former (p. 61). If such sands contain free alkalies or alkaline carbonates, they should be treated with dilute sulphuric acid. In some cases the sand is neutral, but the water mixed with it contains dissolved carbonates, which spoil the sand unless it has been previously treated with acid.

Building sand should be a highly quartzose sand, with sharp, angular grains, and should entirely pass through a No. 30 but be retained on a No. 60 sieve. Loam or clay, if present, is harmful, and should be washed out with running water, preferably in a suitable washing plant.

Sand for Concrete is chiefly of four kinds: (a) pit sand (other than that of glacial origin); (b) river sand; (c) sea sand; (d) grit or sand made by crushing coarser material. According to the Test Committee of the Concrete Institute, it is important all sand that is not retained on an aperture of one-fiftieth by one-fiftieth inch should be rejected so far as the manufacture of concrete is concerned, as the fine dust-sand seriously weakens the resultant concrete.

The *British Standard Sand* for use in testing Portland cement and hydraulic mortars is obtained from Leighton Buzzard, and consists of clean grains of quartz. It must pass completely through a sieve having twenty meshes per linear inch, and be retained on one having thirty meshes per linear inch, the diameters of the wires being 0.0164 and 0.0108 inch respectively. This agrees with the standard of the Tests Committee of the Concrete Institute in rejecting all dust. As comparatively small variations in the sizes of the sand particles exercise an important influence on the results of the tensile tests of cement and mortar, the use of a standard sand is imperative.

The following sands require to be mentioned, though largely on account of the "impurities" they contain.

Clayey or argillaceous sand must only be used when its clay content is not harmful (see *Building sand*). For mixing with clay for brick and tile-making it is an excellent "opening substance," and more plastic than quartz. Usually it is more readily mixed than is an entirely non-plastic material, but some clays behave curiously in this respect, and will not form a homogeneous mixture with others. At Windsor, Ewell, Epsom, and in Wales, Derbyshire, and other localities, clayey sands are used for making fire-bricks (see pp. 61 and 181).

Calcareous sands contain chalk, limestone, gypsum and other lime compounds in notable quantities, and can only be used in clayworking where the lime is in an extremely finely divided

state. The injurious action of large grains of limestone has already been noted (p. 200).

Calcareous sands are more fusible than others.

Sea sand is yellowish in colour, though at the junction of some rivers with the sea it may be almost pure white, as **Calais sand**. The less pure varieties contain much iron, sometimes a large proportion of fine chalk, and almost invariably some salt. The latter can seldom be completely removed by washing, so that sea sand is harmful to the clayworker and forms "scum."

Monazite sands and others bearing the names of special minerals are valued for their content of such minerals.

Silicates are compounds of silica with one or more bases or metallic oxides, the silica acting the part of an acid. Their constitution and properties form the subject of an increasingly important branch of chemistry, but is too large and complex to be discussed here. The majority of minerals included under the terms "clay," "shale," and "sand," with the exception of quartz, have at one time or another been considered as silicates, though recent investigations by Mellor and Holdcroft have indicated that the term "alumino-silicic acids" is more appropriate for clays and some shales.

Many of the materials occurring adventitiously in clays and shales are silicates, and will be found under their individual names. Felspar and mica form the two most important groups of these silicates, but these may also be regarded as salts of one or other of the alumino-silicic acids just mentioned.

Alumina (Al_2O_3), like silica, occurs naturally in all clays: (a) in combination as an essential constituent; (b) in combination as an "impurity"; and (c) in the free state. Free alumina is, however, seldom observed in raw clays, though according to Van Bemmelen it occurs in many of them in the form of *laterite* or *hydrargillite* $\text{Al}(\text{OH})_3$, both of which are decomposition products of diorites and granites. Alumina is also produced by heating clays to redness.

Alumina behaves sometimes as a base and sometimes as an acid. In clays its action is apparently neutral, so far as it is a constituent of the clay molecules and not as an "impurity"; but the molecular constitution of clays and some allied minerals is so complex as to make investigation very difficult.

In the form in which it exists in relatively pure clays—as a hydrated aluminium silicate or an alumino-silicic acid—alumina may be considered to be the chief refractory oxide; indeed, pure alumina is practically infusible.

The other chief compounds of alumina occurring in clays are felspar (p. 15) and mica (p. 19). A variety of other aluminous

minerals described in the last section of this chapter, and as constituents of igneous rocks (Chaps. I. and II.), may also be present.

The effect of adding free alumina (either artificially prepared or in the form of native *bauxite*) to a clay is similar to that of adding free silica, but a somewhat more refractory material is produced, and clays rich in alumina are apparently more viscous, and so retain their shape well when heated to the softening point.

Compounds of alumina other than clay appear to reduce the plasticity and to increase the fusibility, impermeability, and strength of the clays to which they are added, but this statement is too general to be entirely accurate, and presupposes firing at a sufficiently high temperature. With underfired goods the alumina compounds act simply as non-plastic materials. For further details see Chap. IX.

In combination with water, alumina forms a colloidal hydrate to which the formula $\text{Al}(\text{OH})_3$ is assigned. On heating this substance the water is removed and alumina formed. Both the colloidal and ordinary form of alumina are soluble in acids, but alumina which has been heated to 1000°C . or above for some time becomes so inert as to be dissolved with difficulty.

Crystalline alumina prepared electrically has been placed on the market under the name of *alundum*. It has a sp. gr. of 4.00, a hardness of 10 on Mohs' scale, and a heat conductivity about four times as great as fireclay. When mixed with fireclay it may be made into crucibles and other articles of exceptional refractoriness, the mixture showing no signs of fusion below 1950°C . Such articles are strong, but too porous for fusing slags and salts, though valuable for metals and alloys.

Iron Compounds.—The chief compounds of iron occurring in clays are the two oxides (more or less hydrated), the carbonate, sulphide, and various minerals containing iron as an essential constituent, such as glauconite, ilmenite, etc. They are obtained from decomposed ferruginous rocks, either by direct admixture or by their becoming dissolved by organic acids, and the solution penetrating into the clay and being decomposed later.

Very few clays are quite free from iron compounds, and in buff and red-burning clays it is essential to the production of the colour. Thus, a clay with more than 4 per cent. of ferric oxide will usually burn red; with 3 to 4 per cent. it will be more brown or even purple, and with less than 3 per cent. it will usually burn white or buff. The colour is not closely proportionate to the amount of iron oxide present, but depends on the size of the particles and whether lime compounds are also present.

In analyses of clay, the total iron present (varying from

0.1 to 35 per cent.) is usually reported as ferric oxide ("iron oxide"), no distinction being made between the various forms in which it may really occur in the clay. To the potter and brick-maker more detailed information is usually necessary, though this is commonly obtained from a study of the material heated under different conditions rather than from an analysis.

In spite of the thorough and careful investigations which have been carried out during the past fifteen years, the state or condition in which iron occurs in burned clay is still a matter of conjecture. The red colour of certain articles, such as bricks and terra-cotta, is apparently due to the presence of free ferric oxide, but this is by no means certain; and in any case the colouring particles must be extremely minute, as the addition of specially prepared iron oxide does not produce the same shade of colour.

Ferrous oxide (FeO) occurs but rarely in clays, though it is sometimes produced in the kilns by the reducing action of the fire-gases on other iron compounds. It readily unites with silica to form a dark slag-like mass.

Ferrous carbonate (FeCO_3) occurs frequently in certain clays, chiefly in the form of concretionary masses or as a film coating other minerals, but occasionally as minute crystals (*chalybite*). The masses of this carbonate (*siderite*) are known as *clay ironstones*, and are particularly abundant in the clays of the Coal Measures. On exposure ferrous carbonate loses carbon dioxide, and is converted into a hydrated ferric oxide, possibly limonite.

Siderite, or native ferrous carbonate, is present in many clays, but is most noticeable in the Staffordshire marls and the buff-burning clays of the Coal Measures (fireclays). It must be removed before these can be used for some purposes, as the nodules of siderite ("ironstone") produce black spots of a slag-like nature which spoils the appearance and reduces the refractoriness of the fired clay. Attempts to remove it usually consist in picking out the larger nodules by hand.

Ferrous sulphate (FeSO_4) sometimes occurs in moist clays, but only to a small extent. It appears to be retained by the clay, and cannot be readily removed by washing. It behaves in a similar manner to ferrous carbonate, from which, in the presence of clay, it is difficult to distinguish it.

Ferric oxide (Fe_2O_3) is the compound of iron most frequently occurring in clays, especially if its hydrated forms are included. **Hæmatite** is ferric oxide which often contains free silica or clay. **Magnetite** (Fe_3O_4) is a black oxide, and is rarely found in clay.

When present in very large quantities, ferric oxide converts the clay into a variety of ochre (p. 215), but in smaller amounts

produces red-burning clays, the colour of which is not strictly proportional to the amount of iron present.

Ferric oxide chiefly occurs in extremely minute particles, distributed so regularly throughout the clay that they cannot be separately distinguished, and even when the clay is washed the greater part of the iron oxide will still be in it. It also occurs as a thin film, coating other minerals, and as small as pellets, though these last are rare. (See also *Nontronite*, p. 248.)

When lime or some of its compounds are present in a clay they combine with the ferric oxide—forming a silicate—on being heated, and the resultant material is white instead of red. This fact is used in the manufacture of malm bricks (p. 205).

Ferric oxide is readily reduced to ferrous oxide on heating in a kiln with an insufficient supply of air. The reduced oxide usually combines with the free silica in the clay, producing a bluish-black or grey slag which forms the chief colouring agent in the “blue bricks” of Staffordshire and elsewhere. When heated with a sufficient amount of air, ferric oxide remains uncombined even at very high temperatures, and then produces the characteristic red colour of certain clay-wares.

Ferric hydrate or hydrated ferric oxide is not a single substance, but includes a wide range of combinations of ferric oxide with water. Its composition is capable of infinite modification, and is dependent on the tension of the aqueous vapour in contact with it. This explains the many variations in colour—from yellow to red. All ferric hydrates behave like colloids; on being heated they lose water and are converted into ferric oxide. The relative volumes of the different hydrates have, apparently, some effect on the colour of the bricks, etc., produced from the clays in which they occur.

Limonite is usually represented by the formula $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, but, being colloidal, it does not possess a really definite composition. It is commonly understood to produce the yellow colour in many surface clays and weathered shales. It occurs evenly throughout the mass, and also in irregular nodules or “kidneys,” particularly in weathered clays. These may be usually removed by hand, but if left in the clay they cause irregularity in colour.

When ferric oxide and the various ferric compounds are exposed to the action of the weather, limonite or other ferric hydrates are produced.

Ferric sulphide (FeS_2)—**pyrites**—occurs in clays in several forms, of the same chemical composition, as *pyrite* or *mundic* and *marcasite*. These occur chiefly in the shales of the Coal Measures, but are also found in ball clays, and are apparently

formed by the action on ferrous carbonate of sulphuretted hydrogen evolved from decomposing organic materials, possibly with the aid of bacteria. These sulphides may be disseminated in the clay, but are usually found in groups resembling petrified roots, or in nodules or "kidneys," though in some clays and shales pyrite occurs as cubical crystals resembling minute blocks of polished brass, this brassy lustre being very characteristic. These crystals are particularly noticeable in coal-pit refuse (shales) which is largely used for brickmaking in some districts. When the nodules are large they are easily removed; when they are small and numerous they are difficult to separate. For coarse articles they may be often left in the clay, though they then form cavities and a blackish slag of iron silicate.

Marcasite is chiefly found in twin rhombic crystals, fibrous masses,¹ or dirty-brown nodules; when bright it is paler in tint than pyrite, though this is not a constant character. It occurs frequently in many sedimentary rocks in the form of very minute particles, or sometimes in irregular layers, but being difficult to distinguish from pyrite, it is often supposed to be somewhat rarer than the latter. It oxidises more readily than pyrite on exposure, a whitish "scum" of ferrous sulphate being formed. This may be washed out of the clay by rain or may be disseminated through it, and later be converted into red ferric oxide. Double sulphides of iron and copper also occur in some clays; they are described under *Cupriferosus pyrites* (p. 276).

In many burned clays iron sulphide may be detected after firing as minute black spots which under the microscope have a semi-molten appearance. No matter how finely the nodules may be ground, they never appear to become converted into red ferric oxide, but, on heating, half the sulphur is expelled at 400° to 600° C. and the remainder at a higher temperature. If the material is heated rapidly and with insufficient air during the second stage the ferrous oxide produced combines with some of the silica present and forms a bluish-black slag. This is of such a nature that it cannot be oxidised under the conditions obtaining in commercial furnaces, and it is therefore necessary in firing clays containing much pyrites to heat very slowly and with an ample supply of air between 600° and 1000° C., or the goods will be marred by irregular blackening of the surface or interior.

The odour of burning sulphur so often noticed in brickyards on the Coal Measures is largely due to the pyrite and marcasite in the clay and coal. The effect of iron compounds on clays con-

¹ Stokes has noticed that much of the fibrous mineral usually termed marcasite is really pyrite.

taining them is chiefly connected with the colour of the fired articles. If added to a refractory clay, iron compounds lower its fusing-point. They do not appear to diminish the plasticity of a clay, and they increase its cohesion after firing. Further particulars will be found on p. 185.

Vivianite, a crystalline ferric phosphate, has been found in some boulder clay as tiny blue flecks, but the amount is too small to be determined.

Glauconite is an amorphous, granular, or earthy hydrated potassic ferric silicate, alumina, magnesia, and lime being often present, as its composition is very variable. It is green in colour, and occurs extensively in marls from the chalk, chloritic marls, and particularly in the Greensands. It tends to give raw clay a greenish colour which becomes reddish on burning, and aids vitrification, as it is readily fusible. It is therefore useful in some clays, but disadvantageous in those which are required to burn to a light coloured, refractory body.

Lime compounds¹ are extremely widely distributed, and scarcely any clays are quite free from them. The purest commercial clays contain only 0·2 per cent. or even less, but some alluvial clays and marls contain as much as 45 per cent. of calcium carbonate.

In clays, lime compounds occur in a variety of different forms, of which the most important are calcium carbonate (calcite aragonite, chalk and limestone), gypsum, selenite, and other forms of calcium sulphate, as a phosphate, and as oligoclase and anorthite feldspars (p. 16) or other silicates.

Calcium carbonate (CaCO_3) is a compound of lime and carbon dioxide, which on being heated loses the latter constituent and forms **lime**. On exposure to moisture the lime becomes hydrated or "slaked," and in contact with carbon dioxide the carbonate is again formed. The calcium carbonate in the clay may be derived from the decomposition and pulverization of limestone or chalk, or it may be deposited by water holding bicarbonate of lime in solution. Primary clays or kaolins do not usually extract more than 2 per cent. of carbonate of lime from such solutions, but secondary plastic clays can absorb 10 to 40 per cent. of it.

Free lime does not occur in raw clays but is produced when clays containing calcium carbonate are heated, and may later cause them to crack and to disintegrate.

Limestone is a sedimentary rock composed chiefly of calcium carbonate, some varieties being very pure, but others containing much clay. These may form natural malms or marls (p. 206) on

¹ Strictly, these should be termed *calcium* compounds, but the term employed in the text is that commonly used by clayworkers.

weathering. Some limestones are rich in magnesium carbonate. (See *Dolomite*, p. 267.)

Particles of crushed limestone in a clay are usually highly objectionable, as they form small lumps of free lime when heated and, as already explained, may seriously damage the goods. It does not appear possible to grind them sufficiently small to be harmless in the crushing plants usually employed in brickmaking. In the manufacture of cement, whereas much finer grinding is customary, mixtures of limestone and clay are largely employed: and in ascertaining the commercial possibilities of a given deposit the association of limestone and clay is always suggestive of a material for the manufacture of cement. This is particularly the case with deposits of the Oolite formation.

When occurring in nodular form in a clay, limestone is frequently termed **race** or **skerry**, and is then particularly objectionable and liable to produce cracked and "blown" goods.

Calcite or **calcspars** (CaCO_3) is a crystalline variety of calcium carbonate, another form being

Aragonite, of identical composition. In clays both these substances form irregular greyish-white, semi-opaque masses, which behave in a manner precisely similar to pieces of limestone of the same size.

Chalk is a soft, fine form of calcium carbonate, and is usually so friable as to be readily ground. Its particles are small and may be very evenly distributed throughout any clay containing it, with the result that it has all the advantages of limestone and none of its defects. Chalk is usually pure, the calcium carbonate in it being seldom less than 95 per cent. In the form of **shells** (unless so minute as to be unrecognizable without a powerful microscope) it is more objectionable. In some clays there are numerous impressions of shells but nothing more, the calcium carbonate having been dissolved and disseminated through the clay.

Clays containing a considerable proportion of chalk are termed "marls" (p. 206), and are much used in the manufacture of the so-called "white bricks" or malms (p. 205).

Calcium sulphate (CaSO_4) occurs in clay in two forms as gypsum and selenite.

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) occurs as a crystalline mineral or as white pearly lumps, some of these being so large as to be readily picked out. It is a soft material, can easily be scratched with a finger-nail, and leaves a white streak when rubbed on a harder surface. It loses its water on being heated to 120°C ., forming plaster of Paris $\text{CaSO}_4 \frac{1}{2}\text{H}_2\text{O}$; at 132°C . it forms anhydrous CaSO_4 ,

and at a much higher temperature sulphur trioxide volatilizes, leaving quicklime.

Gypsum is seldom distributed throughout a clay, but occurs in irregular layers or small pockets.

Selenite ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the "petrified water" or "congealed water" frequently mentioned by brickmakers. Like gypsum, it is crystalline, but is much more frequently seen. Large and beautiful transparent crystals—some of them radiating or in fibrous masses—are found in many clays, particularly those of the London basin (p. 86).

Beeby Thompson has found that crystals of selenite placed in a solution of ferrous sulphate neutralized with lime water increase in size, and suggests that the selenite in clays is due to the simultaneous presence of ferrous sulphate and chalk or limestone.

Anhydrite (CaSO_4) is of a similar composition to gypsum, but is devoid of water.

Coprolites, Phosphorite, or Phosphatic rock is an impure phosphate of lime, and when the term is used, strictly relates to the fossilized excrements of animals, occurring in clays above the chalk. Many clayworkers use the term in a looser way to designate all phosphatic nodules, particularly those in the "Greensands." True coprolites are common in Oxford clay and gault, but their influence is inappreciable if they are finely ground and not too numerous.

The effects of lime compounds on clays are very varied:—

1. As already stated, if free lime is produced by the heat of the kiln and the goods are later exposed to moisture, they will probably crack. If sufficiently strong to resist the disruptive action any free lime in them will probably slake and fall out ("blow"), leaving a cavity corresponding to the size of the mass of free lime (p. 200).

It is very important that the chalk or limestone added or present in the clay should be in a sufficiently fine state of division, as the presence of lumps far smaller in size than a pea will sometimes cause a brick to fall to pieces. With certain clays pieces of limestone as small as $\frac{1}{25}$ inch have been found capable of bringing about the destruction of the article in which they occur. When sufficiently finely ground as much as 25 per cent. of chalk may be present in a clay; but for bricks intended to resist the action of the weather, 12 per cent. is usually the upper limit. Much, however, depends upon the original composition of the clay used. Instead of grinding the material very fine it may often be washed in a mill and the coarser particles removed in this manner. Washing is preferable to crushing very fine, but is somewhat more expensive.

It is precisely for the reason that the lime compounds in boulder clay or drift are in the form of stones which cannot be ground to an impalpable powder with ordinary appliances that this material is so difficult to use and so unsatisfactory to clay-workers, whereas marls which contain the same material in a very finely divided condition (as chalk) are capable of being made into excellent bricks.

Sometimes, instead of falling out, the lime or plaster forms unpleasant white spots on the surface of the goods.

2. If the lime compounds are in the form of chalk and very evenly distributed throughout the mass they will combine with any iron oxide and some free silica in the clay, destroying the red colour normally produced by iron and yielding a buff or whitish article (see *Malms*). Hence it is impossible to produce a good red brick from a clay containing much lime.

3. Lime in the form of silicate, though frequently present in clays, as oligoclase and anorthite feldspars, etc. (p. 200), is seldom in sufficiently large amounts to be important. Its chief effect is to (slightly) reduce the refractoriness and plasticity of the clay.

4. Clays containing lime compounds fuse more readily and become impervious (vitrified) at a lower temperature than others. They are always difficult to burn, as when the finishing temperature is reached vitrification takes place very rapidly and the articles are particularly liable to lose their shape. For this reason most malm bricks are underfired and "baked" rather than burned. The effect of the lime compounds depends upon the size of the grains, the extent to which they have been diffused throughout the clay mass, and the kiln temperature. If the kiln temperature is over 1000° C. the lime compounds will usually act as a flux, but at lower temperatures they act merely as non-plastic substances, making the clay more porous and altering its colour. (The effect of lime on clays containing iron has already been described.) Calcium carbonate (chalk) or lime thoroughly blended with the clay operates as a very active flux, the thermochemical reactions between the nascent oxide and clay taking place with great rapidity, and in some instances so quickly as to make it very dangerous to approach the vitrification temperature. If the calcium carbonate is present in nodules (limestone) the reaction just described can take place only at the points of contact of the lime and clay, the remainder of the carbonate being converted into quicklime. The different effects of lime in these two physical conditions on the rate and regularity of fusion of the clay mass is obvious. Calcium sulphate (gypsum) only reacts at

temperatures above 1200° C., but it is then converted into lime and behaves like this substance.

5. Lime compounds diminish the plasticity of clays to which they are added, but to a less extent than silica.

6. If a raw clay containing calcium carbonate in any of its forms is treated with hydrochloric, sulphuric, or nitric acid a violent effervescence of carbonic acid gas is produced.

7. Calcium sulphate is sufficiently soluble in water to form a superficial scum on bricks, etc., made from some clays containing it. This may be prevented by adding barium carbonate in suitable proportions.

A small proportion of **barium compounds** occurs in some clays. They act so similarly to the corresponding lime compounds that they need not be described separately.

Magnesium compounds are of rather less importance than lime compounds in clays. They are derived in a similar manner from the destruction of magnesian rocks, and in many ways act like the corresponding compounds of lime.

Magnesite ($MgCO_3$) is pure magnesium carbonate and occurs in clays as fibrous crystals, but more usually in so finely powdered a condition as to be unrecognisable. The proportion in British clays is never large, 5 per cent. apparently being the maximum, even in the lowest grades of clay. On heating, it forms **magnesia** (MgO)—a material very similar to lime but much slower in its action. When magnesia is added to a clay it greatly increases the vitrification range on account of the high viscosity of magnesium aluminosilicates, and is convenient as a flux which does not induce loss of shape or warping. In this respect its action is precisely the opposite to that of lime, which causes a rapid loss of shape as soon as a temperature is reached at which a large proportion of the lime can enter into combination with the clay.

Dolomite is, strictly speaking, a mineral composed of 46 per cent. of magnesium carbonate and 54 per cent. of calcium carbonate, but in commerce the term is not confined to the true mineral but is used to designate any mixture of calcium and magnesium carbonates containing a considerable percentage of the latter. If low in magnesia such a mineral might be called a dolomitic limestone, but there is no definite proportion of magnesium carbonate which forms a border-line between limestones which are dolomitic and those which are not so. The amount of dolomite occurring in clays is invariably small, and it is seldom possible to ascertain whether dolomite or free magnesium carbonate and calcium carbonate is present.

Dolomite, when it occurs in clays, is derived from the dolomite rocks by the action of the weather.

The effects of magnesium compounds on clays to which they are added are similar to that of the corresponding lime compounds, with the exception that magnesia acts much more slowly than lime, and consequently a high degree of vitrification can be secured in a clay with less risk of loss of shape than when lime compounds are used. This is due to the greater difference in the temperatures at which vitrification and loss of shape respectively commence when magnesia compounds are used.

Alkalies is a term used to include all compounds of potash and soda which occur in clay, as these act so similarly as to render their differentiation unnecessary. Ammonium salts are also present in some raw clays, but their proportion is seldom determined; they may slightly increase the fusibility of a clay or modify its plasticity, but their effect is usually negligible. They are volatilized on heating the clay.

The fixed alkalies (potash and soda compounds), on the contrary, remain in the clay after firing, and are the most powerful fluxes known. At the high temperatures reached in some kilns a partial volatilization of alkalies occurs, the material then becoming slightly more refractory. This fact is the chief reason for the use of chamotte (p. 152) for retorts and fire-bricks on the Continent.

Although reports of analyses usually state the percentage of alkalies in terms of potash (K_2O) and soda (Na_2O), these oxides seldom exist in this form in clays. The most usual forms are *alkali-alumino-silicates*, such as the feldspars, micas, Cornish stone, greensand (glauconite contains potash), and hornblende, but only the first three are really important in this respect. All these minerals are practically insoluble in water, and they form a convenient means of supplying fluxing materials to clays which are not sufficiently vitrifiable, the feldspars and Cornish stone being much used for this purpose.

It is by no means essential that the whole of the alkalies should be in a combined form, and Binns has shown that free alkali is present in small quantities in some clays; ordinarily, however, they exist in the form of feldspar, mica, or other silicates, which are described later in the present chapter.

It was at one time thought that the alkalies contained in clays were found exclusively in the state of impalpably powdered feldspar, but Vogt has shown that this opinion is erroneous, and that they also exist in the form of finely divided mica. It is not a little curious that most British, American, and German experts consider that the alkalies occurring in the finest particles of clays are in

the form of felspar, whilst the French experts maintain that they exist as mica. As a matter of fact in some clays they exist as felspar, in others as mica, and in others again in both forms, as may readily be found by careful investigation.

Occasionally clays contain soluble alkali salts—usually potassium and sodium sulphate, though sodium chloride (common salt) is not infrequent. In the Triassic clays of Cheshire soluble iron sulphates due to the oxidation of pyrite or marcasite may also be present. If the proportion of these *soluble salts* is small the effect is a slight reduction in the refractoriness of the clay, but if larger they tend to be drawn to the surface of the goods made from the clay and to form an unpleasant white scum or slight irregular glaze on the fired articles. If this scum is due to soluble sulphates it may be prevented by the addition of a suitable amount of finely-ground barium carbonate to the raw clay, but the scum produced by common salt cannot be avoided, though it may often be converted into a glaze which is less noticeable by increasing the temperature in the kiln.

The following soluble substances reduce the plasticity of a clay: ammonia, caustic soda, caustic potash, lime, sodium carbonate, potassium carbonate, borax, and water-glass. They do this by coagulating the colloidal portion of the clay, but their action may be prevented by the addition of a quantity of weak acid sufficient to neutralize the alkali in the clay.

The effects of alkalis on clays containing them are therefore (a) to increase the fusibility, (b) to produce a scum on the surface of the goods, and (c) to diminish the plasticity of the clay when it is made into a paste with water.

Titanium compounds occur more frequently in clays than is commonly supposed, though only in small quantities (under 2 per cent. titanium oxide), and in the ordinary methods of analysis it is (unconsciously) included in the figures for alumina. Titanium compounds occur chiefly as **rutile** (TiO_2), **ilmenite** (TiFeO_3), and **titanite** (CaTiO_5), and act as somewhat powerful fluxes; hence clays which are required to be highly refractory should not contain more than 2 per cent. Several investigators have independently examined the effects of titanium oxide on china clay and on artificial mixtures of alumina and silica. Their results show that within the limits in which this substance usually occurs in clays, the reduction in refractoriness is less than 40°C . and is therefore negligible if less than 2 per cent. of titanium oxide is present. Ten per cent. of this oxide lowers the softening-point of kaolin about 100°C ., but on fireclays richer in silica it has a considerably less effect.

Sulphur compounds occur in clays in the form of pyrite and marcasite (iron sulphides), and as various soluble sulphates. The sulphides are objectionable because of the odour produced when the clay is burned (see *Pyrites*, p. 261), the slag-like residue which disfigures the goods, and the difficulty often experienced in preventing the formation of a black "heart" or core.

Sulphates may dissolve in the water in the clay, and rise to the surface of the goods, being carried thither by capillary attraction, and may form an objectionable scum. They may also be dissociated in the kiln, sulphur trioxide being volatilized at 800° to 1000° C., and then do but little harm to the goods.

If a clay contains free alkali or a carbonate and the fuel used in the kiln is pyritiferous, the latter will produce sulphur dioxide which may combine with the alkali or carbonate and produce a sulphite, or a sulphate, which has all the objectionable properties already described. This formation of sulphates in the kiln may be prevented by using coal free—or nearly free—from sulphur and, in continuous kilns, by heating the goods to at least 120° C. with hot air instead of with fire-gases.

The scum due to dissolved sulphates in the clay may be prevented by adding a suitable proportion of barium carbonate. Barium hydrate and chloride are also occasionally used, but whilst very effective they are somewhat risky, as an excess of either may form a fresh scum on the goods. Barium carbonate being insoluble, is free from this objection.

The recommendation to allow such clays to leach thoroughly or to use them only after thorough weathering is only occasionally of value. Many clays retain soluble salts so persistently that they cannot be washed clean. Coating the goods with a colloid material such as tar, glue, or flour paste will prevent the salts rising to the surface, and so may avoid the formation of scum.

If sulphates, but no sulphides, are present in the clay, burning with a strong reducing flame (smoky flame) will sometimes be advantageous.

Numerous other effects are attributed to "sulphur" by many kiln-men, but these have yet to be accurately proved. Orton and Stanley, who investigated the subject in 1908, consider that the loss of sulphur in the interior of the clay goods is usually very small, and that in whatever form it may occur sulphur is not likely to cause any serious disturbance until the clay becomes vitrified, after which the evolution of gas may occur and a swollen and spongy body be produced. This is to a large extent prevented by heating very slowly with plenty of air so as to secure the complete combustion of the carbon at a low temperature, after

which the volatilization of the sulphur compounds follows easily and rapidly. Any treatment which enables the goods to reach a temperature high enough for the silica to react on the sulphates before all the carbon has been removed will cause swelling and slagging.

With some clays the heat-treatment at 900° C. or lower must be so prolonged as to be commercially impracticable.

Phosphorus compounds exist in trifling proportions in most clays (probably as phosphates), and are purposely added to soils to increase their fertility. They have no apparent influence on the physical or chemical properties of the clays in which they occur, though in much larger quantities (in the form of **bone ash**) they are added to give translucency to English china-ware.

Water occurs in three forms in clay, viz. (a) as moisture or dampness; (b) as water of formation, this being that which is added to produce a workable paste; and (c) combined water. Of these the last cannot in any sense be regarded as an impurity unless it is combined with materials other than clay.

The moisture in a clay is sometimes troublesome, as it may produce a sticky adhesive material which is difficult to manipulate and must therefore be dried or mixed with some absorptive, such as burned clay (grog), very dry clay, or sand. Usually when the clay has been made into bricks, tiles, pottery, or other articles of definite shape, the moisture becomes part of the "water of formation," but it is in the grinding of the clay where the presence of moisture *per se* is apt to be troublesome.

Clay is naturally hygroscopic, and when fully dried and then exposed to the air it rapidly absorbs moisture from the latter, even though it may not become actually wet.

The water of formation and the chemically combined water with the precautions which must be used in connection with them are described in Chap. IX.

Water is added to clay for a definite purpose—viz. to make it of convenient consistency and plasticity, and cannot, unless it be present in excess, be regarded as an impurity. Any excess of water may usually be removed by exposing the clay to the atmosphere, or, more rapidly, to a current of warm air. If the clay has been made into articles of definite shape, however, great care is necessary to prevent it cracking (see Chap. IX.).

Most analyses of clay show the proportion of moisture correctly, but the combined water is included with carbonaceous matter, sulphur, carbon dioxide (from any carbonates present) and sulphur trioxide (from any sulphates), and its amount is therefore seldom known.

The effect of water on clays containing it largely depends on the form in which it is present. If it exists as moisture or water of formation it makes the material plastic and generally workable, and as it evaporates (by drying), the material shrinks in size (see *Shrinkage*), and may crack if the water is removed too rapidly. If too little water is present the material will be too stiff to be readily shaped, though it may usually be more easily crushed than when in a moist condition. If a large quantity of water is added to and mixed with clay a slip or slurry is formed, from which many of the coarser impurities may be separated by allowing the slurry to remain standing for a short time and then running off the fluid portion. This process may be repeated frequently, and is known as elutriation or washing. Instead of allowing the slurry to stand, it may be passed through fine sieves and so freed from coarse particles.

The water of combination is quite different. It is only expelled at a temperature of 400° to 600° C., and is accompanied by a slight shrinkage; the clay then loses its plasticity and cannot recover it by any treatment yet devised, but becomes hard and stony. It is, indeed, probable that this so-called water does not exist as such in the clay, but is formed when the clay molecule begins to decompose in consequence of its being heated (p. 154).

Organic matter is a frequent constituent of clays, particularly of those which are plastic, and some chemists consider that the plasticity of clays is due in some way to this material. The organic matter may be of animal or vegetable origin, but in either case it is distinguished by the fact of its being chiefly composed of carbon, hydrogen, and oxygen, and is driven off by heating the clay slowly in the presence of sufficient air. Organic matter contained in clays may be derived from: (1) Infiltration of soil suspended in water into a bed of clay. (2) The deposition of the clay on land containing vegetable matter, the existence of animals and plants on the surface of the deposit, or the presence of plants and animals carried by the water at the same time as the clay. (3) Various bituminous rocks which become mixed with the clay. In the first and third cases the proportion of organic matter is not usually large, but in the second it may become so. As its origin is usually of minor importance, but its carbon content is an essential characteristic, the term **carbonaceous matter** is frequently used. This has the further advantage of including such organic material as has undergone so complete a change as to render it almost impossible to describe it in more definite terms. Indeed, the composition of the major part of the organic matter in clays is very imperfectly understood.

Carbonaceous matter may be present in such a form that its vegetable or animal nature is clearly recognizable, in the form of leaves, wood, roots, etc., and as such is frequently found in surface clays. The fossilized remains of animals and plants are found in most clays, but these are usually little more than facsimiles of the original, the carbonaceous matter having been largely replaced by earthy material.

In the form of humus, peat, lignite, coal, shale oil, and bitumen, or materials allied to these, carbonaceous matter occurs frequently in clays—notably those of the Oxford and Coal Measure series and certain Scotch shales. If not excessive in amount, and if present in a finely divided state, such material is often an advantage, as it reduces the amount of fuel needed to burn the clay in the kilns. If irregularly distributed and in large fragments, however, it may cause uneven burning, and may be a source of perpetual annoyance and trouble. The precautions necessary for the successful working of clays rich in carbonaceous matter are given in Chap. IX., under the heading *Effects of Heat*.

Clays or shales containing more than 10 per cent. of carbon can seldom be worked profitably; even half this amount sometimes produces black cores or "hearts," and necessitates such slow burning as to waste fuel. If, like some ball clays, they are very plastic and are mixed with a large proportion of non-plastic material, much less trouble with carbonaceous matter will be experienced.

The colour of clay is seldom any guide as to the proportion of carbonaceous matter present, though the darker clays are often rich in this substance. That the colour of many raw clays is due to it may be concluded from the fact that they change their colour on being heated, though this is by no means a reliable criterion.

The effects of carbonaceous matter in clay are numerous. The most important are: (1) the colour before and after firing; (2) the plasticity of the clay; (3) the size and number of the pores in the fired clay (porosity); (4) the quantity of water the clay can absorb, and consequently its shrinkage; (5) the smaller amount of fuel required to burn the clay, except when the carbonaceous matter creates special difficulties in firing. These are all described more fully in Chap. IX.

The most troublesome effect of carbonaceous matter is that due to the fact that carbon has a more powerful affinity for oxygen than iron has, and so it will keep any iron oxide in a clay in a reduced (ferrous) state, and as this is objectionable in most cases, it is necessary to exercise great care to burn off the carbon with a plentiful supply of air, without allowing the temperature of the

clay to rise sufficiently for the reduced iron oxide to form a black fusible slag or core. The amount of trouble and attention involved in this will depend on whether the pores in the clay are large or small.

Stones in clay are so frequent and so objectionable that in spite of the numerous materials included in this one term it may conveniently be mentioned separately. If the stones are of a siliceous nature they may frequently be crushed along with the harder pieces of clay and may be disregarded, but if they contain alkalis, lime, or magnesia, they must usually be removed from the clay, or they will spoil the goods made from it.

Large stones, *i.e.* those more than 2 inches in diameter, may usually be picked out by hand, or may be removed by means of a coarse grid, but stones the size of peas, hazel-nuts, or walnuts are more difficult to remove, though the use of a clay-cleaning machine, in which the material is made into a soft paste and then compressed against a perforated plate, or passed into a cylinder with perforated walls, is often effective. By mixing the material with an equal weight of water, mixing thoroughly, allowing the slurry to stand for a short time, and then running off the fluid portion, all the stones may be removed, but this process is somewhat expensive—about one shilling per ton of clay.

The effect of stones in clay varies with their composition, but in general terms they increase the cost of preparation, reduce the plasticity of the clay, and may cause irregularity in colour, texture, and strength in the goods made from the material containing them. The most serious effects are obtained with limestones (see *Lime Compounds*), as these may cause partial vitrification, white blotches on the surface of the goods, or “blow-holes.”

Other minerals may be, and usually are, present in clay. The most frequent of these are felspar, mica, and various forms of silica, but, as will be understood from a study of the origin of clays (Chap. I.), almost any mineral may be present. A large proportion of these latter may be separated as sand, gravel, or stones, by mixing the clay with water or slurry and passing as much of it as possible through a No. 200 sieve, the residue being well washed with a further supply of water. Or a process of washing and settling, similar to that used for china clay, may be employed, but no method has yet been devised for completely separating the finer minerals from clay.

Usually it is unnecessary to distinguish between the different minerals present as coarse particles, the terms sand, gravel, and stones being sufficiently comprehensive, but the finer particles need more detailed consideration.

Felspar and *Mica* are frequently present in clays in so finely divided a state that they cannot be completely separated from the clay by any mechanical process, though a thorough and careful washing will frequently remove all but about 5 per cent.

Their chief characteristics have already been described (pp. 15 and 18), as they are important constituents of igneous rocks, from the decomposition of which clays are obtained. In clays, felspar represents some of the original rock which still remains undecomposed, whilst the mica is set free at the same time as the original rock was kaolinized. Felspars and micas must usually be recognized by their microscopical and chemical characteristics, though the peculiar glistening frost-like particles in many clays usually afford a ready means of detecting even small quantities of mica. The particular mica most frequently found in clays is muscovite (p. 19), and it consequently introduces alkalies as an impurity. Biotite (p. 19) is found, but more rarely, as it decomposes on weathering. Apart from this and its appearance, mica is not objectionable, and is, indeed, slightly plastic.

It is a curious fact that whilst the commoner varieties of clays, such as those used for brick- and tile-making, often contain a notable quantity of felspar, they seldom contain more than an insignificant amount of mica. The crude china clays, ball clays, and fireclays, on the contrary, often contain a considerable proportion of mica, but scarcely any felspar.

The effect of mica and felspar on refractory clays is to increase their fusibility, but with others they merely reduce the plasticity. If clays containing felspar are heated to a sufficiently high temperature an impervious vitrified body (stoneware) is produced, providing that sufficient felspar is present in a finely divided state. Coarse particles have less influence, and are refractory below 1300° C. The softening effect of mica is seldom noticeable below 1200° C. and that of felspar below 1300° C., though it, when finely divided, begins at a much lower temperature.

Where an intense whiteness is required in the burned clay, mica (especially biotite) is objectionable on account of the iron it contains, but for other clays (except fireclays) its influence is usually insignificant compared with other impurities simultaneously present.

Other minerals existing in clay are present in smaller proportions. They are chiefly interesting as indicating the origin of the clay, or on account of some special properties which they possess. The most important of these are mentioned below, but it must be understood that the number of different minerals possible in a given clay is almost innumerable, particularly if those containing

rare elements are included. Many of the silicates found in clays are very difficult to recognize, because of the small amounts in which they are present, and because there is no method by which they can be separated. The microscope is often of great importance in this connection, especially when thin semi-transparent sections of clay can be obtained (see Plates I. and II.).

Small proportions of silicates are not of immediate practical importance, as they do not appreciably modify the plasticity or notably affect the softening temperature of a clay.

Hornblende is a mineral constituent of certain igneous rocks (p. 18), and may frequently be seen when impure clays are examined microscopically. Being a silicate containing iron it gives a dark brown or black colour to clays containing it, but is seldom present in sufficient quantities to exercise much importance on their chemical or physical characteristics.

Tourmaline is a constituent of several primary clays as well as of the igneous rocks from which they are derived (see p. 19).

Cupiferous pyrites—chalcopyrite, bornite, and erubescite—occur in some fireclays, notably those of Northumberland, Durham, South Scotland, North Staffordshire, and Shropshire. This term includes several compounds of sulphur, copper and iron combined in various proportions, closely related to iron pyrites (p. 261) and behaving in a similar manner, except that the stain produced in fired clay is green rather than black. Manufacturers of sanitary ware are often troubled with curious green stains with a shiny black centre which penetrate the white engobes used to cover the clay employed for these articles. These stains, which have a very characteristic appearance, react for both copper and iron, and Mellor has found that precisely similar stains may be produced by adding chalcopyrite to a fireclay.

Chalcopyrite is more weather-resisting than the other copper-iron sulphides; it therefore resembles pyrite (p. 261), whilst they behave like marcasite (p. 262).

Vanadium compounds cause a greenish discoloration in some buff-burning clays of the Coal Measures when exposed to moist air, but as this discoloration can be washed off with water—like the “scum” from soluble salts—it is not a serious disadvantage. By heating the clay until it is partially vitrified Seger found the colouring agent was rendered insoluble and the discoloration prevented.

CHAPTER IX.

THE PHYSICAL AND CHEMICAL PROPERTIES OF CLAYS.

MANY years ago the two subjects of chemistry and physics were regarded as quite separate, but in recent years, following the growth of an intermediate science of physical chemistry, the line of demarcation has largely disappeared. This is particularly the case in the study of the properties of clay, and it has therefore been considered desirable to make no distinct classification of those properties which are accompanied by a change in chemical composition and those which are not. It frequently happens that the effect of a particular force may, within certain limits, be purely physical, but if its range of action is extended or increased, chemical changes may result. Thus the application of heat to a piece of wet "clay" is, at first, purely physical in its action, then as the water is driven off changes in composition commence, and if the heating is sufficiently prolonged, a rearrangement of the elements in the clay may take place and a partial crystalline material may be produced quite different in every way from the original "clay." This newly formed substance has different physical characteristics, and it is therefore more convenient to study the various characteristics separately, rather than to group them into physical and chemical properties respectively.

The colour of raw clays varies within extremely wide limits, and though to a certain extent useful as a means of distinguishing different varieties, but little reliance can be placed upon it. Some dark-coloured — even black — clays behave in a manner almost identical with others of a much lighter colour; and as the tint is usually due to organic or carbonaceous matter in the material, it burns away when articles made of the clay are placed in the kiln.

Variations in colour in different clay strata in the same general bed are common, but do not necessarily indicate any appreciable

difference in composition, nor is the colour any guide to the purity of a clay, as the amount of material producing it may be too small to be determined, so much of it being of the nature of a dye, like the brown colouring matter obtainable from peat.

China clays, kaolins, and pipeclays are usually white or very pale grey. Ball clays are bluish-grey, often mottled or streaked, but are sometimes dark brown to black. Other clays vary from yellow, red, and brown to various shades of grey, and shales are chiefly grey but are not infrequently brown or yellowish in colour.

The colour of clay is partly due to organic (vegetable) matter and partly to the minerals it contains; the latter exercise a greater influence on the colour of the fired material than on that of the raw clay. The grey, bluish, black, and other neutral tints of unburnt clay, although occasionally due to mineral impurities, are usually of vegetable origin, the composition of the colouring matter being very imperfectly understood but usually assigned to peat-like matter. Clays absorb soluble dyestuffs readily, and many of the colours due to organic matter may really be of this nature. These organic colouring matters are destroyed on firing, so that a clay may be strongly coloured in the green state and yet burn perfectly white. The red, yellow, brown and greenish colours of clays are more commonly of mineral origin, and are chiefly due to iron compounds or, very rarely, to manganese. The colour produced by mineral matters in the clay is changed by heating (see later). The difference in colour effected by drying or moistening clays is very marked.

The **odour** of clay is indescribable though characteristic, and is most observable when the material is freshly cut. Its source is not positively known, but is ascribed to organic substances in the clay. On shaking a highly plastic clay possessing a powerful odour with a solution of iron saccharate, the odour and taste of the clay are completely transferred to this solution. In this fact Rohland finds a further confirmation of the presence of colloids in clay.

The **hardness** of clays varies according to the moisture and other materials present, and to the extent to which the "clay" has been compacted and indurated by pressure and other natural forces. Some comparatively dry clays (china clays and pipeclays) are almost as soft as flour; others have a hardness similar to gypsum or talc; whilst others, again, being rich in quartz grains, are, when quite dry, sufficiently hard to scratch glass. Clays may thus be found which have all the degrees of hardness from that of talc to quartz (numbers 1 to 7) on Mohs' scale as given

below. Occasionally a shale is found which is hard enough to scratch quartz, but so indurated a clay is rare.

MOHS' SCALE OF HARDNESS.

- | | |
|---------------|----------------|
| 1. Talc. | 6. Orthoclase. |
| 2. Gypsum. | 7. Quartz. |
| 3. Calcite. | 8. Topaz. |
| 4. Fluorspar. | 9. Corundum. |
| 5. Apatite. | 10. Diamond. |

When moist, most clays are much softer, and may be as soft as butter or so stiff as to bear the weight of a man. If they contain still more water a soft, muddy mass of the consistency of a thick soup, technically termed "slip" or "slurry," is formed.

Dry clays are usually somewhat **rough** when rubbed between the finger and thumb, but the finer qualities of ball and china clay consist of such minute particles that no grittiness can be perceived in them, even when a piece of such clay is placed in the mouth and "tasted." The finer the clay the smoother it is, but most clays are quite smooth when moist enough to form a paste. Clays suitable for making bricks, tiles and refractory goods feel quite rough, but for terra-cotta and pottery smoother clays—composed of finer grains—should be used. The smoothness of clays may be increased by removing the coarser particles by washing or by grinding them to a sufficiently fine condition, though this is costly and troublesome with those containing a considerable percentage of siliceous matter ("sand").

The **stickiness** of certain clays (*e.g.*, London clay) is very pronounced, but must not be confused with true plasticity. Ashley has stated that if the granular constituent is removed from a plastic body it loses plasticity and becomes sticky until the granular constituent is restored. This suggests that the practice of adding granular material of a non-plastic nature, so common amongst users of London clay, is based upon a sound principle. Sticky clays are difficult to mix with water, and crushing rolls of special design must be employed.

The **Plasticity** of clays is described later (p. 314).

Toughness and stickiness are commonly associated, and cause much difficulty when a uniform, homogeneous material is required, as a tough, sticky clay permits the rollers used for crushing them to slip, unless they are specially designed to obviate this difficulty.

Oiliness is a characteristic of some clays, and is distinguished from stickiness in the smoother feel and less adhesiveness of the material.

Some clays contain material of an oleaginous nature, and when treated with alkaline solutions produce a soap. This saponification of certain clays increases their plasticity on the addition of alkali, which is precisely the opposite of what occurs with ordinary clays.

Clays are always **opaque** when examined with the naked eye; under a microscope they are seen to be composed of fragments, some of which are transparent but most remain opaque, though many of these particles are so small as to render it difficult to state definitely whether they are really opaque or not.

Sectility, or the capability of being easily cut, is a characteristic of clays which occur in a plastic condition, such as ball clays and many surface clays. This property often serves as a simple means of distinguishing "clays" from many other minerals, though the "clays" so found may be too impure to be of any commercial value. Anyone constantly engaged in examining clays soon learns to recognise certain varieties by their sectility and by the slightly glossy appearance of the freshly-cut surface, though these cannot be clearly described.

Fissility—or the capability of being split up into slabs or thin flat pieces, or even into flakes or foliations—is characteristic of many indurated clays, and especially of shales. If the splitting can be effected so as to form plates of extreme thinness, the material is said to be laminated; if the tendency to split is strongest in the direction of bedding, the material is termed shaly; if this tendency is strongly marked in any other direction it is said to be fissile, as are slates and certain limestones and sandstones.

The terms **ductile** and **malleable** are seldom applied to clays, as the term plasticity to some extent includes them both, though not completely. Most plastic clays are ductile—*i.e.* easily drawn out or extended, and malleable—*i.e.* easily altered in shape when hammered¹; but before these properties are fully developed it may be necessary to mix the clays with water. The ductility of clays is, however, much less than that of metals when this term is limited to its narrowest meaning; but if, as is usual, it is understood to include the capability of being shaped into a long bar by compression through a small orifice, plastic clays are remarkable for their ductility. This property is much used in the formation of bricks, pipes, etc.

The **texture** of clays is usually that of a solid, dense mass, with no obvious "structure," but if examined with a microscope, clays

¹ Most clays may be altered in shape by so slight a pressure that the use of a hammer for this purpose is unnecessary. Hence, instead of the term "malleable" being applied to them, they are described as plastic (see later).

are seen to be composed of small irregular grains of various sizes, aggregated closely together.¹ If the clay is comparatively pure, these grains are so small that on mixing the clay with a sufficient quantity of water they will all pass through a sieve with 200 holes per linear inch. Shales, slates, and rock clays may require boiling with water to which a little ammonia has been added before they can be effectively treated in this manner. If any particles remaining on the sieve are washed and examined, they will be found composed of materials other than clay, such as sand, small stones, pieces of roots, grass, or other adventitious matter. It is, in fact, a peculiar characteristic of clay that its particles are so extremely minute that they may, for this reason, be easily separated from much of the other material occurring along with them in ordinary clay deposits, though no complete separation of these other materials is possible. This remarkable fineness of the clay particles is well shown by the following definitions proposed by Seger and generally accepted as "standard."

*Clay.*²

All grains with a diameter less than 0.01 mm. washed out by a stream of 0.18 mm. velocity per second with 20 mm. pressure in piezometer. This gives a grain of not more than .010 mm. diameter.

Silt.

All grains between 0.01 mm. and 0.025 mm. in diameter washed out by a stream of 0.7 mm. velocity per second with 8.900 mm. pressure.

Dust Sand.

All grains from .025 to .040 mm. in diameter, which are washed out with a stream of 1.5 mm. velocity per second.

Fine Sand.

All grains between 0.04 mm. and 0.33 mm. diameter.

Coarse Sand.

All particles with a diameter above 0.33 mm.

The coarse sand is taken out by sifting, and the "clay," silt, and dust sand are washed out with successive streams of water

¹ The study of the texture of raw clay has not, as yet, yielded results of much importance to clayworkers. The texture of burned clay wares is, on the contrary, a characteristic of the highest importance.

² Mechanically separated, but not chemically pure clay.

having velocities of 0·18, 0·7, and 1·5 mm. per second respectively ; the fine sand can then be washed out with any higher velocity, or it may be found by taking everything out which is left in the vessel after the dust-sand is got rid of, and weighing it.

Only the most valuable clays are sufficiently fine for a slip made by mixing them with water to pass through a 200 sieve ; the majority of clays employed in the manufacture of bricks, tiles, terra-cotta, and coarse pottery will leave a residue of 15 per cent. or more of their weight on the sieve. Thus, clays which are rich in sand (*Loams*, p. 202) often contain a large proportion of coarse particles, and boulder clays ("drift") may contain stones of all sizes, from that of linseed to a mass weighing several tons. These "coarse particles" can scarcely be considered as "clay," and the larger ones must usually be removed before the clay can be used.

The limiting proportion of coarse particles which may be present depends largely on the binding power of the clay. If the binding power of the finer particles is very great, they may be associated with a much larger proportion of non-plastic (coarse) particles than when the particles are of a leaner nature. Hence no definite rule can be laid down ; each material must be judged according to the purposes for which it is proposed to use it. Clay for large articles should not be too fine, hence the alluvial clays are, as a rule, unsuitable for this class of work, as the method of their formation has caused them to consist of extremely fine particles, so that they cannot withstand repeated changes of temperature so easily as a coarser clay. It is in consequence of this that the rock clays, shales, terra-cotta, and fireclays—whose particles are much larger—are the most suitable for the production of large ware, particularly if it is to be heated and cooled repeatedly.

In order to effect a simple comparison of the fineness of different clays, W. Jackson suggested the use of a **surface factor** for clay. This is based upon an assumed mean diameter of particles separated into groups by sifting or elutriation. Adopting Seger's figures for the extreme diameters of each group of particles obtained in a Schoene's elutriating apparatus and taking their arithmetical mean, Jackson states that the average diameters of the four fractions obtained are 0·005, 0·0175, 0·0325, and 0·185 mm. respectively, and that the surfaces of equal masses of each group will be in the proportion of

$$\frac{10,000}{50} \quad \frac{10,000}{175} \quad \frac{10,000}{325} \quad \frac{10,000}{1850}$$

or

$$3367 : 962 : 518 : 91.$$

He therefore multiplies the weight of each group by its appropriate ratio, adds all the products together and divides by 100, terming the figure so obtained the "surface factor."

Purdy has suggested a modification of this calculation in which he adopts a more correct figure for the average diameters of the particles in the coarser portion (viz. .080), and instead of finding the highest common factor of the fractions, he divides out and obtains the following ratios:—

$$12.50 : 30.97 : 57.14 : 200.00,$$

which he treats in precisely the same manner as Jackson, but obtains a factor which is only about one-seventeenth as large.

Mellor has shown that both Jackson's and Purdy's factors are of the form

$$\frac{6}{s} \left(\frac{W_1}{d_1} + \frac{W_2}{d_2} + \frac{W_3}{d_3} + \frac{W_4}{d_4} \right),$$

in which s is the specific gravity of the particles W_1, W_2, W_3, W_4 , the weights of each group of particles per unit weight of sample with average diameters d_1, d_2, d_3, d_4 . He has also shown that more accurate values for the mean diameters are obtained by using the formula

$$\sqrt[3]{\frac{(D+d)(D^2+d^2)}{4}}$$

where D is the diameter of the largest and d that of the smallest particle in each group. He prefers to use only three groups of particles (Table XII.), and to include the specific gravity.

TABLE XII.

Maximum Velocity, mm. per sec.	Manometer Height for Flint, cm.	Extreme Diam. Spherical Particles, mm.	Average Diam., mm.
0.18	1	Below 0.010	0.0063
0.30 or 200's lawn	60	0.01 to 0.063	0.042
120's lawn	...	0.063 to 0.107	0.087

Mellor thus obtains a surface factor of the same type as Jackson and as Purdy, but probably somewhat more accurate, and adopting the case where the specific gravity of the material is 2.65 (shown by Hecht to be true for most clays),

$$\text{Mellor's surface factor} = 359W_1 + 53.9W_2 + 26.0W_3,$$

in which W_1 represents the weight of the finest fraction in the above table, W_2 that of the middle fraction, and W_3 that of the coarsest one.

Until some definite agreement is reached it is necessary to state which of these factors is used to represent the fineness of a clay or other material. Whichever is employed, the fineness of the clay will be proportional to the size of the factor, a coarse clay giving a low value and a very fine clay a high one. The surface factor is seldom applied to those portions of clay which will not pass through a No. 100 sieve. A value for the surface factor is necessary in finding the relation of absorption to plasticity.

Coarse clays of granular texture have usually been subjected to some exceptional force since their deposition. In many instances the pressure and other forces expended upon them have compacted them into rock-like materials which are termed "rock clays" (p. 224), "shales" (p. 228), or "slates" (p. 233). These usually have a laminated structure, though this is not so well developed in the rock clays as in the others. This possession of well-defined lines of cleavage is the essential characteristic distinguishing shales and slates from other varieties of clay (see *Sectility* and *Fissility*, p. 280). Some of these indurated clays are composed of grains which are intrinsically fine, but are so compressed that the mass appears to be solid. They may, however, be completely disintegrated by crushing them and then boiling them with water to which a little alkali has been added.

There is a considerable difference of opinion as to the shape of clay particles,¹ some authorities considering them to be *crystalline*, whilst others regard them as truly *amorphous*. The grains of the purest clays are usually too small for their crystalline nature to be definitely observed,² even with the assistance of polarised light, though some crystals or crystalline fragments are almost invariably present. Some of these are obvious impurities, such as fragments of quartz, mica, and other minerals, but others have the same ultimate chemical composition as true clay, or a composition so similar as not to be readily distinguished from it. The nature of these particles has been described under *Kaolinite* (p. 196) and *Materials similar to Clay* (p. 246). The major portion of the particles in a relatively pure clay appears to be amorphous,

¹ The extremely minute particles of clay are so small that their shape cannot be accurately seen even with a powerful microscope. If mixed with several times their weight of water they remain in suspension for several days, and this characteristic *suspensibility* is sometimes used as a test of quality by purchasers of china clay for the manufacture of ultramarine, etc.

² Van Bemmelen states that "clay crystals" average $\frac{1}{100}$ to $\frac{1}{1000}$ of an inch in diameter (see footnote on p. 315).

though various observers have recorded indications of its definitely crystalline character. Thus, Aron supposed the smallest particles to be spherical in shape, but Bierdermann and Herzfeld, on the contrary, considered clay to consist of microscopical hexagonal and rhombic crystals. Hussak confirmed the crystalline constitution of several washed clays examined by him, but found that the crystals were so broken that identification of the crystalline form was almost impossible. Ashley states that any crystalline matter is usually masked by a coating of colloid material.

The possible presence in plastic clays of a considerable proportion of **colloid** matter has recently attracted much attention, though originally suggested in 1874 by Schloesing. It appears highly probable that colloid substances are present in most clays and that they exercise a distinct influence on the plasticity, though the extent to which they do this is not yet clear, some authorities believing that the chief value of clays is due to the colloids they contain. Clays certainly appear to be composed of granular matter covered to some extent with colloidal gels derived from organic matter such as peat, colloidal silicates, silica, and more rarely from alumina and iron oxide. The presence of the granular matter is important, though its influence appears to have been overlooked by some writers (see *Stickiness*).

It may be desirable to explain here that all solid substances when in solution exist in two forms: (*a*) *crystalloid*, in which case the particles can be deposited from the solution in crystals of regular form and possessing definite and constant shapes; and (*b*) *colloid*, in which the particles are so minute that though they appear to be in suspension they also act as though they are in solution. Solutions of crystalloid substances have a high boiling-point; the substances themselves have a comparatively low molecular weight, and only a definite amount can enter into solution; but colloidal solutions have only a slightly supernormal boiling-point; the substances have an indefinite but very high molecular weight and no distinct solubility coefficient. In no case can colloid substances produce a crystalline mass; if they change at all it is to be coagulated. Most colloid solutions are easily coagulated either by heating or by the addition of an electrolyte.

Colloids also differ from crystalline substances in being soft and irregular in form, with only a weak power of combining with water, though they absorb it readily.

Colloids exist in two forms: (*a*) in suspension in a liquid in which they mostly behave like solutions and are termed **sols** or **hydrosols**, and (*b*) as a jelly, whose pores are filled with a liquid, termed a **gel** or **hydrogel**. If they can change from the sol to

the gel state and back again, they are termed "reversible," but gels which cannot be converted into sols are "irreversible." The process of passing from sol to gel is termed "coagulation"; the reverse process is "deflocculation." If a gel cannot be converted into a sol it is said to be "set," and any process which effects this is termed "setting." The cause of this coagulation is still in dispute. Rohland believes it to be due to the direct action of electrolytes, particularly those which on dissociation produce hydrogen-ions, the reverse action, *i.e.* the formation of a clay suspension (sol) being due to an increase in the opposite particles amongst which hydroxyl-ions are the most important, as in the case of water. If the coagulated material is washed with water it may again enter the sol state and become so susceptible that it will not settle and cannot be removed by filtration. The addition of any suitable electrolyte will cause it to coagulate again.

Although colloid matter in the "sol" state may appear to be in suspension it cannot be removed by any process of filtration, but as such a sol is very sensitive to electrolytes it will coagulate immediately on the addition of hydrogen-ions, such as occur in dissociated solutions of most acids, the speed of the coagulation being proportioned to the hydrogen-ions present.

Thus, the presence of hydroxyl-ions usually favours the formation of colloidal solutions, whilst hydrogen-ions act contrarily. This is due to the fact that particles of colloid matter in suspension acquire an electric charge which is positive or negative to that of the liquid, the metallic hydroxide colloids being charged positively with respect to water and others negatively.

Clays, like colloids, are very sensitive to the action of electrolytes, a few drops of a solution of caustic soda or barium hydrate making a stiff clay paste into a fluid. It becomes stiff again on the addition of sufficient acid to neutralize the alkali present. This corresponds very closely to the action of electrolytes or the coagulation and re-suspension (sol formation) of colloids.

An essential difference between colloidal solutions and true solutions lies in the fact that the former do not diffuse, or only very slowly, through membranes of animal tissue, parchment, or similar material, whereas substances in true solution will easily pass through such membranes. Sols may thus be separated from solutions of crystalline substances by allowing the material to dialyse against pure water; the crystalloid then passes through the membrane into the outer vessel of water, whilst the colloid remains behind. When the colloid under investigation is a clay containing salts this process of dialysis is extremely slow, on

account of the clay forming an impermeable membrane of its own, unless means are adopted to prevent it from settling.

Colloidal solutions are seldom perfectly clear, but usually show an opalescence, just as do clays suspended in water. In many cases these colloidal solutions are merely fine suspensions from which the solid can be separated after a long period of settling. Much time is needed, as the particles are so small, though occasionally they are enlarged by their absorption of water, just as gelatin swells on soaking in water. Gelatin may, in fact, be regarded as a typical colloid, from the Greek name of which (*ἡ κόλλα*) the word colloid is derived.

Various investigators have shown that with a negative sol, such as clay in colloidal suspension, the most powerful factor in coagulation is the positive ion of the electrolyte added, the negative ion having but little influence. The power of different positive ions appears to be the same for those of one valency, but divalent and trivalent ions are far more powerful than monovalent ones. Thus Foerster has shown that if a clay contains just enough calcium-ions to keep the colloidal matter in gel form, and sodium carbonate is added, the sodium will combine with the colloid clay and will form a sol, the plasticity being reduced according to the completeness of the reaction, but if an excess of sodium-ions is added they will re-coagulate the colloid. This has been confirmed by experiments on the viscosity of clay slips by Mellor and others.

Adolph Mayer has determined the limiting amounts of electrolytes which will permit a fine clay (freed from soluble salts by treatment with hydrochloric acid) still to be kept in suspension in water (100 grammes clay, 500 cubic centimetres water). The limits are: ammonia, 2.5 per cent.; sulphuric, hydrochloric, and nitric acids, and the alkali salts of these acids, 0.025 per cent.

Although 2.5 per cent. of ammonia caused precipitation in Mayer's experiments, a less amount favours the deflocculation, or breaking-up of the lump.

According to Hardy, the concentration of acid or alkali necessary to coagulate the particles is determined by the ordinary laws of chemical equilibrium, and the specific electric conductivity varies as the sum of the velocity of the two ions and as the fraction of the total number of molecules dissociated at any one moment.

The best-known inorganic colloids are hydrated silica, alumina and iron oxide, the hydroxides of various other metals, copper ferrocyanide, "Berlin blue," gold, silver, platinum and copper.

The chief organic colloids are peat, starch, dextrin, white of

egg (albumen), tannin, rubber, inulin, glycogen, agar-agar, glue, gelatin, and various gums. Van Bemmelen states that soils contain colloids—colloidal silicates, ferric oxide, silicic acid, humic substances—all of which can show the above effects. The absorption (adsorption) effects on treating soils with solutions are principally to be attributed to the colloidal silicates. The colloidal matters in clay are therefore non-crystalline, hydrated, gelatinous alumino-silicates, organic colloids, gelatinous silicic acid, and hydrated ferric oxide. Colloidal aluminium hydrate may also be present.

The absorption of water by a colloidal mass in the form of a gel is accompanied by a large increase in the volume of the mass, as is familiar in the case of gelatin and starch grains, but the total volume of colloid and water diminishes during the absorption, so that the net effect is a small contraction. Hence, when clays containing colloidal matter are mixed with water the volume of the mass of clay is largely increased, but the total volume of water and clay—before mixing—is always slightly greater than that of the clay-water mixture.

Colloidal substances in the gel state also absorb dyes, to which crystals are largely inert, so that it is possible to stain colloids without affecting the crystalloids in a mixture, and so to render the colloids more easily distinguishable. The amount of colloids in clays has been measured by staining a small portion and measuring, under a microscope, the total area of the stained portion, and comparing it with the total area of the sample so treated. The amount of dye absorbed has also been used for measuring the plasticity of clay.

Coagulated substances (gels) possess a peculiar kind of porosity, whereby they can form a filter which will only permit certain substances to pass through it, even though all are in solution. Such semi-permeable membranes are used to separate certain crystalloids from others, but are useless for separating two colloids. The reason for this behaviour is unknown, and the speculations upon it are beyond the scope of the present work; but the curious properties of colloids are highly important, as they explain many facts observed in the behaviour of clays, notably as regards plasticity and absorption.

Just as colloid solutions become stiff and jelly-like as soon as they have absorbed sufficient water to dissolve the colloid matter, and being super-saturated are ready to coagulate, so clays become stiff in a precisely similar manner.

Colloid gels, on drying, shrink greatly, and if organic, they have both a drying shrinkage and a kiln shrinkage just like plastic clays.

By mixing an inert substance, such as sand, with a colloid, the shrinkage is lessened, and the cohesion of the dried colloid, including its adhesion to the inert substance, are the causes of the increased mechanical strength of many such mixtures. This is another characteristic common to all colloids and to plastic clays.

The presence of colloids in solution hinders the formation of crystals; this may explain why so few crystals are found in clays, and may confirm the view originally proposed by Johnson and Blake, that the composition of the purest china clays (kaolin) is identical with that of kaolinite, though the former is, apparently, largely amorphous and the kaolinite is crystalline.

In addition to the properties already mentioned, plastic clays behave in a manner so similar to colloid substances as regards viscosity, surface tension, and plasticity, that there can be little doubt that some clays contain colloidal matter to a very important extent, though the proportion of it varies greatly.

The study of colloids is highly complicated on account of their indefinite nature, but the close parallelism between the behaviour of many clays and colloid substances renders an elementary knowledge of the subject desirable to all interested in the constitution of clay and in its plasticity and shrinkage.

The particles of clay and other substances in a deposit often appear to arrange themselves so as to form a structure similar to that of an extremely complex arrangement of minute tubes (**capillary structure**), so that on allowing the mass to dry, the moisture at the surface first evaporates and is replaced by other water from the interior of the mass, which travels outwards by "capillary attraction," until all the water which can be carried to the surface has been evaporated (see *Drying*, p. 343).

The **specific gravity**, density, or relative weight of a clay is of theoretical rather than of practical importance.

The term **density** is often used very loosely in connection with clay. Strictly speaking, it relates to the specific gravity of the particles forming the mass, but it is occasionally used to indicate impermeability, a sample of clay being, in this sense, said to be dense because water will not penetrate easily into it.

Occasionally the term density is used as distinct from specific gravity, the former indicating the relative weight of the whole mass and the latter that of each particle considered separately or the average of all such particles. In this sense the density changes with the treatment undergone by the clay whilst the specific gravity remains constant. This use of the term density is better replaced by the more cumbersome but clearer term **volume weight**, which indicates the weight of a mass of ascertained

volume, that of an equal volume of water being taken as unity. It is ascertained by measuring the volume of such a mass as accurately as the nature of the material permits, weighing it, and dividing this weight by that of an equal volume of water. Various appliances for determining the volume weight of clay have been devised, that of Seger's (fig. 17) being usually adopted. This consists of a four-litre, wide-mouthed, glass-stoppered jar. A circular opening in the centre of the stopper is fitted with the ground-end of a short glass tube *m*, which expands above into a bulb *b*, and is again contracted above it. The jar has a glass stopcock *e* near its base, which is connected above with a burette *a* of 125 c.c. capacity, and graduated to tenths. The upper end of the burette also widens to a bulb *f*, from the top of which there extends a bent tube for the attachment of a rubber, this tube being used to draw the liquid into the burette.

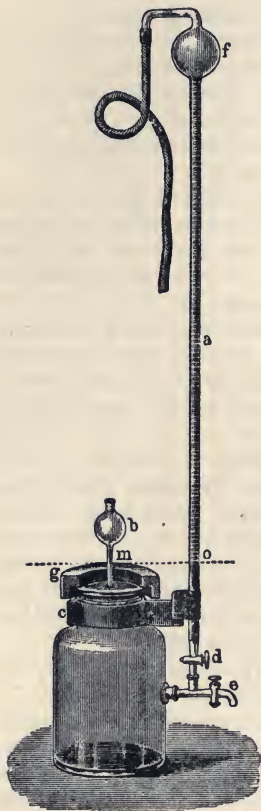


FIG. 17.—Seger's Volumeter.

When the stopcock in the lower part of the burette is open, and the liquid filled in jar up to the mark on small glass tube *m*, the liquid stands at the zero-point in the burette.

The method of using the apparatus is as follows:—

“To use the volumeter for determining the volume of clay, it is filled with oil, ordinary kerosene with a specific gravity of 0.8 (which must be accurately known) having been found to give satisfactory results.

“After filling the jar the burette is drawn full of the liquid by suction through the rubber tube, and held full by turning the burette-valve or by means of a pinch-cock on the rubber. The stopper is now removed and the test piece of the clay, which is still plastic and permeated with water, is carefully wiped dry of the coating film and put in the volumeter.

“The stopper is now replaced, and by turning the tap or cock *d*

oil from the burette is allowed to flow back into the jar until it again stands at the mark on the short tube *m*.

“The volume of the clay is then indicated by the height of the liquid in the burette above the zero mark. The piece of clay is taken out and placed to dry, while the volumeter is again filled to the zero point to be ready for the next test.”

The **specific gravity** of a clay is the average weight of its particles considered separately relatively to that of an equal volume of water. It is constant for any sample of clay, no matter what mechanical treatment it undergoes, and its determination is only required in ascertaining the porosity of the material.

There is but little variation between the specific gravity of different raw clays, the range being from 2.5 to 2.7. Lower figures generally refer to the volume weight of the clays, or are due to the inclusion of air in the mass. They thus represent the “apparent specific gravity,” but this term is so liable to confusion as to make it desirable to use the term volume weight, and to restrict the use of the term “specific gravity” to that of the true gravity or true density of the actual substance, determined on a portion of the material which has been reduced to so fine a powder that the existence in it of sealed pores is a matter of great improbability. The true specific gravity is most conveniently determined in a pycnometer of the ordinary type, care being taken to extract all air by constantly shaking the material and water together and repeatedly exhausting the air. If the clay is in large pieces and it is not desirable to crush it to powder, a Seger’s or other volumeter may be used, and the specific gravity found by the following formula:—

$$\text{Sp. gr.} = \frac{W}{V - P},$$

where W = actual weight of the sample,
 V = apparent volume (including pores),
 P = volume of pores, ascertained from porosity.

As clays tend to retain air very tenaciously, the figures quoted for specific gravity are often too low. It is therefore desirable to adopt Hecht’s suggestion and employ a much larger pycnometer than usual—one of 300 c.c. capacity being convenient—and to boil the clay with water for several hours with constant stirring. The slip thus produced is allowed to become quite cold and is then placed in the pycnometer. The latter is filled up with water and then weighed accurately. After the clay has settled, the bulk of the clear water may be syphoned or decanted off, the

remainder evaporated, and the weight of dry clay in the pycnometer thereby ascertained.

Where the specific gravity of a highly plastic clay is required, Hecht recommends that some of the material should be well kneaded with water to remove all the air and then divided into two portions. Each of these is weighed accurately, and the volume of one ascertained in a volumeter. The other is dried thoroughly, and from the weight of dry clay present the weight of dry clay corresponding to the other portion is calculated. The volume of dry clay may also be calculated and the specific gravity ascertained by dividing the former by the latter.

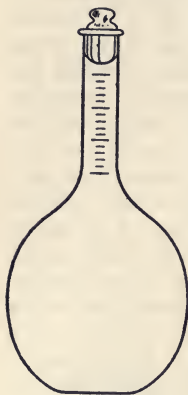


FIG. 18.

A method which is particularly convenient for ascertaining the true specific gravity of burned clays is that suggested by Stanger and Blount for cement. The pycnometer used has a graduated neck (fig. 18), the capacity to the lowest mark being exactly 65 c.c. and to the top mark 80 c.c. In making a determination, 50 c.c. of paraffin or water are introduced into the instrument by means of a pipette, and afterwards exactly 50 grms. of the powdered material are introduced through a small funnel. If it is not convenient to use exactly 50 grms., a portion weighing slightly more than this may be introduced into the apparatus, and its exact weight determined by weighing the pycnometer before and after the introduction of the material; it is, however, usually more convenient to weigh out the exact quantity.

After tapping and shaking, to dislodge any air bubbles, the level of the liquid is read off on the graduations. The volume of liquid displaced is equal to the volume of the clay added, and the specific gravity is found by dividing the weight of clay added by the volume of liquid displaced. Thus if 50 grms. of material occupies a volume of 20 c.c., the specific gravity will be 2.50.

The change in the specific gravity affected by heating clays is discussed later (p. 379).

The **porosity** of a raw clay, as distinct from its permeability, is much less important than that of the same clay after it has been heated, though the more porous the clay the easier it is to dry without disintegration. The addition of sawdust and other combustible materials does not affect the porosity of a raw clay, but on firing they become important (see p. 336).

The determination of porosity is sometimes made by soaking the material in a suitable liquid, such as xylol, as described below, or by using a Seger's volumeter (p. 290).

Heath and Mellor have improved upon this instrument by arranging so that all the air may be exhausted from the pores of the material before it is placed in the fluid. Unless this air is removed (and it cannot be by simple immersion, owing to the small size of the pores) the porosity figures will be low, and if the instrument is used for measuring the volume of a clay, in order to ascertain its specific gravity, the latter will also be low.

In the improved volumeter C is a glass vessel about 250 c.c. capacity closed with a ground-glass stopper A, sealed on to a capillary tube B. The capillary has a mark B. The bottom of the vessel C is sealed on to a glass tube connected with a stoppered burette E, and a 250 c.c. bulb F¹ blown at the opposite end. This is closed by a perforated stopper, fitted with a glass and rubber tube G, as shown in diagram.

Heath and Mellor operate as follows:—

1. About 270 c.c. of liquid is introduced, and by blowing or suction at G the liquid is adjusted until it reaches the mark B. The level of the liquid in E is read off. The liquid is then run from C to F by suction at G and the stopcock D closed, the apparatus being tilted, if necessary, to secure the removal of the whole of the liquid.

2. The weighed sample is then placed in C, the stopper re-inserted, and connected at B with a good water pump. After about fifteen minutes' exhaustion the stopcock D is opened and sufficient liquid is allowed to run from F to cover the piece of ware in C. The rubber tube connecting the apparatus to the pump is then removed from B, and the liquid allowed to run from F into C until it reaches the mark B. The level of the liquid is again read in the burette. The difference between this and the first reading gives the volume of the air spaces inaccessible to the liquid plus the volume of the solid (= a).

3. The liquid is again drawn back to F, the piece removed from C by means of a pair of forceps, and wiped with a piece

¹ In the illustration the bulb F is shown smaller than the vessel C; it should be nearly the same size.

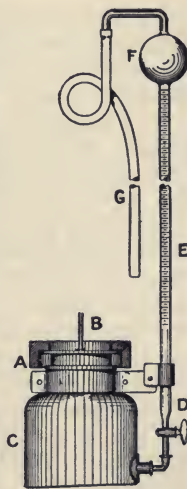


FIG. 19.

of blotting-paper. The liquid is again returned to C, and the volume of the liquid in E again read off.

4. Finally the liquid is sucked up into F and the piece returned to C. The liquid is allowed to run back into C until it reaches the former level B. The difference between this reading and the one immediately preceding gives the total volume of the piece (including all pores) ($=\beta$).

$$\begin{aligned} \text{Then} \quad \text{Volume of pores} &= \beta - \alpha. \\ \text{Porosity} &= \frac{100 (\beta - \alpha)}{\beta}. \end{aligned}$$

In order to prevent movements of the stopper A while the measurements are in progress, the stopper may be clamped by two screws on to the body of the vessel C, but a heavy weight (as shown) is usually sufficient.

The **magnetic** properties of clay have not been extensively studied, though Laurence has found red bricks in the University of Rochester, U.S.A., which were distinctly magnetic, though all the white ones examined were free from this property. This implies the presence of magnetite (magnetic iron oxide) or of other minerals capable of affecting a magnet. Sidot has shown that at a "white heat" ferric oxide is converted into magnetite and so becomes magnetic. So far as is known, clay is in itself non-magnetic, but in addition to the well-known magnetic minerals (of which magnetite is typical) several feebly magnetic ones occur in clays, the most important being limonite, hæmatite, pyrites and chalcopryrite, though unless they were formed during the cooling of the kiln it is difficult to see how such materials could retain their magnetism when made into bricks. Hopwood has drawn attention to the fact that the black specks present in many red clay wares are generally magnetic, as are all ferrous silicates. Zirkel has found that fused phyllite ($\text{FeOAl}_2\text{O}_3\text{SiO}_2\text{H}_2\text{O}$) is magnetic.

The **conductivity** of clays for electricity is tolerably constant for the raw material, but varies considerably in the fired goods, and it is only when the latter are used for electrical instruments, etc., that it becomes important commercially.

The electrical conductivity of clay may prove of value in its purification, as Blake, Morscher, and Swarte have patented machines for separating good conductors from other materials, the most important of which to the clayworker are:—

Good Conductors.—Native minerals, pyrite, chalcopryrite, erubescite, galena, graphite, molybdenite, copper glance, argentite, metallic sulphides, tellurides, and copper and silver ores.

Bad Conductors.—Quartz, sandstone, granite, porphyry, schist,

spinel, blende, calamine, barytes, gypsum, fluorspar, and silicates including clays.

The process has not, however, been applied on a large scale to clays on account of the small size of the clay particles.

The electrical conductivity of clays is also important in studying their physico-chemical nature, particularly their viscosity and plasticity.

The so-called **chemical properties** of clays are, chiefly, those which concern its behaviour to various other substances (reagents) and the changes which occur in its composition when heated.

Pure clay is insoluble in dilute hydrochloric, nitric, or sulphuric acid, but is readily decomposed by boiling sulphuric acid and hot solutions of soda or potash. It may also be decomposed and rendered soluble by fusion with alkalis, or with alkaline carbonate, or with lime and ammonium chloride.

J. M. van Bemmelen has found that some clays yield a much larger percentage of soluble matter to hydrochloric acid than others. He uses this feature as a means of distinguishing clays produced by weathering from those produced by pneumatolytic action, on the assumption that the latter are practically unaffected by boiling hydrochloric acid. His method of separation is admittedly defective, but in the present state of knowledge it appears to be of distinct value. The method of procedure is as follows:—

Three grammes of finely powdered clay is boiled with 50 c.c. concentrated hydrochloric acid (sp. gr. 1.2) for a quarter of an hour. The liquid is decanted and the residue boiled with a fresh quantity (50 c.c.) of acid for a further fifteen minutes. The liquid is again decanted and the residue boiled a third time with 50 c.c. hydrochloric acid, this time for half an hour. The liquid is decanted a third time and the residue neutralized with caustic soda and then heated with 50 c.c. caustic soda solution of sp. gr. 1.04 for five minutes at a temperature of 50° to 60° C. The acid and alkaline solutions are diluted, filtered separately, and then mixed; the alumina and silica in the mixture are determined in the usual manner.

Although the value of this method cannot be ascertained until a very large number of experiments have been made, the use of sulphuric acid in a corresponding manner (see *Rational Analysis*, p. 298) has proved unsatisfactory, except for a very limited number of clays.

Hydrofluoric acid attacks clay readily if warm, the silica being converted into gaseous fluoride which volatilizes.

Boiling sulphuric acid decomposes clay, though not always completely, and this property has long been used as a means for ascertaining the proportion of other minerals contained in "clay." Unfortunately this so-called "rational analysis" is not reliable, though with comparatively pure clays like china clays its results are sometimes valuable.

Ordinary clays naturally behave to reagents according to their constituent minerals. Thus, when heated in a blow-pipe flame and then treated with cobalt solution they give a blue colouration characteristic of alumina, though this is only clearly visible with white-burning clays.

The effects of the different constituents in a clay have already been partially described in Chap. VIII. (impurities). They are most notable in connection with plasticity, shrinkage and when clay is heated (see later).

The effect of adding other substances to a clay depends on the nature of each. Thus, a highly refractory clay will be rendered more fusible by the addition of any flux such as lime, potash, soda or iron compounds or even silica, but an easily fusible clay will be less affected, and the addition to it of siliceous material may make it less fusible.

The addition of combustible matter to a clay increases its porosity when fired, but may make it more difficult to burn.

The addition of an alkali to a raw clay has the effect of making it more fluid, but if the alkali is neutralized by an acid the stiffness of the material returns. This property has been made the basis of a method of manufacturing glass-pots and other large articles by Weber.

The substance of most importance in its action on raw clay is water, the effect of which is described in a later section.

The behaviour of clay to other substances depends largely on the extent to which they are mixed together and the temperature to which they are subjected. Clay is curiously sensitive in many ways whilst correspondingly inert in others, and the presence of other materials in it is often of great importance. Their effects are most noticeable on its plasticity and behaviour when heated, and are therefore considered separately.

Owing to their similarity in composition to many other minerals, and to the frequency with which these occur in deposits of "clay," there is no distinct means of separating the true clay in such a deposit from its constituents, though much may be done by careful washing in an elutriating apparatus. Hence the "chemical properties" of clay are by no means easily definable.

All that can be done is to separate the material into different

portions, according to the size of the particles, by means of an elutriating apparatus, and then to make an analysis of as many of these portions as may be considered necessary. It is seldom necessary to make more than two such analyses—one of the portion which includes all the coarser particles, and another of the finest portion, but each case must be determined on its own merits. It will usually be found that two such analyses and a careful microscopical examination will supply sufficient information to enable the proximate composition of the clay to be estimated with sufficient accuracy for all practical purposes, though it must be remembered that in most industries using clay its behaviour under certain conditions of manufacture is usually of far greater importance than a knowledge of its composition.

For this reason it is useless to attempt to define strict limits of composition in clays to be used for certain purposes, though in practice this is often done. Thus it is usual to consider that a fireclay is of poor quality if it contains more than 4 per cent. of lime, magnesia, and alkalis, or 3 per cent. of iron. These figures are purely arbitrary, but being based on practical experience are often convenient.

It is sometimes stated a clay for brickmaking should contain 60 per cent. of silica and at least 20 per cent. of alumina and iron oxide, but this is not to be regarded in any sense as a true standard of composition, as bricks may be made successfully from the purest clays with only 45 per cent. of silica and from pure sands containing 98 per cent. or more silica.

The chemical composition of a clay must, therefore, be regarded as valuable within certain very narrow limits, its importance being much increased when it is accompanied by other data, though it is seldom sufficient by itself to determine either the value or uses of a clay, even when accurately made. The number of incorrect analyses of clays found in various publications is appalling, and throws doubts on many which may be worthy of full confidence.

In order to make analyses of different clays more readily comparable, the material should be dried at 100° to 110° C. until its weight is constant before being analysed. Its *ultimate composition* may then be stated as in Table XIII. (p. 298).

Such a statement merely expresses the proportion of the different ingredients in the form of oxides, without showing their state of combination.

It is seldom that all the constituents in Table XIII. are determined, the loss on ignition being considered a sufficient guide to the amount of sulphur trioxide, carbon dioxide, organic matter and combined water present.

TABLE XIII.

	Silica	(SiO ₂)	per cent.
	Alumina	(Al ₂ O ₃)	"
Fluxing Impurities.	Ferric oxide	(Fe ₂ O ₃)	"
	Ferrous oxide	(FeO)	"
	Lime	(CaO)	"
	Magnesia	(MgO)	"
	Potash	(K ₂ O)	} alkalis
	Soda	(Na ₂ O)	
	Titanic oxide	(TiO ₂)	"
Loss on Ignition.	Sulphur trioxide	(SO ₃)	"
	Carbon dioxide	(CO ₂)	"
	Organic matter	"
	Combined water	(H ₂ O)	"

In some instances the alkalis are not determined, but are obtained by subtracting the sum of the other ingredients from the total weight or percentage of clay. This estimation "by difference" often gives seriously erroneous figures, and it is far better to determine the alkalis and to take the silica "by difference," if a complete analysis cannot be made. An error of 0.5 per cent. in the alkalis may be serious, but one four times this size in the silica will seldom be of commercial importance. In the case of clay intended to be used for Portland cement the alkalis are less important than the silica.

The methods of making an ultimate analysis of clays vary greatly in different laboratories. A general outline may be found in any text-book on analysis; a more detailed description is outside the scope of this volume.

The value of an ordinary (ultimate) chemical analysis consists chiefly in showing the presence or absence of an excess of any desired constituents—as the alkalis, lime, magnesia, and titanium oxide in a refractory clay, the iron in a buff-burning clay, the silica in a clay to be salt-glazed, etc., but it gives little or no information on the behaviour of a clay in the manufacture of ordinary goods.

The **rational analysis** of a clay purports to show the percentage of various ingredients of a clay and to state the proportion of true clay, quartz, and felspar or mica present. At the first sight this is a great advantage, but greater familiarity with this method of analysis shows that it is far too unreliable for its indication to be used except in special cases.

Many precautions and so high a degree of skill are required in making a "rational analysis" of a clay, and the results, when obtained, are so unreliable, that a full description of the process is unnecessary; suffice it to say that it consists in treating the

finely powdered material with hot concentrated sulphuric acid for a considerable time. It is then allowed to cool, is diluted with water, and filtered, the residue being treated several times with boiling solutions of caustic soda and hydrochloric acid alternately. The residue finally obtained (consisting of felspar and quartz) must be

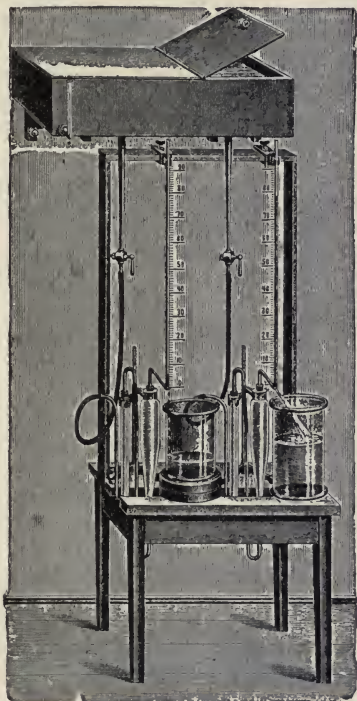


FIG. 20.—Schoene's Elutriating Apparatus as used at the Seger-Cramer Laboratory.



FIG. 21.—Schoene's Tube (see fig. 20).

analysed. The matter dissolved by this treatment is presumed to be the "clay" in the original material.

The **mechanical analysis** of clay consists in treating the material with sufficient water to enable it to be separated into particles of different sizes and densities. It may be carried out in a variety of ways, but is, in any case, merely an elaborate form of sifting, and is not concerned with the composition of the different ingredients.

The finest particles—those less than 0·010 mm. in diameter—are sometimes termed “clay-substance,” but there is not sufficient justification for so naming them, as on analysis they will often be found to contain other ingredients than true clay, such as iron oxide and extremely minute particles of silica and other minerals.

The method of mechanical analysis commonly used in Great Britain is that devised by Schoene and modified by Seger. It consists in passing a carefully regulated stream of water through a series of vessels (figs. 20 and 21) so arranged that the speed of the liquid may effect a separation into several groups. Seger used five groups for this purpose for all “clays” of which the particles are less than 0·33 mm. in diameter (Table XIV.), but as this involves the use of a large amount of delicate apparatus, and is inconvenient in many ways, it is convenient to employ (standard) sieves more extensively (see the author’s *Clayworker’s Handbook*, p. 315), and Mellor has proposed to effect the separation of only one group by elutriation (Table XV.). (See also p. 283.)

TABLE XIV.

SEGER’S FRACTIONS BY ELUTRIATION.

Maximum Velocity, mm. per sec.	Extreme Diam. Spherical Particles, mm.	Manometer Height, cm.
0·18	Below 0·010	1
0·70	0·10 to 0·25	8
1·50	0·25 to 0·04	50
Residue.	0·04 to 0·333	...

TABLE XV.

MELLOR’S FRACTIONS BY ELUTRIATION AND SIEVES.

Maximum Velocity, mm. per sec.	Manometer Height for Flint, cm.	Extreme Diam. Spherical Particles, mm.	Average Diam., mm.
0·18	1	Below 0·010	0·0063
0·30 or 200’s lawn	60	0·01 to 0·063	0·042
120’s lawn	...	0·063 to 0·107	0·087

In order to overcome the fragility of Schoene's apparatus, Krehbiel in 1904 suggested the use of a series of metal containers. In this apparatus the sizes of the different vessels are so arranged that if the speed of the water is regulated for the first of the series, the others need no attention. For most purposes Krehbiel's apparatus (fig. 22) is the most convenient yet devised, though it takes several days to effect a good separation; the amount

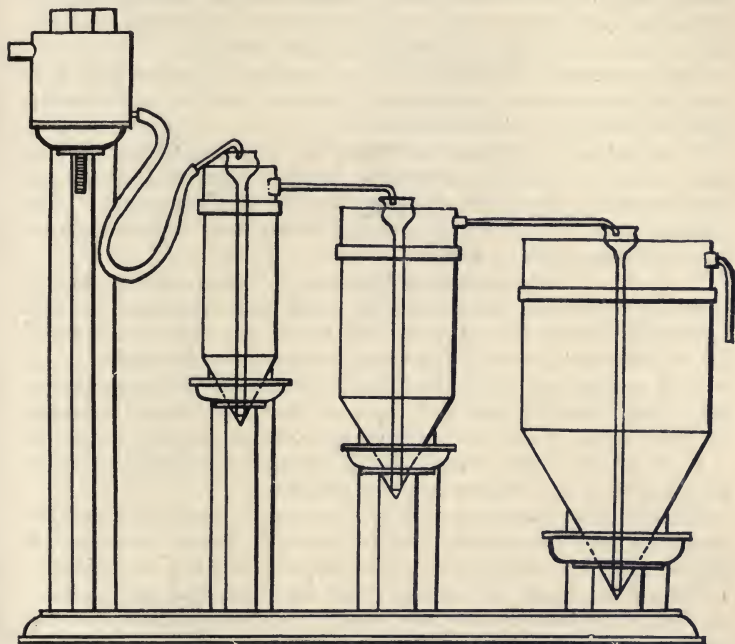


FIG. 22.—Krehbiel's Elutriating Apparatus.

of water used is very large and the results obtained are not strictly comparable with those obtained by Schoene's apparatus.

A centrifugal apparatus for separating clays has been employed regularly since 1900 in the United States, and is stated by Ries to be "the most satisfactory method." As ordinarily employed, the cylinders containing the clay are hung by one end on trunnions, so that in action they swing upwards and rotate horizontally, but it is often much more convenient to use a wider cylinder which rotates on its vertical axis at a high rate of speed (Gee's patent,

p. 166). In this way a dual action is obtained, the various particles being first driven to the sides of the cylinder, and afterwards creeping down it so that they arrange themselves in order according to their size and density. With this machine the amount of water used is much less than with the Schoene or Krehbiel apparatus, and the material is obtained in the form of a soft paste. So far as the author has been able to check results obtained with it, the Gee apparatus yields perfectly reliable results, if the speed of rotation, the amount of material and water, and the rate at which the slip is supplied are kept constant.

The proximate analysis of a clay consists in endeavouring to separate the various constituents from each other and stating their proportions. It is based on—

1. A preliminary separation of the clay into particles of various sizes, these being named according to their physical rather than their chemical properties, as stones, gravel, sand, dust, etc. This separation is effected by the use of sieves and, if desired, by a mechanical analysis (p. 299).

2. By an ultimate analysis of the finer portions, it being usually sufficient to take all those particles which pass through a No. 200 sieve together for this purpose. If necessary, similar analyses of the coarser portions or of the whole material are also made.

3. A microscopical examination of the various portions, preferably with the aid of polarised light, so that the various minerals present may be identified and their proportions roughly computed.

4. By a calculation, based on (1), (2), and (3), of the probable proportions of the various minerals present.

Whilst by no means perfect this proximate analysis gives the most complete information obtainable at the present time regarding the chemical composition of the clays to which it is applied.

Where the work of testing must be shortened as much as possible, a sufficiently accurate idea of the composition of a clay may sometimes be obtained by means of an ultimate analysis, the alkalis, lime, and magnesia being calculated as mica or felspar (unless a considerable quantity of calcium carbonate is present, when this must first be calculated from the lime and carbon dioxide), the iron oxide retained as such, and any alumina and silica not required in calculating the bases to mica or felspar being calculated as true clay. Any excess of silica still remaining is considered to be in the free state. The amount of combined water in the material analysed is sometimes puzzling when this calculation is made. As true clay contains 13 to 14 per cent. of water, it is clear that a certain proportion must be present in any material containing clay. Frequently, however, there is a serious

deficiency of such combined water, and the analyst must then decide for himself the best course to pursue. It is, of course, always open for him to consider that hydrated aluminosilicates other than clay, as well as hydrated mica, etc., may be present in notable quantities. There are obviously certain clays to which such a method of calculation cannot apply, and in any case its value will depend on the nature of the minerals present, and these cannot always be accurately ascertained by a cursory microscopical observation. Yet, in spite of its limitations, such a calculation is fully as reliable for most clays as is a "rational analysis."

The Effects of Exposure on Raw Clay.—The general effects of exposure of clay are included under the term **weathering**, but they are sometimes subdivided into (1) wintering, (2) summering, and (3) maturing. The first of these subdivisions includes all the effects produced by exposing a clay to rain, wind, and frost, the second is limited to the exposure of the clay to dry warm air and sunlight, with possible occasional showers; and the third is concerned with the effects which occur when clay paste or slip is stored. These last are described under *Souring*.

The object of weathering a clay is to separate the particles by natural mechanical and chemical means so as to save expense in crushing, and to yield a more convenient product, but in addition to this mechanical advantage many clays undergo marked changes in character on exposure. These changes are usually advantageous, but some clays are better if used direct from the pit, though these are comparatively rare.

Many of the effects of exposure on rocks have already been described in Chap. II. Some of these occur equally with clays, but the chief results of exposing the latter are a reduction in the density and cohesion of the material as a whole, an increase in its porosity, the oxidation of some of its constituents, and the removal (when water is present) of some of the soluble substances.

A number of minor changes, such as the decomposition of certain minerals contained in the clay by water containing carbonic acid, humic acid, and other substances in solution, and a number of obscure chemical reactions, also occur.

Clays vary greatly in the extent to which they are affected by exposure; some show a marked difference when exposed in a shed for a single day, but others are scarcely affected by several years' exposure in the open air without any protection whatever, and eighteen months is generally considered the minimum exposure desirable for some shales. Yet to work some clays without first exposing them is often to court failure, and not a few shales have been exposed for years before they were in a fit condition for use.

So important is weathering, in some cases, that bricks made from clay direct from the bank and broken down by powerful machinery will not dry sound, whereas the same clay, after a preliminary crushing and two days' exposure to the air, will make a brick which is in every way satisfactory.

For mechanically breaking up raw clay, no means yet devised by man have proved so effective as frost, and many works would be closed were it not for the beneficent influence of this agent.

Frost acts chiefly by converting the moisture of the clay into ice, which occupies a larger volume than the original water, and in expanding it tends to drive the clay particles asunder, whilst the water enveloping these same particles tends to compress them together in other directions by its own expansion. The result is compressive shear and an expansive movement, both taking place at the same time and producing a result which, if it were only under more complete control, and could be carried out with somewhat less labour, would do much to remove most of the grinding and crushing machinery from the brickyards of this country.

Attempts have been made on a small scale to winter clay by artificial means, but the employment of freezing chambers has hitherto been found to be more expensive than grinding the clay by machinery. On this account it is necessary that the clay should be exposed as much as possible, and that it be kept sufficiently moist. The clay should be spread out in thin layers—the thinner the better—so that it may be as fully exposed as possible to the rain and frost, or to the effect of the sun and air, which is equally satisfactory with some clays. Some firms tip the raw clay out of the small waggons or "tubs" in which it has been raised from the pit, so as to form long stacks or "banks," fresh banks being started as existing ones become of too great a length. As each tub is tipped down the bank it is carefully looked over, and all visible bats and lumps of ironstone, locally spoken of as "cannocks," are picked out. If possible, the material should be frequently turned over and mixed so as to expose each particle to the action of the weather; and water should be sprinkled on once or twice daily, especially during dry, cold weather, in order that it may be fully capable of benefiting to the utmost when the frost arrives. The fact that many Midland tile-makers claim that wet weather retards rather than helps the weathering of their clay only confirms what has already been stated above, that clays differ so much in their constitution that what may be well suited for one may prove to be unsatisfactory with another clay. Frost

is far more powerful in its action than any machinery can be, as with it disintegration takes place from within the particles, rather than from outside them, and produces a number of other effects which cannot be exactly produced by the use of machinery at the present time.

In this country the weathering of clay is not carried out to so large an extent as in many others, because of the relatively high cost of labour and on account of the comparatively mild winters. The result of the latter is that the weather has little or no effect on clay at a depth of more than 12 or 14 inches below the surface, so that a large amount of land is required to weather a comparatively small amount of clay. In some other parts of Europe the frost penetrates to a depth of three feet or more, and proportionately less ground is required for storage of the clay.

Clays vary greatly in the number of times they require to be frozen and thawed to reduce them to a convenient state for working, but it is seldom possible in practice to expose to more than one intense frost, as the amount of clay to be dug requires that a comparatively thick layer be spread on the land (land for this purpose being usually somewhat scarce), so that the frost only affects the topmost layers. On this account special attention must be paid to the weather, in order that after a frost a fresh lot of clay may be dug and spread over the previous layers.

It is a mistake to suppose that no weathering takes place except in wet or frosty weather. Many clays simply need exposure to the air for them to break up, and it frequently happens that a couple of days' exposure in dry summer weather will have almost as much effect as subjecting them to a whole winter's rain, frost, and snow. When this is the case, no pains should be spared to secure the advantage thus easily gained. Thus, it is always as well to let a surface clay lie in a shed for some weeks before using, as this exposure disintegrates or air-slacks the particles, and distributes the moisture evenly throughout the material. A better and more even colour, and denser goods, can be obtained in this way.

This is one reason why machine-crushing is not so effective as weathering. Machinery does all the work of frost, but it cannot do the chemical work effected by exposure to air, this latter being so powerful with some clays, as those of Ruabon, that an exposure of forty-eight hours at *any* season is sufficient, though exactly what reactions occur in this short time is by no means clearly understood.

When clay is exposed to air in sheds, the reactions which occur are chiefly of an oxidising nature, as when ferrous compounds are

converted into ferric ones by the oxygen in the air. The same reactions also occur when clay is exposed in the open in fine weather. Thus nodules of "ironstone" which may have been overlooked, or hidden away in the heart of large lumps, may, if exposed to the air, be oxidised on the surface, thus enabling them to be more easily seen and picked out. This superficial oxidation covers them with a brownish film of limonite and ferrous sulphate.

If such nodules are composed of marcasite or pyrite they may be converted into sulphate and be rendered harmless in the kiln, though pyrite is far less susceptible to weathering than is the marcasite. The copper sulphides chalcopyrite and erubescite behave like pyrite and marcasite respectively, but form iron and copper sulphates. Selenite and gypsum break up readily under atmospheric influences, and some lime and sulphur are thereby removed from the clay. Alkaline impurities also, unless a high percentage be present, are to a great extent broken down and washed away by water, the clay being thereby freed from these injurious fluxes. Sometimes additional reactions occur as the result of this oxidisation, as when pyrites which has been oxidised to sulphate reacts with limestone, forming gypsum and iron carbonate. Sunlight appears to have some effect on clay and to facilitate the oxidation.

A general effect of weathering is to cause the clay to become more open and more homogeneous than when first dug, so that it mixes better with water, and produces a paste which passes more evenly through the brick machine. In this way it makes less trouble and increases the output by reducing the number of stoppages and the amount of power needed to work and grind the clay; this saving being, in clays really requiring weathering, greater than the additional cost involved. After being left to weather during the winter the clay is usually drier, and sometimes has less tendency to shrink in the kiln.

More frequently, clay which has been weathered has increased in plasticity and is thereby rendered more valuable.

Some clays are not sufficiently influenced by exposure to make "weathering" desirable; certain fireclays and some marls are of this class. Others are spoiled by exposure, as the pyrite in them may oxidise and be distributed throughout the whole mass, thereby spoiling the colour of the fired goods; these cases are, however, rare.

The reason that wintering the clay has gone out of fashion so much in recent years is chiefly the result of competition, which causes brick manufacturers to eliminate all processes which do not seem to them to be absolutely necessary in the production of a

saleable brick. The pride of the manufacturers of the earlier days was to make the best bricks they could, and no pains were spared to effect this end. At the present time the average brick manufacturer cares little for the durability of his product, and is content as long as he can turn out something which he can sell as "bricks." He does not concern himself with the durability and some other desirable characters of his goods, but judges them chiefly by their appearance and other properties of a more temporary character.

Where an exposure of not more than one week is ample, as it is in certain clays, the cost of weathering is not more than a few pence per ton, for all that is needed is to let the clay lie as it falls, and to so arrange that before it is placed in the waggons it shall have had the necessary exposure. Unless the clay-hole is unusually small this is easily arranged.

When careful records are kept of the relative cost of grinding and making up clay which has been weathered, with that which has been used directly it has been mined, it is easy to show the saving effected by weathering, even though this exposure of the clay may seem to add so much to the cost. In the first place, a clay which is really worth weathering will be ground at practically double the rate, or with a saving of about one-third of the power required for the fresh clay, so that the saving in fuel in the boiler should alone make up for most, if not all, the cost of weathering, or the increased output with the same quantity of fuel burned below the boiler should produce the same financial effect, quite apart from the other advantages gained by exposing the clay.

The Characteristics of Clay when mixed with Water.—All raw clays have a special and peculiar behaviour towards water, though they differ greatly in the extent to which they are affected by it. The china clays (kaolins) and other lean clays are much less altered in character than are the fat clays. This difference in behaviour is due to the variation in plasticity shown by different samples.

When any clay is completely dry without having been excessively heated it is highly **hygroscopic** and absorbs moisture readily—sometimes up to 15 per cent. of its weight—without becoming appreciably moist. It is, therefore, extremely difficult to keep clay perfectly dry, and most specimens contain a considerable percentage of moisture which may, in some cases, cause the clay to be tough and plastic. If a lump of dry clay is placed in water it gradually softens and falls to powder or **slakes**, the time required depending on the clay and varying from a few minutes

to several months. Sokoloff considers this due directly to the plasticity of the clay (see *Binding Power*).

Seger considered that the hygroscopic nature of clay enables it to be distinguished from silt and fine sand, as these do not so readily absorb moisture from the air.

The **absorption**¹ of water by clay may be studied from two points of view, viz. the effect of placing a clay mass in water and allowing it to slake (p. 326), and by adding water to clay and subsequently kneading or mixing them together. The absorption of hygroscopic moisture has already been mentioned (p. 307).

When a piece of air-dry clay is placed in water the latter enters the pores and drives out the air, lifting up the smallest particles of clay. This disturbs the structure of the material, and a partial or complete breakdown occurs. The absorption of water is accompanied by a slight rise in temperature; this, though scarcely noticeable, is characteristic.

The amount of water absorbed varies greatly with different clays; in some cases it is equal to 80 per cent. of the weight of the clay.

Rohland suggests that this power of imbibing a definite amount of water is due to the colloids in the clay, and that as soon as a clay has absorbed sufficient water to dissolve its colloids and to form a colloid solution its ability to absorb water reaches a saturation-point and ceases; this is proportional to the colloids present, and probably, roughly, to the plasticity of the clay. It may, however, be proportional to certain capillary spaces between the clay particles, though not to the porosity of the clay, as the large pores may be unable to retain so much water by capillary attraction relative to their size.

In the manufacture of articles it will be found that each kind of clay requires a definite proportion of water for its efficient manipulation. If more is added it will become too weak, if less it will be too short. The amount of water needed for the purpose is less in proportion as the ratio of non-plastic material in the body increases. Therefore the leaner the clay the less water it will need to temper it. This water is known as **water of formation**, and its amount has a theoretical as well as a practical importance, being closely related to plasticity. Unfortunately, there is no certain method of measuring the consistency of clay paste nor of ascertaining when the correct proportion of water has been added to a clay. The ordinary method consists in adding a definite quantity and working it up into a paste. If this paste

¹ The phenomena classified under the term *adsorption* must not be confused with those of *absorption*; the former are described on p. 333.

adheres to the fingers, too much water is present ; if it cannot be worked into a smooth paste which readily receives the impressions of the finger-prints, but does not adhere to the skin, more water must be added. After a few trials the correct amount of water may be ascertained, but the test is too rough for scientific purposes. The most suitable amount of water to be added to clays to form a good modelling paste varies enormously. In some cases only 5 per cent. is needed, in others it may be equal to more than half the weight of the clay used. If, to a moderately plastic dry clay, water is added in increasing quantities, the clay can at first be moulded with difficulty, then more easily, and finally it may be formed with the greatest facility. But if from this moment the proportion of water is still increased the clay begins to adhere to the fingers and it soon becomes impossible to form it into a definite shape.

If the same experiment is repeated with a more plastic clay, using the same proportions of clay and water as before, it will be observed that it will adhere to the fingers and will allow of no further shaping unless its plasticity is diminished by adding non-plastic material or altering the proportions of clay and water.

An excessively lean clay, on the contrary, only acquires the desired plasticity when it has a very soft consistency, which does not allow it to remain in the given form, and it must therefore be rendered more plastic if it is desired that it should be shaped by hand. If the formation is done by mechanical means, in which the clay is subjected to a much stronger pressure, less water must be added to the body, in order to obtain the same plasticity, and it will be expedient to make it of a stiffer consistency. Pressure in this case plays the same part as water in relation to the plastic qualities of clays ; the one can be partially replaced by the other, so that if the amount of pressure used is increased the water should be diminished, and *vice versâ*.

Bourry has observed that : 1. With a clay of definite plasticity there exists a maximum of pressure and a minimum of consistency between which the clay can be given a definite form. If the clay is too plastic, this maximum pressure will be less, and, on the other hand, the minimum of consistency will be too great to permit of formation by hand, or by a slight pressure. If the clay is too short, the maximum pressure will become considerable, and the minimum consistency will yield a body which is too liquid to be shaped.

2. With a mode of formation corresponding to a pressure and consistency which are fixed, the plasticity of the clay employed can only vary between certain limits. If it is too plastic it will

adhere to the moulds; if too short its grains will not unite among themselves, and it will be impossible to make a compact mass of them. It is, therefore, of the highest importance that a careful choice should be made of the mode of formation for a body of a given plasticity, or to produce in a given body the plasticity suitable for a given mode of formation.

If a sufficient quantity of water is added to a clay and the whole thoroughly mixed, a slip or slurry will be produced which has certain characteristics, according to the proportion of water and clay, to the nature of the clay and the purity of the water. If the proportion of water is very large and the clay particles difficult to separate, they may fall to the bottom of the water soon after the mixing ceases, or the greater part of them may so fall, leaving the smallest particles suspended in the water for many hours.

Slips containing about an equal weight of clay and water are largely used in various branches of clayworking, for covering other clays of inferior colour when burned, and for making objects by the process of **casting**. In the former, the articles to be covered are immersed in the slip, and in the latter the slip is poured into plaster moulds and allowed to remain for a short time, after which any superfluous slip is poured away. On allowing the mould to dry, the water is absorbed by the plaster, and the clay article may be removed in due course.

In both cases it is necessary that the proportions of clay and water should be carefully adjusted, in order to obtain the best results. When a suitable mixture has been obtained it will usually be sufficient to weigh exactly one pint of it accurately, and to dilute other mixings with stronger slip or with water, until they reach the same weight per pint. The specific gravity of the slip may be determined with greater exactness in a pycnometer, if desired, but this involves unnecessary trouble for most purposes.

Schwerin has found that water and alkalis in clay slip may be removed by electro-osmosis by connecting the bottom of the tank containing the slip with the negative pole, and the cover with the positive pole, of a battery, when the water and alkali will collect at the bottom, the slip becoming very stiff and dry.

The **viscosity** of clay-slips is a characteristic property, and throws some light on the peculiar physical nature of clays. The viscosity of a fluid may be regarded as its resistance to flowing, and is usually measured by ascertaining the time taken by a given volume of the fluid to flow through a given orifice when under a constant pressure. In order to eliminate difficulties due

to a proportion of the material being deposited, and so making the flow irregular, some means of keeping it in motion may be necessary. Mellor, Green, and Baugh used a modification of the Marriott flask (fig. 23) which prevents the slip from settling by the air-bubbles drawn through it. Viscosity may also be measured, as suggested by Bleininger and Brown, by immersing a light shaft carrying paddles in a given volume of the slip and noting the time taken by a given force to produce a definite number of revolutions of the paddles.

By treating distilled water in the same manner as the slip, and dividing the figures obtained for the latter by those for the former, a ratio is obtained which is of considerable value in comparing the viscosities of different clays, or of the same clay to which various substances have been added.

Mellor, Green, and Baugh have made the chief experiments on the viscosity of clay slips¹ published in this country, their work being done with a special view to ascertaining the effect of small quantities of added chemicals. They conclude that such added substances may be arranged in five groups:—

1. Substances which first make the slip more fluid, while further additions stiffen the slip. Examples: sodium and potassium carbonates, fusion mixture, potassium sulphate, potassium bisulphate, potassium hydroxide, potassium nitrate, sodium sulphide, tannin, and gallic acid.

2. Small amounts thicken the slip; increasing amounts make the slip more fluid. Examples: copper sulphate, dilute ammonia, and potassium-aluminium sulphate.

3. Substances which make the slip thinner: Magnesium, mercury and sodium sulphates, sodium sulphite, sodium acetate, sodium chloride, sodium phosphate, ammonium gallate, hydrochloric acid, water-glass. It is just possible that

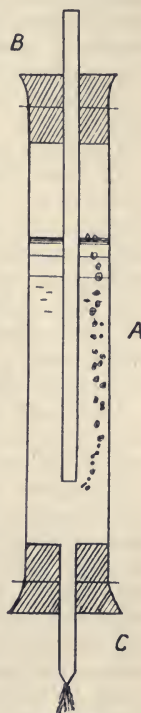


FIG. 23.

¹ It should be noted that the slips used were not made from a single clay, but from a body-mixture composed of 16 g. ball clay, 19 g. china clay, 13 g. Cornish stone, 20 g. flint, and 110 c.c. of water. To this mixture, varying quantities of acid, alkali, or salt—ranging from 0.1 to 6 g. or 0.1 to 35 c.c.—were added. This may account for the difference between these results and those obtained by some Continental investigators (pp. 312 and 313).

some of these substances may have to be transferred to the first (or second) group if greater (or less) concentrations be tried than those employed by Mellor, Green, and Baugh.

4. Substances which only stiffen the slip: Grape sugar, humic acid, borax, ammonium chloride, calcium chloride, calcium sulphate, ammonium urate, aniline, ethylamine, methylamine. Here again some of these substances may have to be transferred to the second (or first) group if greater (or less) amounts than those just indicated are used.

5. Substances which have no appreciable effect on the slip; *e.g.*, alcohol.

Rohland's results are given on p. 313.

R. Rieke has stated that most soluble sulphates increase the viscosity of a clay slip, but their effect may be neutralized by the addition of a solution of barium hydroxide. The most harmful sulphates, according to this investigator, are those of calcium, aluminium, and the heavy metals. Alkali sulphates stiffen the slip when only 0.1 per cent. is present; larger proportions render it thinner until more than 1 per cent. is present, after which they stiffen it again. Zinc and copper sulphates exhibit this phenomenon of variable influence in a marked degree.

Bleininger found that the first addition of clay (up to 3 per cent.) decreased the viscosity of water on account of the deflocculation of the clay by dilution and of the solution of the contained electrolytes. When, however, the addition of clay became so great that no further matter went into solution and the effect of the gel showed itself, the viscosity increased with each addition of clay. This negative viscosity is peculiarly characteristic of some clays. Simonis, Bleininger, and others have suggested that there is a direct connection between the viscosity of a clay slip and the plasticity of the clay from which it is made, the plasticity being considered to be represented by the amount of water which must be added to produce a slip of definite viscosity. This definition of plasticity is by no means complete, as the viscosity of a clay slip is really a measure of the amount of the coagulated colloid material in it, and therefore, indirectly, of the plasticity due to this cause. As the various properties of clay summarized under the term "plasticity" are, in all probability, not due exclusively to the presence of colloid matter, it appears unlikely that plasticity can be completely measured in terms of viscosity, though this latter property may prove sufficient for many purposes.

The viscosity of clay paste is an important factor in the manufacture of bricks, pipes, etc., by "expression." A paste which is

too fluid cannot be used for this purpose; one which is too viscous will require too much power to force it through the die of the machine.

The acidity or alkalinity of clay slips has a marked influence on their viscosity and plasticity. If an alkali is added to a viscous clay slip or clay paste the latter will become more fluid until a certain limit is reached, after which it will become stiff again. If, on the contrary, a suitable quantity of acid is added to a fluid slip, the latter will become more viscous and may even become apparently solid.

The acid or alkaline solutions used must not be too dilute, about twice normal ($\frac{2N}{1}$) solutions being usually satisfactory. The slip must be well stirred.

According to Rohland the addition of hydrochloric, nitric, sulphuric, acetic, or propionic acid increases the plasticity of a clay slip by coagulating the colloid matter present. Solutions with an acid reaction such as sal ammoniac, aluminium chloride, ferric chloride, and bichromate of potash behave similarly. Alkalies, such as ammonia, caustic soda, caustic potash, lime-water and baryta, and basic salts, make the slip more fluid and reduce the plasticity of the material, but their behaviour depends on their concentration.

The fluidity of clay slips containing comparatively little water is of practical importance in casting (p. 310), and it has long been known that the addition of small quantities of alkali (usually about $\frac{1}{4}$ per cent. of the dry clay) enables a slip containing much less water to be used, and so facilitates the manufacture of cast ware. As the alkali affects the plaster of which the moulds are made, it is necessary to use as little as possible, and each clay must therefore be examined separately so as to determine the most suitable amount of alkali or alkaline salt to be added. The use of potassium carbonate and sodium carbonate for this purpose has been known for many years, but the most important development is found in Weber's patent process for casting large pieces of ware made of fireclay and grog. Weber uses lime-water, baryta, or lime-water and caustic soda, and adds it to the water to be used for mixing with the dry clay. The latter is then fed into this dilute alkaline solution at a regular rate, the mixture being stirred mechanically so as to secure a thorough mixture of the two. After remaining for a short time in a second vessel or reservoir, the slip is run off into the moulds. Where suitable clays for this purpose can be obtained this method of increasing the fluidity of the slip is found advantageous, as it produces a

strong dense body of more uniform composition, and therefore more free from internal strains, than when the ordinary methods of moulding fireclays are employed.

The **plasticity** of clay is one of its most important properties, and many industries depend upon it. Clays occur in a plastic state in many parts of the country, but others possess only potential plasticity, which is converted into actual plasticity when they are mixed with a suitable quantity of water. Although some plasticity is valuable in a clay, an excessive plasticity is troublesome, as it causes irregular contraction; and highly plastic clays are therefore particularly liable to crack on drying and burning. No reliable means of preventing this trouble without reducing the plasticity have yet been discovered. Acheson claims that the addition of 2 per cent. tannin does it, but this requires further study.

Plasticity may be defined as that property of a material which enables it to change its form without rupture, the new shape being retained when the deformative force is removed. In other words, a material is said to be plastic when it can be kneaded or pressed into any desired shape, and remains in that shape when the kneading ceases or the pressure is removed; this alteration of shape being capable of being repeated indefinitely. It is a characteristic of many substances besides clays,¹ though these latter possess it to the most marked extent. Ashley has pointed out that very few people agree exactly in their conception of plasticity. Thus a brickmaker terms a clay plastic when it will work well in his machine and is capable of being kneaded into a "good" paste, but a potter usually places more emphasis on the binding power of a clay, though he terms this its plasticity.

Although these definitions are sufficient for practical purposes, they are not entirely satisfactory, nor is there any explanation of the causes of plasticity which meets all the needs of the case.

As already stated, most clays require the addition of a suitable amount of water before they become appreciably plastic, but other materials, such as wax and lead, are plastic in the absence of water, and various metals and glass become so when heated. The amount of water required varies greatly, and will be considered later. Liquids other than water may be added to clay to produce

¹ Atterberg has stated that all minerals which readily split into plates or scales—such as heavy spar, muscovite, biotite, talc, and kaolinite—are found to be strongly plastic when ground and elutriated so that the particles do not exceed 0.002 mm. diameter. Flett has stated that if any rock, even pure quartz, be crushed to an extremely fine powder it will be plastic and will show other characteristics of clays, such as shrinkage and impermeability.

plasticity, but they must usually contain water, and even then sometimes produce quite different characteristics. Thus glycerine may be used, but prevents the clay from drying, and Krupsay has pointed out that if plastic masses made from clay with water and oil respectively be kneaded together the resulting mixture is quite non-plastic. Fatty liquids, such as oils, seem to make a more plastic body than water, especially if the clay has been previously dried to take away from it the hygroscopic water, but alcohol, ether, and turpentine produce bodies with little or no plasticity.

Plasticity does not appear to be connected with chemical composition, as clays which yield the same results on analysis may differ widely in plasticity, yet on heating to a temperature above 415° C. most clays lose their plasticity and it cannot be restored. In this way plasticity in clays differs from malleability in metals, as the latter can be restored by appropriate tempering or heat-treatment. It is also a curious fact that the clays which are richest in "true clay" are seldom so plastic as those which are less pure, and for these reasons any peculiar structure of the clay molecule can scarcely account for its plasticity, though many eminent scientists have laid stress on this suggested cause.

Several investigators have attributed plasticity to the shape or size of the clay particles. Thus Aron considered plasticity to be due to the particles being spherical, but Zschokke and Biedermann and Herzfeld dispute this, and attribute it to the presence of flat and laminated crystals,¹ a view early put forward by Johnson and Blake, and held later by Bourry, who stated that plasticity becomes greater in proportion as the volume of the grains diminish, and that all minerals, if reduced to a sufficiently impalpable powder, on the addition of a liquid produce bodies having a certain amount of plasticity. This may be expressed in another way by saying that the great plasticity of clay proceeds from the fact that it consists of lamellar crystals entangled with one another, so that the grains are closer together than if they were polyhedral or spherical, and this is equivalent to increasing their attraction to each other in a strong degree.

According to Le Chatelier, this lamellar structure and the well-known properties of capillary attraction suffice to explain the

¹ The particles are so extremely minute that it is exceedingly difficult to ascertain their shape even with a powerful microscope. Le Chatelier has noticed that if the material is disturbed when under the microscope, the crystalline form may be observed for a fraction of a second by polarised light if their symmetrical axis is perpendicular to the microscope axis. As soon as they are flat they are isotropic. (See footnote on p. 284).

cause of plasticity. He has shown that all plastic masses contain a large proportion of air, as may easily be shown by comparing the density of a plastic mass with that of clay and of water, and that in each plastic mass there are innumerable capillaries of not more than one-three-thousandths of an inch diameter. He concludes that the tension of the menisci, between the water surface and the air surface in these capillaries, explain the toughness in a plastic mass, as the capillary force prevents the mass from breaking up under pressure, but allows the minute particles to slip over each other and yet to adhere so strongly that the mass retains the new form when the pressure is removed.

The theory that plasticity, instead of being a special property, is simply the result of molecular attraction, and that all bodies which are made up of laminated particles must become plastic when they are reduced to a sufficiently impalpable powder, has been confirmed by Vogt as regards mica, which is very laminated, being made up of thin layers, and when reduced to an impalpable powder becomes distinctly plastic if water is added. The insistence laid by Bourry on the laminated structure of the particles has been frequently overlooked, and the suggestion that, because burned clay may be ground equally fine and yet never become plastic, his experiments are not conclusive, is irrelevant.

Seger, and independently Schumacher, consider plasticity to be due to molecular differences in the clay particles, and Bischof agrees with the latter in considering that clay has undergone great changes in the density during deposition, and a kind of "felting" of the particles has resulted so that they adhere much more closely to each other than the quartz and other particles in which this felting process has not taken place.

Wolff, basing his study on Newton's law that "the attraction of two bodies is proportional to the mass and inversely as the square of their distance," has calculated the attraction of particles of various substances to each other on the assumption that they are spherical. He finds that the mutual attraction of clay particles is very high, and that the ratio between the mutual attraction of clay particles for each other and for water is much higher than for any other substance examined. He states in confirmation of this theory that other substances can be made plastic if they can be made sufficiently small, as by precipitation.¹ He also pointed out that the combined water in a particle increases the ratio considerably and is accompanied by an increase in plasticity not only in clay, but in alumina and iron oxides. Zschokke confirms

¹ This has recently been confirmed by Cohn and Atterberg, who find that precipitated barium sulphate and calcium fluoride are both plastic when fresh.

this theory, and has shown that clay particles will have a thicker film of water around them than do particles of non-plastic materials such as sand.

Atterberg has made the interesting suggestion that the clays of Northern Europe consist of plates of mica, and those of Southern Europe of plates of kaolinite.

It is extremely difficult to find satisfactory reasons for attributing the plasticity of clay solely to the plate-like shape or lamellar structure of the particles or to purely mechanical or chemical characteristics in the atoms and molecules of clay and water, though these are undoubtedly important. Nor has the effort of Le Chatelier to find the source of plasticity in the presence of small amounts of impurities proved really helpful.

The smallness and shape of the particles appear to be important, as clay ground in a pan mill is more plastic than when a ball mill is used, as the former flattens out the material, but this does not really affect the plasticity, except in so far as it facilitates its production. It is not a *cause* of plasticity, though Johnson and Blake claim to have rendered non-plastic china clay plastic by fine grinding. It has also been suggested by Olschewsky, who based his experiments on those of Daubrée, that the water used has a chemical action, and that plasticity is due to the formation of a system of capillaries in the clay, a felt-like or spongy material being formed, and in this way the clay particles are able to come into closer contact owing to the production of a kind of gelatinous film, but the presence of an alkali appears to be essential for this alteration to take place. Thus, Mellor found that ground pottery, felspar, and Cornish stone become plastic on heating with water under pressure to 300° C. for several days, but china clay and flint are scarcely affected.

The finer a substance is ground the more complete is its reaction with water, because a small particle has a greater surface in proportion to its volume than a coarse one. If the particles are sufficiently fine, water may, indeed, act in a manner similar to a solution of caustic alkali; thus very finely divided silica becomes colloidal in contact with boiling water, just as coarser particles of silica do on boiling with a solution of caustic potash.

Koerner has found that other substances (as alumina) become gelatinous when sufficiently finely divided in water, but that their power of cohesion is lost on drying, and he argues that the plasticity of clay may be brought about in a similar manner. This would explain why it is not possible to produce highly plastic clays from kaolins.

As many organic substances possess certain characteristics of

plasticity, several suggestions have been made that these may be the cause of plasticity in clay. It is found, however, that there is no definite relation between the plasticity and the proportion of carbon in the clay, dark-coloured clays rich in carbonaceous matter being no more plastic than lighter ones almost free from this material.

Several observers have suggested that bacteria produce plasticity, but Hecht and Gosmann have not found sufficient data to warrant this suggestion, especially as it has not been found possible to increase the plasticity of clays by inoculation. The effect of bacteria on the souring of clay is described later (p. 321).

Whenever plastic clay is subjected to pressure it tends to obey the laws of fluids, transmitting its pressure equally to all parts of the mass and flowing through any orifice through which it can escape, though it is far from being a perfect fluid. From this arises the modern conception of clay as a very viscous fluid in which every particle of solid matter is surrounded by a liquid film, so that the particles are virtually in a state of suspension, and hence that a plastic clay is, at any rate in part, in a colloidal condition.

As far back as 1876 Schloesing suggested that the plasticity of clay was due to its colloid nature, and claimed to have found an amorphous material of the same composition as kaolin which had all the characteristics of a colloid, and was termed by him *argile colloïdale*.

But little notice was taken of this suggestion or of the allied work of other observers until 1896, when Rohland investigated the subject further, and found indications that the colloidal nature of clay appeared likely to explain many of the facts noted in regard to plasticity.

The nature of the colloid material apparently existing in many clays has already been described (p. 285). In attempting to explain plasticity as due to these colloids, it is assumed that some or all of the pores of the clay are filled with a colloidal solution (gel) obtained by the partial hydrolysis of the clay, and that the larger the proportion of pores so filled the more fat and plastic will be the clay, providing that the proper ratio of granular material to colloid gel is retained.

Rohland has further shown that the addition of trifling amounts of electrolytes often produces great changes in the plasticity of a clay, and suggests that this characteristic of colloids is a strong argument in favour of the connection between the colloidal material in clay and plasticity (p. 313). All electrolytes (such as acids) which yield hydrogen-ions on dissociation increase the

plasticity of clay, whilst those (such as alkalis) which yield hydroxyl-ions make a clay paste more fluid.

Plasticity is not, however, entirely due to the presence of colloidal matter in clays, though the effect of organic colloids in increasing plasticity cannot be denied. Many highly plastic clays are so free from organic matter that this cannot be the cause of their plasticity, yet according to Hermann the most delicate tests for inorganic colloids have yielded negative results in these cases. Indeed, some investigators maintain that the presence of inorganic colloids in clay has never been conclusively proved.

Another difficulty has been pointed out by J. M. van Bemmelen, viz. the rapidity with which most colloids lose their power of absorbing water. This suggests that clays of great geological age cannot contain active colloids produced when the clay was formed, though they may contain colloidal substances derived from adventitious materials—organic or otherwise—at a comparatively recent period. The fact that many highly plastic clays appear to be free from such extraneous colloids only increases the difficulty.

Other objections of equal or greater weight may be urged against any single theory yet published on the causes of plasticity, so that much further work remains to be done.

Summarizing the results of the numerous theories and experiments made, plasticity may be said to be due not to one cause, but to several causes, of which the chief are:—

1. The nature of the molecules of the "true clay" present.
2. The extremely small size of the particles, their large surface (due to their porosity), and (possibly) their fissile character.
3. The effect of water on the particles and the probable production of inorganic colloid matter by its hydrolysing action on the clay, the amount of colloid material so produced being dependent upon the hydroxyl-ions present. If these are absent, or neutralized by hydrogen-ions, added purposely or occurring naturally or through fermentation of the organic matter in the clay, the plasticity will continue to increase until an excess of hydroxyl-ions is again produced; when the concentrations of hydroxyl-ions is large the negatively charged clay particles will go into suspension. As the extent to which water can be dissociated is very limited, the plasticity of clay can only be increased at so slow a rate that it is unlikely that very slightly plastic clays (kaolins) can even be made highly plastic by artificial means, though the increase in plasticity may be sufficient to show the nature of the reactions which take place.
4. The presence of organic colloid matter, due to impurities in

the clay, or added purposely, may still further increase its plasticity.

5. The presence of minute quantities of soluble salts may exercise a pronounced effect on the plasticity. Their action has been mentioned under *Viscosity* (p. 310). The limits within which the plasticity of a clay can be increased by the addition of soluble salts are very small; but there is such an abundance of naturally plastic clays that it is only where materials of exceptional purity are required that an increase in plasticity is desirable.

As plasticity appears to be a resultant of several properties, see also *Viscosity, Cohesion, Adsorption, Tensile Strength, Binding Power*, etc.

A small increase in plasticity may be obtained—

1. By increasing the hydrogen-ions in the material, by allowing the organic matter in the clay to decompose (ferment) and become acid, or by adding a weak acid, or by keeping the clay in intimate contact with fresh water by stirring the two together. This hydrolyses the clay and forms colloid matter on the particles. In this connection it is important to have the particles of clay as small as possible in order to facilitate the hydrolysis. If water alone is used for this purpose the clay must be allowed to stand until fermentation of the organic matter sets in and the mass reacts faintly acid. In any case the time required for an appreciable increase in plasticity may be several years.

2. By keeping the moist clay in a cool, damp cellar.

The ancient practice of storing clay in cellars for a long time, and known as *maturing* or *ageing*, is now seldom practised to anything like the extent which was formerly thought necessary. Where hollow goods of very fine clay are made there is an undoubted advantage in thus storing the clay before it is made up into goods, but the keeping of the clay in air-tight boxes for several years, as practised by Wedgwood and other famous potters, is no longer considered essential, though its beneficial effect on the clay is not denied. In Germany, the use of sumps, in which the clay and water remain in contact for a considerable time, is still regarded as necessary.

A much shorter storage of clay paste, frequently in open sheds, the material being covered with wet sacking, is known as *souring*. Its effect is undoubtedly to increase the plasticity of the clay, though there is a great variation in the extent to which it does this. The apparent effect of storing or souring is the formation of acid substances by the decomposition of the organic matter in the clays, and the coagulating effect of these acid-ions on the colloid material in the clay. If this is the true explanation, it

should be possible to reduce the time of storage by the addition of acid to the clay and then mixing it thoroughly. This treatment has proved successful in some cases, but not in all, probably because a certain amount of time is required before the whole of the mass can become permeated with the acid and water.

There is a widespread impression that souring is the result of bacteria or ferment organisms, and some potters have even added sugar or honey to the clay to assist the "fermentation"; but whilst this may account for some of its effects, the hydrolysing action of the water present in the mass on the clay, silica, and iron oxide particles must not be overlooked. Rohland in 1903 suggested that the fresh clay paste is slightly alkaline, owing to the felspar, etc., present in the clay being hydrolysed and converted into a colloidal form. The acids produced by the decomposition of the organic matter also present neutralize the alkali-ions; and the excess of hydrogen-ions produced coagulates the colloid matter and correspondingly increases the plasticity of the clay. This explains why the old vinegar "tip" of bygone potters increased plasticity. Previous to this, Seger had found that clays which remain alkaline do not increase in plasticity on storage, but do so if they are acidulated with acetic acid.

As heat is a disadvantage, the souring must usually take place in a cool, moist shed or cellar, if it is to be really effective; though, in opposition to this, it may be noted that slips which are dried by heat are often more plastic than those treated in a filter-press.

Some firms apply souring or storage to clays which are highly plastic, not to develop more plasticity but to secure a better distribution of the moisture in the mass, and, as they express it, "to bring it into a better and tougher condition."

3. By the addition of other colloids, such as colloidal silica, alumina or iron hydrate, hot starch, dextrin, tannin, rubber, sumach, inulin, caramel, gelatin, gum, glycogen, or various ferments and enzymes, the plasticity of clay may be increased, but care must be taken to avoid confusion between true plasticity and the pseudo-plasticity caused by the addition of materials of an oily, gelatinous, or gummy nature.

Some very interesting experiments by Acheson and Ries on the effect of a 2 per cent. solution of tannin (gallotannic acid) on clay show that the addition of this substance notably increases the plasticity of the clay, and at the same time apparently deflocculates it and breaks it up into much finer particles. The tensile strength of the clay was nearly doubled.

In a later patent Acheson first adds tannin and alkalis or ammonia and stirs the clay into a fluid state, and then by the addition of a suitable quantity of acid he coagulates the colloids and forms a stiff, plastic paste.

A problem which confronts many clayworkers, particularly those engaged in the manufacture of bricks and tiles, is how to keep the plasticity of a clay within convenient limits. So many clays on drying warp and crack to such an extent as to be very troublesome, and some means must then be found to lessen it. This is because very plastic clays dry unequally and with difficulty; they tend to lose their shape and crack because the particles cannot move over each other with sufficient freedom, and have not sufficient rigidity to remain in their original position. Hence it is necessary to reduce the plasticity of such clays in order to overcome these defects, and the correct adjustment of the plastic and non-plastic materials composing the clay mass requires the most careful attention.

To Reduce Plasticity.—(1) Hydroxyl-ions may be added and the temperature raised (direct reduction). (2) Non-plastic material may be added so as to spread the plasticity over a large volume of material (indirect reduction or dilution). (3) The material may be heated to 200° C. or other suitable temperature.

For the first method any basic material, whether organic or inorganic, may be used, though lime-water is the cheapest. If it is too weak in hydroxyl-ions, caustic soda solution may be used, as may any salt composed of a strong base and a weak acid, or soda, potash, phosphates and silicates, all of which readily dissociate and liberate hydroxyl-ions, though the cathode constituent of the salt may exercise a considerable effect. Thus, borax reduces the influence of the hydroxyl-ions and potassium carbonate increases it, yet both are salts composed of a strong base and a weak acid. The concentration of the alkaline or basic material added is also of importance, and it may be necessary to render sulphates and other soluble salts insoluble by the addition of baryta, as suggested by Weber.

There are certain clays, as Weber has shown, which act in precisely the reverse manner. These are free from sulphates, and rich in colloid matter.

Certain clays containing organic acids of a fatty nature are saponified on treatment with alkali, and the soap so produced increases, instead of diminishing, the plasticity, owing to the coagulation effected.

The reduction of plasticity by raising the temperature considerably is described later. A comparatively small rise in

temperature—produced by the action of mechanical stirrers—will reduce the plasticity of a clay if free hydroxyl-ions are present.

The addition of non-plastic material, such as sand or grog, effects a reduction of the plasticity in an entirely different manner, by separating the clay particles from each other. It thus reduces the strength of the material, but by diminishing the shrinkage it enables the clay to be used in a manner which would otherwise be impossible, and the strength is seldom reduced to such an extent as to make any notable difference to the user of the material. The proportion of non-plastic material to be added depends upon the size of its grains and on the binding power of the clay. As the latter is closely connected with its plasticity, it will usually be found that the more plastic the clay the larger the proportion of non-plastic material which may be used.

Some sands are quite useless for this purpose, so that great care is needed in their selection (p. 254). For some clays, chalk is preferable to sand.

The Measurement of Plasticity is a problem which has not yet been satisfactorily solved, probably for the reason that plasticity is the result of the united action of several forces some of which may not, as yet, have been recognized as important. Early attempts to measure plasticity usually resulted in only measuring one or more of these forces. Thus Bischof added sand to clay until the dried mixture was so soft that it could be rubbed away between his finger and thumb. Bischof's figures are, however, a measure of the binding power of clay, but not of its plasticity. Measurements of tensile strength, viscosity, the amount of water required to produce a mass of given consistency, the consistency or depth to which a Vicat needle will penetrate, Sokoloff's slaking test, and other single characteristics, are all useful in their way, but they fail to include all the properties involved in the use of the term plasticity. Zschokke, who has examined the subject very fully, considers that the percentage of extensibility multiplied by the tensile strength of a freshly-moulded clay cylinder of standard size (60 mm. high by 30 mm. diameter) is a coefficient of the plasticity. Modifications of this method have given excellent results in the hands of several experimenters in different countries and with a very large variety of clays. Grout considers that plasticity is proportional to the product of (*a*) the load required to sink a Vicat needle to a definite depth in the mass of clay and (*b*) the deformation of the clay under stress, which he measures by the increase in area of a clay cylinder produced by a load which just causes cracks to appear. Both Zschokke and Grout really consider plasticity to be the product of the deformability and the force

resisting deformation, though they differ in the manner in which they measure these forces. More recently, Ashley has adopted the same general idea as to the forces involved, but has assumed that the force resisting deformation is exerted by the colloids in the clay. He therefore regards the plasticity of a clay as

$$\frac{\text{Relative colloids} \times \text{Shrinkage of clay}}{\text{Jackson-Purdy Surface Factor.}}$$

The term "relative colloids" is explained in the section on *Absorption* (p. 333).

As the ratio of surface factor to shrinkage is approximately constant, Ashley concludes that the plasticity of a clay is directly proportional to the colloids present. The objection to this conclusion is that it appears unlikely, from other considerations, that the whole of the plasticity in a clay is due to colloidal matter.

Rohland, also assuming that colloidal matter in clay is the chief cause of plasticity, has suggested that the ratio obtained by dividing the coagulable colloids by the non-coagulable material is a measure of the plasticity. He ascertains this by measuring the amount of water required to make a clay into the consistency of good modelling paste, and argues that this is a measure of the colloids, because as soon as sufficient water is present to dissolve the coagulable colloids a saturation point is reached and no more water can be absorbed without the clay losing its stiffness.

Störmer has summarized the various factors needing consideration in estimating the plasticity of a clay, by stating that plasticity may be judged by the following characteristics:—

1. The proportion of water which must be added to a clay to make a good modelling paste (*absorption*). This is not always reliable.

2. The "feel" of the paste when it is rubbed between finger and thumb (*binding power*).

3. The behaviour of a paste when rolled into a "sausage" (*toughness*).

4. The adhesiveness of the clay (*adhesion*).

5. Twisting a cylinder of clay into a spiral and noting its behaviour (*torsion*).

6. Noting the length of the threads produced by expressing the clay from a vertical pug mill before they break off by their own weight (*tensile strength and extensibility*).

7. Forming balls of the clay and pressing them until the edges crack (*crushing strength*).

8. Bending cylinders of the clay into a ring (*bending moment*).

None of these characteristics taken alone can form a measure of the plasticity of a clay, though they are many of them closely related to each other. The most reliable measure of plasticity appears to be that devised by Zschokke (p. 323), or by Rosenow, who multiplies Zschokke's figure by the percentage of water added to the dry clay to make it into a workable paste, *i.e.* by Rohland's figure (p. 324).

The **binding power** of a clay is the property it possesses of uniting with non-plastic material and water to form a uniform plastic paste, and is consequently closely related to its plasticity. This absorption of non-plastic material by clay with the spread of plasticity throughout the whole mass has been attributed to the power of the saturated colloids (*gels*) to retain non-colloid particles in a state of pseudo-solution. Other colloids are known to possess the power of preventing insoluble matter from settling, and this is, in some senses, a parallel case. The binding power of a clay may be determined by measuring the tensile strength of mixtures of the clay with various amounts of standard sand, but a skilled clayworker can tell by the "feel" whether such mixtures are sufficiently strong to be useful. In order to determine how much lean clay or other non-plastic material can be added to a clay without unduly destroying its value for moulding into shape, Bischof's test may be used. In this the two materials are mixed in various proportions and the same measured quantity of water added to each. The pastes are then rolled into small balls as equal in size as possible, and allowed to dry. They are then rubbed gently between the finger and thumb or with a small "camel-hair" brush. The mixture, which just resists the action of the rubbing, may be taken as the standard. Some authorities make up small balls of mixture in this way and then notice to what length a cylinder can be rolled from each without cracking.

Bischof has suggested that the binding power of a clay is a function of the cohesion and adhesion of its particles, but later investigators have questioned this, and have ascribed it to the presence of coagulated colloid matter (see *Plasticity*, p. 314).

Clays with a high binding power are known technically as "fat" clays; "lean" clays are deficient in binding power.

Where highly refractory goods are to be produced, and have to withstand sudden changes in temperature, it is desirable to use clays with a high binding power (see *Binding Clays*, p. 138) in order that a larger proportion of grog may be employed.

Some writers appear to consider that binding power and plasticity are synonymous; this is by no means the case, as a

clay may be very plastic and yet not be able to bind much non-plastic material into a uniform plastic paste. At the same time, there is clearly some relationship between these two properties of clay. Sokoloff considered that the length of time taken by a clay to fall to pieces, or slake, in water is a measure of its plasticity, particularly if it is mixed with various proportions of standard sand and each of these mixtures submitted to a soaking test. The results plotted on a chart with the percentage of clay

as ordinate and the time required for the mixture to slake as abscissæ will show a critical point indicating the limit of the binding power of the clay.

Such a test is carried out as follows:—

The air-dry clay is passed through a sieve of fine mesh, and is then mixed with quartz grains of definite size in the following proportions: (a) nine volumes of clay and one volume of quartz sand; (b) eight volumes of clay and two volumes of sand, and so on up to (f), (g), and (h). Occasionally intermediate proportions are required. A convenient measuring instrument is a porcelain crucible

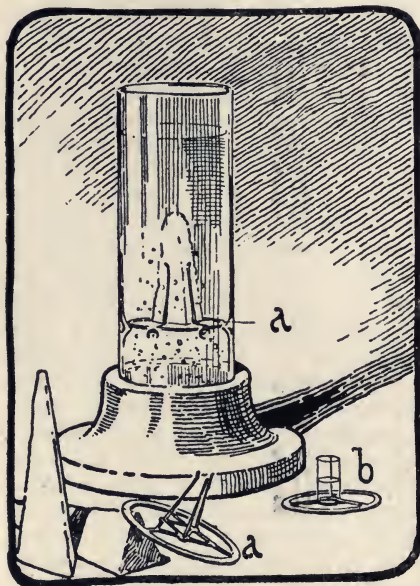


FIG. 24.—Sokoloff's Slaking Test.

holding about half an ounce; this is filled with the material, and any excess removed by drawing a knife blade horizontally across the mouth of the crucible.

The materials are carefully mixed together in the dry state, and are afterwards moistened and well kneaded together into a uniform mass. The stiff paste thus produced is then made into pyramids (like Seger cones, p. 353) in a brass mould, or small cylinders can be made by means of a small piston press, with an opening $\frac{1}{2}$ inch (or 1 cm.) in diameter. The test pieces are first allowed to dry in the air, and afterwards are dried to constant

weight at 100° C. (or preferably 110° C.), after which they are allowed to cool in an exsiccator to prevent them absorbing moisture.

The test is first made in still water in an apparatus similar to fig. 24, the clay pyramid or cylinder being held in a small wire frame, shown empty in *a* and *b* in the illustration. The clay having been placed in position in the glass cylinder, water is carefully poured in, and the whole allowed to remain in a quiet place where it will be free from vibration.

The moment when disintegration of the mass is made visible is remarkably constant, if the apparatus shown is used. The effect is most easily seen in the leanest mixtures, which absorb the water fairly rapidly, and after a short time pieces of sand and clay become loose and fall through the open wirework stand to the bottom of the cylinder. The test piece disappears like a lump of sugar in water, until the whole of it has fallen, with the exception of a few odd pieces which may remain attached to the wire. These last should be gently touched with a glass rod.

Very fat clays do not fall so readily, and the end of the test is less easily observed, as so much of the clay remains in suspension that it is difficult to see inside the vessel. For this reason Sokoloff found that sometimes it is desirable to make a similar test with running water, as shown in fig. 25. Numerous tests have shown that the time required is the same in both forms of apparatus, providing the stream of water is not too rapid, and in the latter one the end point is readily seen, as the flowing water carries away the fine particles, which in the apparatus shown in fig. 24 obstructs the vision with fat clays.

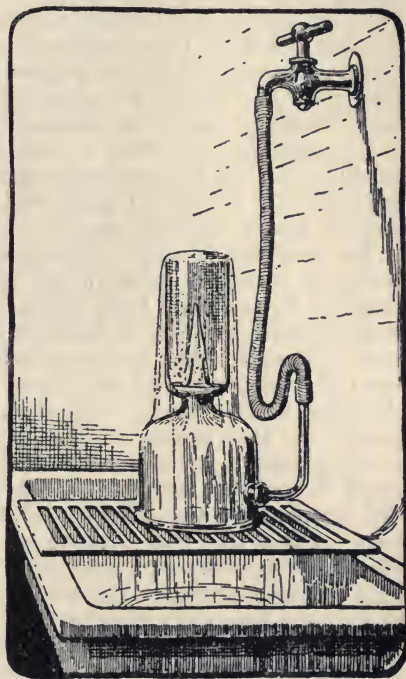


FIG. 25.—Sokoloff's Slaking Test.

The **strength** of dried clay is very important to some firms ; *e.g.* to those engaged in the manufacture of roofing tiles, pottery, and other thin-walled articles. The factors which determine it are not all known, but they appear to be closely connected with the plasticity of the clay.

The strength of a clay is measured by determining (*a*) the tensile strength or resistance to pulling ; (*b*) the resistance to crushing ; (*c*) the cross-breaking strength ; (*d*) the resistance to torsion. It is seldom that all these resistances are determined ; usually one is selected according to the purpose for which the clay is to be used : tensile strength for pottery, crushing strength for bricks, cross-breaking strength for roofing tiles, and so on.

The strength of a clay is due to (*a*) its plasticity, (*b*) its cohesion, and (*c*) its toughness ; other factors, less easily ascertainable, also appear to play an important part, as porosity, binding power, fusibility, etc.

The **cohesion** of clay is that property which counteracts the tendency to fall to pieces or to crack in drying, and so gives strength to the clay, both before and after firing. Any clay which lacks this quality is therefore liable to bring disaster to the user. Freedom from loss in manufacture is greatly dependent upon this property, and clays from different deposits vary considerably in this respect. It must be considered from two distinct points, *viz.* the capacity of the clay to resist tension and the power to resist a crushing strain. Leppla has suggested that the cause of plasticity may be found in the cohesion and adhesion of the clay particles, the adhesion of the water to the clay particles being greater than the cohesion of the clay particles for each other. Bischof considers that clays which can be easily kneaded have a greater cohesion than adhesion, whilst those which adhere to the hand have more adhesion than cohesion.

The addition of non-plastic material to a clay materially reduces the cohesion of the whole, as measured by the loss in tensile strength and resistance to crushing, but although there are several explanations of the cause of this reduction, no general consensus of opinion has been reached, some authorities maintaining that it is due to the particles being prevented from interlocking, whilst others consider it is to be explained by the coagulated colloid matter being too widely distributed to bind the particles firmly together.

The **toughness** of clay in a plastic condition is also supposed by some to be due to the same cause, but it may be equally referred to the high binding power of the clay particles in the mass. Toughness is expressed scientifically in terms of: (1)

extensibility, or the ability of the clay to stretch when pulled, which is measured by ascertaining the fullest extent to which a clay of a given size will stretch without breaking (p. 321); (2) **torsion**, or the extent to which a piece of clay can be twisted, which is measured by clamping one end of a bar rigidly and rotating the other slowly by means of a screw and counting the number of complete revolutions which can be made before the bar breaks; (3) **bending moment**, or the angle through which a bar of clay of given size can be bent without rupture; (4) **elasticity**, or the extent to which a piece of clay can be stretched and yet return to its original length when the tension is removed. Many plastic clays show slight elasticity, though it is usually too small to be measurable.

The **tensile strength** of a clay is its resistance to tension or to being pulled apart. It is often determined on air-dried specimens, of the shape shown in fig. 26, such as are used for testing cement, but more satisfactory results are obtained if the pieces are tested when "black hard," or even when they are only just stiff enough not to adhere to the fingers. For special investigations on plasticity, etc., bars of cylindrical shape are preferably used. The clay must be very carefully prepared so as to be uniform in composition, and the brass mould must be properly filled at a single stroke. A considerable amount of skill is required to do this, and many methods have been suggested for avoiding it, though without success.

It is essential that the clay paste shall be soft and thrown in accurately and forcibly. Incidentally it may be noted that the same difficulty occurs in making bricks by hand, and one of the reasons this branch of clayworking has so largely disappeared is the lack of skilled moulders.

There is a further difficulty, which arises from the shrinkage of clays on drying, whereby the area of the cross-section of the test-piece differs slightly with different clays. This is not of much importance unless clays with an unusually high shrinkage are tested, when it must be allowed for.

The dry test piece is placed in the rubber-lined clamp of a cement-testing machine (fig. 27), and the force necessary to

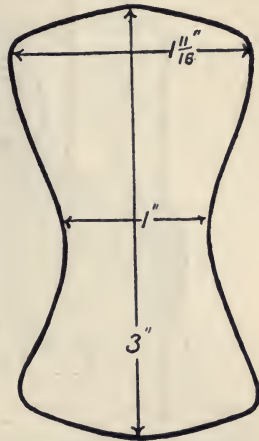


FIG. 26.—Test piece.

break it is measured in lbs. per square inch of cross-section of the fractured surface of the test-piece. If the test piece has an area of one square inch at the point of fracture, the weight in lbs. per square inch required is found without calculation. It is convenient to mark two small dots exactly two inches apart on the test piece before breaking and to measure the percentage of increase in length brought about by the tension of the weight. The results obtained vary greatly for different kinds of clay; a clay tested in a highly plastic state will have a breaking strain

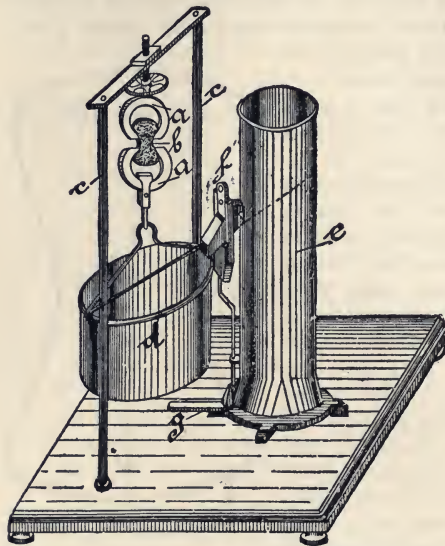


FIG. 27.—Tensile Strength-testing Machine for raw clay. (*Seger-Cramer.*)

of 50 lbs. per square inch, but if tested when dry may resist 400 lbs.; whilst other clays tested while soft will break under a strain of a few ounces, or under a few pounds when dry. Eight pounds is a fair average for ordinary brick clay as it comes from the machine, or 100 lbs. when tested dry. Rapid drying diminishes the tensile strength.

It is exceedingly difficult to get the pieces to break at the centre, but they must do so to yield serviceable results. Great care in fixing the piece in the machine evenly and in applying the tension uniformly are the chief essentials. At least ten tests should be made of each clay, and variations of 20 per cent. will frequently occur, even with skilled operators; in basing conclusions on the tensile strength of clays this may be borne in mind.

Where a rough measure of the tensile strength of a plastic mass is required it may be ascertained by observing the length of the piece which can be pressed through a $\frac{3}{8}$ -inch hole in the bottom of a vertical cylinder before the extruded mass breaks.

Ries and Orton have independently investigated this problem and find that the non-plastic ingredients of a clay influence its

strength inversely as the diameter of their grains, so that fine-grained clays will usually be strongest, though an excess of either very fine or very coarse grains will break the clay. In support of the theory that the grains of clays interlock to some extent, Ries has found that mixtures of two clays can be made which have a higher tensile strength than either clay taken separately. This fact has long been known by the makers of crucibles for melting steel in this country, as many as four different clays being used sometimes to produce a sufficiently strong crucible.

The tensile strength of the clay has, in fact, an important bearing on its resistance to accidents in the processes of manufacture, particularly from the commencement of the drying to the commencement of the firing. It is sometimes stated that the tensile strength of a clay enables it to carry a large quantity of non-plastic material, but this is rather confusing the effect with the cause. It is the binding power (p. 325) of a clay which enables it to carry such a large quantity of added material and still retain a sufficiently high tensile strength. Olschewsky has proved that there is no direct relationship between the binding power of a clay and its tensile strength when dry. It was at one time thought that the tensile strength of clays is proportional to their plasticity, but this is only true, if at all, when the pieces are tested in a moist (plastic) state. If air-dried the definite relationship ceases (see pp. 323, 325).

The **deformability** of a clay is the force required to effect a definite alteration in its shape. As crushing tests are unsatisfactory, the deformability is usually understood to mean the percentage of extensibility (p. 329), and is ascertained by placing a freshly-moulded cylinder of clay, of such a consistency that it will not adhere to the fingers, but is soft enough to receive delicate impressions, in a tensile strength machine and noticing its increase in length after fracture. Zschokke has found that more constant and higher results are obtained if the bar is stretched rapidly.

Ries prefers to determine deformability by noting the weight required to immerse a Vicat needle to a depth of 3 cm. in half a minute.

Ashley considers as deformability the cast air-shrinkage divided by the Jackson-Purdy surface factor or the concentration of colloids multiplied by their specific air-shrinkage. The relative colloids are determined by ascertaining the amount of malachite green adsorbed by a given weight of the clay (see *Adsorption*, p. 333), that adsorbed by a standard ball clay being taken as 100. The amount of relative colloids divided by the surface factor gives

the surface concentration, and the specific air-shrinkage of the colloids is calculated by dividing the linear shrinkage of the clay by the relative colloids.

The crushing strength of raw clay is seldom determined, as it has not, hitherto, yielded intelligible results. It is measured by forming a cube of clay of convenient size (usually 2 inches, but Zschokke uses cylinders 60 mm. high and 30 mm. in diameter),

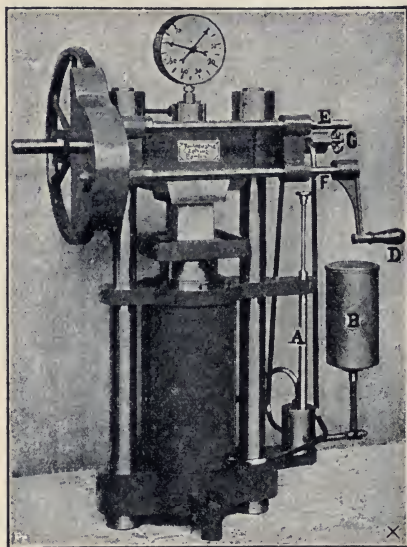


FIG. 28.—Machine for testing crushing strength of clay. (*Seeger-Cramer.*)

allowing to dry under the best conditions, and then crushing this test-piece in a machine (fig. 28) devised for the purpose, in which the pressure used can be registered.

Crushing should be measured on pieces as nearly cubical in form as possible, obtained with ordinary bricks; for example, by putting two half-bricks on another and joining them together with a thin layer of Portland cement paste.¹ The surfaces to be compressed should be made exactly parallel by a covering of cement or plaster. The force required for crushing should be supplied by a special lever apparatus or hydraulic press. As

tests on different-sized pieces are not strictly comparable, the dimensions of the bearing surfaces should be shown in all reports of the test. At least three test pieces of the same sample should be crushed and the mean of the results calculated. If the clay is crushed in an air-dry condition the results do not appear to be of any value, whilst if it is crushed in a moist state no definite end-point is reached, the clay beginning to lose shape under very small pressures. The crushing strength of

¹ The Institution of Gas Engineers' standard specification for fire-bricks requires a whole brick to be placed vertically in the crushing machine, and instead of levelling the faces with plaster or cement, it directs that they shall be sawn or ground flat.

fired clay is, however, valuable in connection with constructional engineering problems.

The **cross-breaking strain** is chiefly of interest to tile manufacturers. It may conveniently be determined by a method suggested by W. G. Worcester. The piece to be tested is supported on two "knife edges" of oak, placed 10 inches or other suitable distance apart. An iron or steel stirrup with a knife edge where it comes into contact with the upper surface of the test piece, and a hook at the other end is then placed over the test piece and a bucket attached to the hook. The stirrup should be placed as centrally as possible. Water is allowed to run into the bucket at a convenient rate until the test piece breaks. The water-supply is then stopped instantaneously, and the bucket with its contents, together with the stirrup, are weighed. This gives the total load on the test piece. This total load, divided by the area of the cross-section of the test piece at the point of fracture, gives the cross breaking strain in "lbs. per square inch."

Bars 12 inches by 3 inches by 1 inch (*i.e.* 3 square inches cross-section) are convenient. W. G. Worcester states that for roofing tiles, clays tested as just described which show a cross breaking strain of more than 5 lbs. per square inch are quite satisfactory.

The effects of **torsion** on clay have been studied by Jochum and others with a view to using them in the measurement of plasticity. A cylinder of plastic clay is clamped at one end to a fixed frame, and at the other to a screw. On rotating the screw slowly the angle through which the clay can rotate without serious fracture is measured. Owing to lack of sufficient data, no general law connecting torsion with other characteristics of clay can be formulated.

Adsorption is the power possessed by certain substances of removing other dissolved substances from solution. Thus, if a highly plastic clay is thoroughly mixed with a solution of dye-stuff and allowed to settle, it will remove the dye-stuff from the solution, and will deposit it on its own surface. If a salt solution be treated similarly, it will be much weakened by the salt adsorbed by the clay particles. Care must be taken to avoid confusion between the terms "absorption" and "adsorption." The latter relates exclusively to the withdrawal of the dissolved substances from solution and the retention of them on the surface of the solid particles. The same power is possessed by charcoal and filter-paper in a very high degree, and is attributed to their colloid nature. The amount of substance which can be adsorbed is apparently proportional to the surface area of the solid

substance, and is a function of the nature of the solid and dissolved bodies and of the concentration of the latter.

As adsorption is a characteristic of colloids (gels) and also of plastic clays, it has been suggested by several investigators that the plasticity of clay may be measured in terms of its adsorptive power (see *Colloids*, p. 285), but it is doubtful whether this includes the whole of the plasticity.

Some authorities suggest that the plasticity of clay is due to the salts it has already adsorbed (adsorption theory), whereas the supporters of the colloid theory maintain that it is due to the formation of reversible gels, which themselves possess the power of adsorption. Owing to the extreme difficulty of removing all soluble salts completely from clay, no absolute knowledge of their action is obtainable.

Ries has shown that tannin is adsorbed by clay with an increase in the plasticity of the latter, and Hirsch and others have found that barium, lead, and aluminium salts are adsorbed more readily than are those of lime and magnesia. Chlorides and nitrates are adsorbed more than sulphates, but alkali salts, with the exception of the carbonates, are not adsorbed. The behaviour of the alkaline carbonates may be explained by the almost invariable presence of calcium ions in clays, which react with the carbonate, forming precipitate of calcium carbonate, and so removing the carbonate ion from solution. Rohland states that some clays which are only moderately plastic may, on addition of alkali and certain salts, or through some chemical change, be made more adsorptive. The adsorptive power of clay is valuable in some industries, and it is on account of this power that if clay is mixed with neutral or slightly acid muddy solutions or emulsions, when the clay settles it will be found to leave a clear liquid. The adsorptive power of fuller's earth for oil is well known (p. 190). The adsorption of a clay is determined by noting the loss of colour of a dye solution, such as malachite green.

The following procedure was adopted by H. E. Ashley:—"Into a 500 cubic cm. bottle with ground-glass stopper greased with vaseline, 20 grms. of clay and the dye were placed, then 400 cm. water was added. The closed bottle was then fastened in the frame of a small ball mill (60 revolutions per minute), so that at every revolution it was up-ended. This gave a vigorous and complete agitation, which lasted for an hour. Although the clay appeared to settle clear in half an hour, the results were too large and erratic, unless the settling continued overnight. On the following day a convenient amount of the clear liquid was taken

out by a pipette and put into one of a pair of 'carbon' comparison tubes, such as those used in steel analysis, and compared by dilution with a standard solution of 3 grms. per litre, using a camera while matching.

TABLE XVI.

Designation of Clay.	Portion Unabsorbed.		C.
	1.00 Grm. Dye used.	3.00 Grms. Dye used.	Relative Colloids.
Fuller's earth, Eimer and Amend . . .	0.00081	0.00351	...
J. Poole, Pike's No. 20 English ball . .	.00371	.0699	97.5
G. Knowles & Sons, No. 12 English ball	.0086	.0764	96.5
Hammill & Gillespie, Whiteway's English ball clay109	92.0
Moore & Munger, English ball clay . .	.00258	.1221	90.7
Wm. Adolph Co., WH ₂ English china clay0461	1.146	29.0
J. Poole, BB English china clay	1.440	24.7
Hammill & Gillespie, A1 English china clay0842	1.459	24.5
J. Poole, No. 1 English china clay0408	1.500	23.8
Moore & Munger, HN English china clay0523	1.554	23.1
J. Poole, I.R. and S. English china clay	...	1.883	18.6
G. Knowles & Son, No. 15 English china clay1042	2.060	16.0
G. Knowles & Son, No. 7 English china clay	2.410	11.5

"The results with 3.0 grms. dye per 50.0 grms. clay in 1000 cubic cm. water are used as a basis for comparison. From these, column C has been prepared by means of fig. 29. The principle is this: If there is a certain amount of colloids in, say, 10 grms. of No. 3 ball clay, there is twice as much in 20 grms., three times as much in 30 grms., etc. Let us call the amount of colloids in 50 grms. 100, in 20 grms. 40, etc. Treating each of these amounts of No. 3 ball clay with 3 grms. of malachite green, we obtain the curve shown in fig. 29. Now suppose we take 50 grms. of any other clay, say, Moore & Munger's ball clay, and treat it with the same amount of dye, the amount of dye adsorbed proves to be 2.8779 grms.; 2.8779 grms. comes on the curve at 43.35 grms. Tennessee ball No. 3, or at 90.7 relative colloids; that is, it is assumed that clays adsorbing equal amounts of dye contain equal

amounts of colloids, and these are expressed in terms of the amount present in Tennessee ball No. 3."

Unfortunately some other clays of widely differing plasticity show identical adsorptive powers, and grog is also adsorptive. These facts detract from the value of adsorption tests as measures of plasticity.

If Olschewsky's suggestion (p. 317) that the particles of clay are porous is true, some of the phenomena ascribed to adsorption may really be due to absorption within the capillaries or pores.

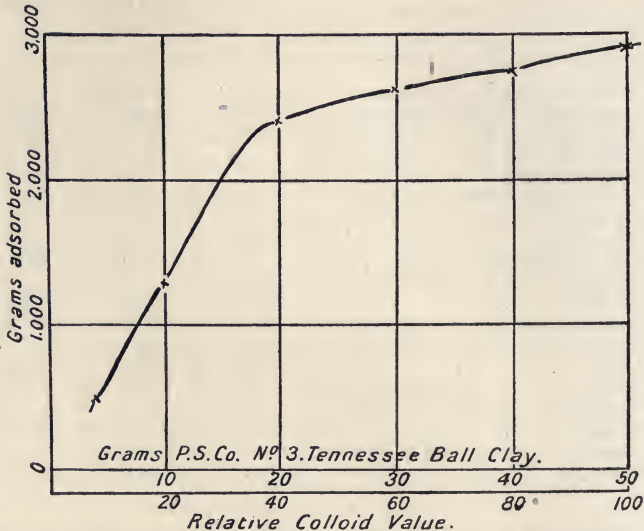


FIG. 29.—Adsorption of Malachite Green by R.S. Co., Tennessee Ball Clay No. 3. (Ashley.)

The permeability (cf. *porosity*, p. 292) of raw clays has been studied by Spring, who found that when such clays are confined so that they cannot expand, they will only absorb enough water to fill the pores. The amount so absorbed varies from 3 per cent. with some fireclays to 25 per cent. with sandy loams. When not confined in this manner the extent to which water can permeate a clay is dependent upon the amount of non-plastic material it contains, and increases when grog or sand is added. The permeability of fired clay is an important characteristic, and is described later.

The more permeable a clay the more easily can it be dried and heated without damage, large pores being preferable to small ones.

Wet clay in the form of a stiff plastic paste is generally considered to be extremely **impermeable**, but, as already mentioned, this is only a relative property, as such a mass of clay if left in water will, in time, fall to pieces (see *Slaking*, p. 307).

Clay which has been suspended in water and allowed to settle is usually quite permeable, as are many natural clay deposits. It is only when the material has been "worked" or pugged that it becomes impermeable.

Semi-permeability is an important characteristic of raw clay which is often overlooked. Graham in 1862 discovered that certain colloid materials, such as parchment paper, glue, etc., if made into a hollow cylinder and filled with a solution of a colloid and a crystalloid substance and then partially immersed in water, will permit the crystalloid to pass through them into the outer water, but will retain all the colloid material. Instead of making a vessel completely of colloid matter it is sufficient to use a vessel of porous earthenware, the pores of which are filled with the colloid matter either by direct application or by precipitation. In this way many substances may be used as "membranes," and are termed "semi-permeable," because they will not permit colloid solutions to diffuse through them, though crystallized ones dialyze perfectly.

When clays are made into "membranes" of this type they behave according to their plasticity. Thus plastic clays effect a perfect separation between colloid and crystalloid solutions and are truly semi-permeable, but very lean clays, such as china clay, are irregular in their action. Thus, according to Rohland, plastic clays will allow ferric chloride and sugar (crystalloids) to diffuse, but not tannin (colloid). In emulsions of oil and water, plastic clays permit the (crystalloid) water to pass but not the (colloid) oil. In alcoholic solutions of fat, such clays permit the alcohol to pass, but not the fat. In aqueous rubber solutions, plastic clays prevent the rubber from diffusing, and in albumen solutions the albumen is retained, both rubber and albumen being typical colloids. The diffusibility, or speed, at which substances dialyze through such a membrane, depends upon their nature. Thus water,¹ which is a crystalloid, and electrolytes, *e.g.*, salts dissolved

¹ There is some difficulty in carrying out these experiments with a clay "membrane," as if a clay paste is formed it may appear to be impermeable to water.

in it, diffuse rapidly, but colloids, such as ferric hydrate, hydrated silica, hydrated alumina, and most products of organic life such as starch, vegetable oils, and gelatin, are either indiffusible or pass through the membrane with extreme slowness. Colours, on account of their complex composition, play a special part. They are retained by plastic clays, though these colours are crystalloid and *not* colloid. Berlin blue, potassium ferrocyanide, aniline blue, sulphated triphenyl rosanilin, aniline red, carmine, malachite green, fluorescin, aurin, and many other animal, vegetable, or tar colours, cannot diffuse through clay, and this in spite of their crystalloid nature.

As the semi-permeability of clays appears to be connected with its plasticity, any treatment which will increase the latter should also increase the former. Rohland has found this to be the case with some lean clays he examined. Some of the phenomena of semi-permeability occur whenever plastic clay is mixed with solutions, as the particles allow the crystalloids in the latter to pass through them but retain the colloids on their surface. In this way an absorption of crystallized matter as well as an adsorption of colloids occurs; but as the particles of clay are so minute the effects are scarcely distinguishable, and clays appear capable of absorbing both colloid and crystalloid substances (see *Adsorption*, p. 333).

Expansion.—When water is added to a dry clay it is first absorbed by the pores, but when these are filled any further supply of water appears to cause a separation of the particles from each other so that the volume of the clay is increased, though not in proportion to the water added. The amount of water which can be absorbed in this manner differs greatly with different clays. That which is absorbed in converting the clay into a good modelling paste is termed the “Water of Formation” (p. 308). It reaches a limit beyond which the pasty mass loses its shape and begins to behave like a thick fluid, so that the stage at which the clay contains a maximum quantity of water of formation is also the point of maximum plasticity; it is said to be the saturation-point of the coagulated colloids (gels) in the clay.

If by any means some of this water is removed, the volume of the mass begins to diminish and contraction occurs.

Contraction or Shrinkage is chiefly, but not entirely, due to the removal of water from clay by evaporation at the ordinary temperature (air-shrinkage), at a somewhat higher temperature in a dryer (dryer-shrinkage), or during the burning (kiln or fire shrinkage).

As all coagulated colloids (gels) which are saturated with water,

shrink when this water is removed, some investigators consider that the shrinkage of clay may be due in part to this cause.

The more general idea (which states facts rather than explains them) is that as the water is removed that which remains draws the clay particles together into a smaller and denser mass. If the clay is not subjected to draughts, the contraction will take place equally in all directions and the shape of the article will be retained. Highly plastic clays are, however, extremely difficult to dry satisfactorily, as they shrink irregularly and set up internal strains which may easily cause the articles to crack.

The amount of shrinkage appears to depend upon the rate at which the clay is dried, for if this operation is performed rapidly the shrinkage will be less, the clay particles not having time to move over each other so freely as when the drying is slower. Rapid drying tends to crack dense clays, owing to the particles near the outer surfaces contracting more than those near the centre of the article. Hence it is necessary to determine the best conditions of drying a given clay. When drying a porous strong clay, the water at first evaporates from the surface and is replaced by capillary action from the interior, the mass contracting by the same amount as the water diminishes. All the pores remain filled with water until the rate of evaporation exceeds the rate at which the pores transmit the water. This point occurs when the clay particles move so much less freely on each other that the rate of evaporation begins to exceed the rate of contraction. After the first stage of surface drying, the exterior of the mass loses water more rapidly than the interior; in the second stage now reached, the pores are no longer filled with water at their outer ends, and begin to form spaces in the clay, filled with air and vapour. Contraction still occurs throughout this second stage until the substance of the clay is so far solidified that the individual particles can no longer slip on each other at all. The third stage is then reached, in which capillary action and shrinkage cease entirely. Evaporation now takes place entirely inside the mass, and spaces are formed exactly corresponding with the volume of water lost. That shrinkage ceases before the clay is completely deprived of its water has been shown by Aron and Brongniart to be characteristic of many, but not of all clays. Aron supposed that the clay shrinks until the particles are practically in contact with each other, so that any further water which may be driven off does not make any notable difference in the volume of the clay; but supporters of the colloid theory argue that the heat used in drying really causes the colloid particles to shrivel, thus reducing their surface and increasing their density.

Aron has further shown that the "pore-space" is constant for each kind of clay, and is independent of the amount of water of formation added to the clay, though this last statement is only true of relatively pure clays.

Thus A. E. Brown has found that taking one hundred parts by volume of an average mild clay the following results have been obtained:—

TABLE XVII.

With the addition to the dry clay of	A shrinkage in volume when dried will occur of	And the ratio of the spaces to the total volume of the dry mass will be
10 per cent. water. ¹	4 per cent.	21 per cent.
15 " "	11 " diff. 7	22½ " diff. 1½
20 " "	20 " " 9	24½ " " 2
25 " "	30 " " 10	27 " " 2½

Table XVII. shows that the less the water used in manufacture the more solid is the resulting mass.

If, now, the pastes made with varying amounts of water of manufacture are subjected to exactly the same conditions of drying, the rate is not proportional to the amount of water added, but is slower in proportion for those with less water. It takes approximately proportional time in the first two stages of drying, but the more solid the mass, the longer it takes to eliminate the water in the last stage. It follows also from this, that want of uniformity in the substance of a brick, such as must exist in bricks made by hand, and in a less degree in those made through a die or in a press, causes a corresponding want of uniformity in the shrinkage and the rate of drying in different parts of it. This is one cause of the warping or twisting of bricks in drying.

In the second stage of drying all clays lose water more rapidly on the outside than in the inside, the angles and arrises in their turn drying more rapidly than the faces. The consequent shrinkage of the outer layer is a frequent cause of cracking, and it is therefore necessary to pursue this stage with great caution, and to effect the drying with air already heavily charged with moisture. It is also for this reason essential to avoid excessive prominence of any part of a complex-shaped article, and it is advisable to follow the shaping with hollows so as to maintain an approximately

¹ Of these quantities 5 per cent. is in each case hygroscopic water, which is not dried out until the clay is placed in the kiln.

regular thickness of material throughout. The frogs or indents on both sides of a common brick are serviceable in drying for the same reason. In a re-pressed brick they serve the additional purpose of rendering the consistency more even throughout.

For objects of reasonable size the rate of drying is approximately proportional to the ratio of surface to volume. Objects of large size, however, take much longer to dry, and require the application of considerable heat to complete the removal of all the water of manufacture from the interior. Many large goods made of fire-clay and stoneware clay require extremely careful treatment, and have to be kept in a heated atmosphere for several days after the moisture has apparently all been removed. Disastrous results are frequently known to occur in the steaming operations in the kiln for want of sufficient care in this particular. Manufacturers frequently adopt a wise precaution in having such goods stamped with the date of making, and in holding their workmen responsible if they are rendered unsound by being burned before the lapse of a stated period of drying.

In order that the goods may not twist or warp when drying, it is essential that they should shrink but little. This means that but little plastic clay can be used in the material, although some is necessary to bind the particles together and to give it the general characteristics of clay. With a carefully compounded mixture the contraction from paste to entering kiln should not exceed 1 inch in 16 (or $\frac{3}{4}$ inch per foot). If it does so, more non-plastic material must be added. The lower the contraction the better the chance of the ware coming true out of the drying-rooms; hence as much non-shrinking material as possible should be used in clay mixtures, so as to keep the contraction at a minimum. The addition of non-plastic material to a clay enables a smaller quantity of water of formation to be used and so reduces the shrinkage; but Aron has shown that if the amount of water used is kept the same as for the clay alone, the addition of non-plastic material will actually increase the contraction which occurs on drying until a certain point (that of maximum density) is reached. After this, the more "grog" added to the clay the less will it shrink and the greater will be the porosity. The nature of the non-plastic material added will also affect the shrinkage to some extent, and will exercise a considerable influence on the quantity of water which must be mixed with the clay. Thus, a porous burned clay will absorb more water than will sand. Providing that the non-plastic material is of a nature suitable to the clay (this must be determined by actual experiment), it may be added in any desired proportions so long as it does not too

seriously reduce the strength of the mass, as it will do if more is added than the binding power of the clay can accommodate.

The shrinkage of clay is usually expressed in terms of original length either as "inches per foot" or "per cent.," as homogeneous clays contract approximately equal in all directions. This is termed the *lineal shrinkage*. The *surface contraction* is almost double, and the *volume contraction* treble the linear shrinkage, within small errors. These errors are due to the fact that no clay mass is perfectly uniform, but for many purposes they may be neglected.

The shrinkage of clay may be measured in a variety of ways, but the following will be found to be one of the most satisfactory, as it is sufficiently accurate without being tedious or complicated. A block (fig. 30) of convenient size (say $9 \times 4 \times 4$ inches) is made of the clay to be tested; the precise size is of little importance provided the ends of the block are as square and the arrises as

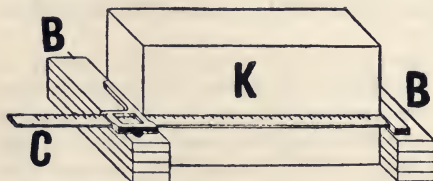


FIG. 30.—Measurement of Contraction.

(Seeger-Cramer.)

sharp as possible. This block (K) is laid carefully on a smooth, level slab or sheet of glass, and a distinctive letter or number marked on the top. This is done so that the block may always be laid in the same position relative to the operator. A sliding caliper (C), graduated in thirty-seconds of an inch, is applied to the block, and its length at the bottom carefully measured. A slip of wood (B), about $\frac{1}{4}$ of an inch thick, is then laid at each end of the block, the caliper again applied by resting it on the wooden slips, and the length of the block again measured. This operation is repeated by the use of additional slips until the top of the block is reached, sixteen or seventeen measurements being taken in all. (In fig. 30 the use of eight such wooden slips—four at each end of the block—is shown.) Very great care must be used not to alter the shape of the block during the measurements, as will occur if the caliper is moved carelessly. The block is allowed to dry white hard and the measurements are repeated, the difference being the contraction on drying. The block is then fired in the kiln, and, when quite cool, it is again measured as before, the difference between these and the first measurements showing the total contraction. The results may be expressed in various ways, but it is most convenient to express them in inches per foot—*i.e.* if a block of the wet clay is exactly one foot in

length and is found to measure only $10\frac{3}{4}$ inches after firing, the total contraction would be $12 - 10\frac{3}{4} = 1\frac{1}{4}$ inches per foot. If the loss in volume is required it may be calculated with sufficient accuracy for most purposes by multiplying the linear contraction by 3, though this is not strictly correct.

Where a sliding caliper is not at hand, a sufficiently accurate result may be obtained by carefully ruling two lines about three inches apart on the clay with a needle and measuring their distance carefully with a fine rule before and after drying and firing. This method, with a pointed caliper replacing the rule, is sometimes preferred to the one previously described.

It is essential that the clay, to commence with, should be of known consistency, and if comparative tests of the clay are to be made at intervals, the actual amount of water in the clay should be determined, as small differences in it have a considerable effect on the contraction during drying.

Shrinkage on drying and heating is a special characteristic of amorphous substances; crystalline bodies—such as quartzose sands—expand on heating.

The **Homogeneity**, or uniformity of physical composition of mixtures of clay and water, is an important characteristic, for unless the material is of the same nature throughout it will be very difficult to obtain satisfactory results. For this reason, clayworkers endeavour by means of crushing and mixing plant of various kinds to temper, pug, or mix the material. Where small amounts of clay are used, *wedging* or mixing by hand may be used, but for larger quantities mechanical mixing appliances are essential. Those most frequently used are pan mills, pug mills, and blungers, according as the clay is coarse, fine, or to be mixed in the form of a slip. The mixture will be more uniform if the clay has been previously weathered, ground, and dried.

Perfect uniformity of composition is seldom, if ever, secured, but by fine grinding followed by repeated pugging, with intervals of rest to permit the water to penetrate the mass completely, a sufficiently uniform material may usually be obtained.

The Effects of Heat on the Characteristics of Clay.—

When moist clays are warmed gently, the chief effect of the heat is to drive off the moisture and so dry the clay. This can only be accomplished in the presence of a quantity of air sufficient to absorb the moisture thus vaporized, so that wet clays heated in closed vessels or chambers do not dry appreciably. The rate at which a clay can be safely dried depends upon the size and shape of the mass, the amount of water it contains, the quantity of colloid present, the power of adhesion possessed by the particles, and the

porosity of the material. Clays may contain, without any special appearance of wetness, as much as 30 per cent. of evaporable moisture, the maximum amount depending on their porosity, and on the amount of hydrated silica, iron oxide, carbonaceous matter, and other active colloids present.

When this moisture is removed, if the exterior parts lose water more quickly than the interior, the clay must be submitted to some internal strain, which must not exceed the adhesive power of the particles, or cracks will be formed.

Tensile tests on a dried clay, alone or mixed with various materials, are often made in order to gain an insight into the best means of enabling a clay to resist the strains produced in drying. They show that the clays capable of resisting the largest strains are those which contain particles of various sizes rather than consisting of wholly fine or wholly coarse particles.

Like all active colloids, plastic clays part with water extremely slowly, and by decreasing the general porosity of the material, the colloidal portions retard the evaporation of water not actually entangled in them. The presence of large quantities of non-absorbent minerals, such as sand, increases the rate at which clays may be safely dried, and, where necessary, materials of this kind are usually added. If the clay is in large pieces and is at all dense it will crack unless special precautions are taken in the application of the heat. These precautions, however important they may be to manufacturers, are outside the scope of the present volume. Many of them may be found in books dealing with the manufacture of bricks, tiles, and pottery.

The removal of the moisture is accompanied by a reduction in the volume of the clay mass (see *Shrinkage*) and a temporary loss of plasticity. Both these can, however, be restored on adding water to the clay, providing that the temperature to which the material has been heated is not sufficient to convert any colloids present into irreversible gels or otherwise to destroy the structure of the clay.

When a clay which has been mixed with water is left in a dry atmosphere the water evaporates progressively. As long as the body preserves a sufficient plasticity, the departure of the water results in the grains of clay coming closer together in proportion to the volume of water removed, but when there is no longer sufficient water to allow the grains of clay to become displaced, the shrinkage ceases and the evaporation of the last portions of water causes the formation of pores in the interior of the mass.

The dry body thus obtained no longer resembles the original clay; it forms a harder mass of a greater density, and the mole-

cular attraction continues to be so powerful after the departure of water that, unlike other (non-plastic) mineral powders, it retains its form and does not fall into powder when dried.

If the temperature of the clay is increased considerably, many notable changes in its characteristics will occur and some new ones will be observed. For example, the clay will gradually lose its softness, sectility, and plasticity, and will become hard and stone-like. It also loses what is known as its "combined water," viz. that which is an integral part of the clay molecule and is represented by $2\text{H}_2\text{O}$ in the formula for kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The evolution of this water is, apparently, accompanied by a decomposition of the clay, though the proximate composition of the residue is not fully proved (p. 363). For some years it has been known to cement manufacturers that under the conditions employed by them, clays when heated to 700° or 800° C. are decomposed, water being evolved and their silica and alumina contents being practically set free.¹ More recent experiments have confirmed this, and Mellor and Holdcroft have shown that china clay, on heating to as low as 500° C., becomes converted into a simple mixture of silica and alumina, and it is probable that other clays behave similarly in so far as their content of "true clay" is concerned. The felspar, mica, and other minerals present may, however, exercise a fluxing action and produce other changes.

If the temperature is raised still further a clay undergoes various changes in volume, and at a sufficiently high temperature it will begin to lose its shape and may (if impure) fuse to a shapeless mass. Hence, in addition to the characteristics already mentioned, the effect of heat on clay reveals its fusibility, or, conversely, its refractoriness.

When a clay is heated strongly it does not behave like a single substance, such as iron, silver, or ice, which has a definite melting-point, but as a mixture of various substances each of which commences to melt at a different temperature, so that it becomes increasingly fluid as the temperature rises. Thus, if a piece of ice is slowly melted, its temperature will be found to remain constant until the whole mass is fused; immediately this occurs the temperature will rise. If a piece of the purest china clay obtainable is heated, it will lose water and, according to Mellor and Holdcroft, will be decomposed into a mixture of silica and alumina, but it will not show a definite melting-point and, except for two points—the first at 500° C., where an endothermal reaction occurs, and the second at 800° C., where an exothermal reaction

¹ Cf. Rebuffat, *Gazz. chim. ital.*, xxx. pt. ii. 182 (1900). Michalis gives a temperature of 600° to 700° C.

is observable—the temperature rises steadily the whole time. Similarly, if the clay contains other minerals than china clay, no single period of constant temperature will be observed, but one ingredient after another will fuse, until finally the whole material is melted. As each of these ingredients softens and partially fuses, it may enter into reaction with other particles, the number of such chemical changes increasing as the temperature rises. Thus clay and chalk, if heated separately, are both almost infusible, but if heated together in certain proportions they form a fused mass at a much lower temperature. It is therefore impossible to calculate the fusing-point of a clay from those of its constituents. If a pure clay is mixed with a fusible mineral or with a substance which can unite with it so as to form a fused mass (such a substance being termed a *flux*) the molten portion may flow into and fill the pores in the clay, and on allowing the whole to cool, an impervious, almost glass-like, mass will be produced. Stoneware and porcelain are well-known examples of clay mixtures which behave in this manner. Such masses are said to be “vitrified.”

Unlike crystalline substances, clays have no definite melting-point, the amount of fused material produced depending on the rate at which the temperature rises, and on the impurities present. Prolonged heating has an effect precisely similar to that of a shorter heating at a higher temperature.

Clays appear to be decomposed at a temperature much below that required for their fusion, the clay molecule breaking down into a mixture of silica and alumina, as already noted. At higher temperatures partial recombination may occur. Thus, Mellor and Holderft consider that if the temperature be raised to above 1200° C. the silica and alumina will, in part, recombine to form *sillimanite* ($\text{Al}_2\text{O}_3\text{SiO}_2$).

In the heating of a clay, therefore, four distinct stages may be noted, each overlapping the others to some extent. These four stages are termed—

1. **Baking**, or heating until the clay particles have lost their plasticity and have formed a moderately hard mass composed of particles adhering together, the mass remaining porous. Fire-bricks, the softer varieties of building bricks, such as “rubbers,” and “biscuit-ware,” are of this type. The end of this stage is sometimes termed the *point of incipient vitrification* or the *sintering point*.

If clays containing much chalk or limestone in the form of a fine powder are baked, the calcium carbonate in these materials will combine with any iron oxide present in the clay, producing a white mass. If iron oxide is present without sufficient calcium

carbonate to combine with it, the product will be red or "blue." (See *Malms* and *Marls*.)

The changes which occur in baking are described more fully on p. 364 *et seq.*

2. **Vitrifying**, or heating the mass until some of the ingredients have melted and have partially or completely closed the pores, as in stoneware and porcelain. The completion of this stage occurs at the point of maximum shrinkage without loss of shape. The vitrification will continue until the whole mass is fused, if the heat be sufficient; but if (as is usually the case) the shape of the material is important, the end of the vitrification stage of firing may be taken as stated. The extent to which vitrification occurs can be altered by increasing the size of the particles, and in this way it is distinguished from the "partial melting" which is noticed when a single compound is heated nearly to its fusing-point.

For further information see *Full fire*, p. 364 *et seq.*

3. **Squatting**, or **Softening**, which occurs when so much of the material has fused that the mass begins to lose its shape and becomes viscous.

The temperature differences at which these changes occur vary with each clay; thus a clay rich in magnesia may be far more completely vitrified without losing shape than another clay containing the equivalent proportion of lime. Hence the influence of the impurities in a clay is often most powerful when the latter is heated to the temperature of vitrification of the mixture.

The difference between the sintering point or commencement of vitrification and that at which loss of shape occurs¹ is very small (about 30° C.) with calcareous clays (marls), but with fireclays and some stoneware clays it is at least six times as much (200° C.). The result is that great care is necessary in heating clays in which this difference is small, or they will warp and lose shape, even if slightly overheated, and for this reason articles made of some clays can never be completely vitrified on a commercial scale. In the manufacture of vitrified articles it is, therefore, advantageous if the clay and silica in the material be highly refractory, somewhat coarse, and with a long "range of vitrification."

The temperature at which the most readily fusible materials soften depends on their nature. Felspar begins to show signs of vitrification at 1190° C., but it is not completely fused below 1300° C.; though, if mixed with clay and chalk, a material becoming quite fluid at 1200° C. may be obtained. Chalk alone,

¹ This is sometimes known as the "range of vitrification," and is an important characteristic of clays to be used for impervious articles

as already mentioned, is almost infusible, but in marls it combines with the clay to produce a material which fuses at a red heat (950° C.). It is, however, very difficult to ascertain the precise temperature at which vitrification begins, as a certain amount of material must be fused before the difference in the porosity of the ware can be noticed. As the temperature rises, the rate at which the fused material is produced increases very rapidly.

4. **Fusion** occurs if the material is changed from the solid to the liquid state, but complete liquefaction takes place so gradually with most clays that a "fusion-range" and not a "fusion-point" is obtained.

Fusion may commence at a temperature of only 500° C., but may be incomplete after the material has been heated to a temperature of 1200° C., though the amount of fused substance has increased all the time.

A reaction commences between the alkalies and the siliceous matter in the clay, then the lime enters into combination, and is rapidly followed by the iron. The finer particles of fusible minerals next fuse, and as the volume of fluid increases with a rise in temperature it attacks the clay particles, then the coarser quartz, felspar, etc., until only the largest particles of the most heat-resisting materials are left. In the manufacture of articles from clay there must always be left a sufficient "skeleton" of unattacked material to enable the shape of the article to be retained.

As previously explained, clays have no definite fusing-point.

The *fusibility* of a clay is a characteristic which is seldom studied, as the temperatures at which most clays fuse are so extremely high as to be almost unattainable. What is usually termed the "fusibility" of a clay is really the temperature at which sufficient of its ingredients have fused to cause the whole mass to lose its shape. This is really the softening temperature, and is defined by Mellor as "the range of temperature in which the substance begins to lose its shape and commences to flow like a mobile liquid. It also indicates the temperature at which the surface tension of the substance becomes greater than those intermolecular forces which hinder the molecule from taking up a position of stable equilibrium, *i.e.* with a minimum surface area." Some very impure clays may be more easily fused, but they do not yield much information with regard to the rest, and all that can be done is to study the reactions which occur previous to actual fusion. For this reason, and because many clays are valued on account of their resistance to heat, it is more usual to refer to the "refractoriness" of clay than to its fusibility.

The nature and proportion of the impurities in the clay and the

size of all the particles are obviously important factors in fusibility. For this reason, the addition of coarse material (sand or grog) may increase the heat-resisting power of the whole.

It has long been supposed that when strongly heated, clays undergo molecular changes, and Abegg and others have found heat reactions taking place quite independently of the heat supplied by the kiln. Glasenapp has observed that all clays become crystalline if sufficiently heated, the clay substance being dissociated at 1400° C. or a somewhat higher temperature,¹ forming a glassy magma containing crystals, apparently of sillimanite, though there is some indication of more siliceous crystals being formed. Mellor has noticed the same phenomenon when fireclays and porcelains have been heated repeatedly. The reactions which occur at high temperatures are sometimes very different to those ordinarily known. Thus at 1000° C. silica can decompose most carbonates, carbon dioxide being evolved, so that, at this temperature, chalk is almost as active as free lime.

The temperature which should be reached in order to secure the strongest goods must be ascertained by actual trial.

Usually it is necessary to make a number of test pieces, to heat these to different temperatures, and to measure their porosity when cold. It is necessary that at least one of the pieces shall have been heated to the stage where it begins to lose its shape. The piece with the least porosity without any loss of shape will be the one which has received the most suitable heat treatment. This method of testing will not apply where the goods are required to be porous.

If a clay is pure the addition to it of other substances, except alumina, will usually lower its fusibility; hence the resistance to heat can only be increased in the case of poor clays by adding more refractory substances to them, and these must be of such a nature that they do not act as fluxes. The presence of free **silica** reduces the fusibility of a refractory clay in proportion to the fineness of the former, and must be regarded as a flux in refractory clays. In a marl or other more fusible clay silica acts as a refractory agent. Relatively coarse sand may have no appreciable effect, or (with a poor clay) may increase its refractoriness.

According to Seger, finely divided silica dissolves in the "true clay," and its action is therefore directly related to its fineness. An excess of silica increases brittleness.

Alumina added to a clay increases its refractoriness, but diminishes its strength. Some alumina compounds, such as felspar and mica,

¹ Mellor and Holdercroft suggest dissociation at a lower temperature—about 800° C.—and partial recombination at the higher temperature (pp. 345, 346).

act as fluxes and greatly increase the fusibility of clays to which they may be added. The case of *felspar* has been studied by Simonis, who worked out a formula for it (see *Refractoriness*), and that of *mica* by Rieke, who found it lowered the softening-point of a kaolin from cone 35 to 31 when the mixture contained 60 per cent. of mica, and still more rapidly as the proportion of mica increased, mica alone softening at cone 13. Hence mica is a distinctly weaker flux than felspar.

Titanium oxide, when 0.2 to 2 per cent. is present in a clay, also increases its fusibility.

Magnesia, lime, iron oxide, potash, and soda increase the fusibility. Richter and Bischof found that the increase in the case of almost pure clays (kaolins and the higher grade fireclays) is roughly proportional to the molecular equivalents of the materials; e.g., 28 parts of magnesia are equal in this respect to 28 parts of lime, 47 of potash, 31 of soda, and 40 of red iron oxide. It will thus be seen that, as far as its weight is concerned, magnesia is the most active of these materials, and iron oxide has the least effect, unless it is reduced to the ferrous state, when it becomes a powerful flux. It must be remembered, however, that magnesia is very slow in action, and is therefore less dangerous as an impurity than lime.

The statement of Bischof and Richter is only true for a very limited number of highly refractory clays, and Flach has found that it does not govern the melting-point of mixtures of metallic oxides or carbonates with quartz and kaolin. Thus, magnesia—which Richter and Bischof claimed to be the most powerful oxide—is found by Flach to be less so than iron and calcium carbonates. In mixtures rich in silicates, magnesia acts as a flux up to 5 per cent., but larger proportions have a refractory tendency. Lead and bismuth carbonates lower the melting-point of a clay mixture far more than the equivalent amount of any other carbonate.

Wheeler has suggested a "fusibility factor" obtained by dividing the sum of silica, alumina, titanitic acid, water, and carbon dioxide by the sum of the total fluxes, the alkalies, and a constant which varies from 1 to 4 according to the fineness and specific gravity of the clay. This has not proved satisfactory when applied to British clays, though apparently useful in America. It is not, at present, possible to ascertain, without a direct test, the temperature at which a given clay will become vitrified or sufficiently viscous to lose its shape, as this does not only depend on the temperature to which it is heated. The duration of the heating is also important, as many clays will fuse if maintained for a sufficient length of time at a temperature several hundred degrees

below that at which they melt when heated somewhat rapidly. Clays are poor conductors of heat, and consequently take a long time for the heat to penetrate them completely. Hence the general rule that "prolonged heating at a definite temperature produces the same effect as a higher temperature applied for a correspondingly shorter time" is sufficiently correct for most practical purposes.

As clays are seldom heated to fusion, other characteristics concerning their fusibility may most conveniently be studied under *Refractoriness*.

The **refractoriness** of a clay is its power to resist the action of heat under a steadily rising temperature and in the absence of disturbing conditions. There is a tendency in some quarters to overlook the fact that whilst flue-gases, fluxes, and other agencies may affect the heat-resisting power of a clay, they do not alter its true refractoriness. For this reason it is not sufficient for a purchaser of refractory clay (or of fire-bricks) to judge it by its refractoriness alone: he must either ascertain its behaviour under the conditions in which he requires to use it, or he must have other information regarding it. Many clays which can withstand a very high temperature when heated under laboratory conditions prove to be useless in works furnaces, and any test of the refractoriness of a clay is therefore chiefly of value in distinguishing it from non-refractory ones, rather than in showing its commercial value as compared with other similar clays. It is for this reason that Loeser finds many supporters in his contention that the rule commonly adopted in classifying clays, viz. to term all those which will bear the same heat treatment as Seger cone 26 refractory, is misleading. He cites several instances, and especially a case where high-class fire-brick did not give any satisfaction in a lining of a lime kiln, while a brick which melted considerably below cone 26 proved to be the best adapted for the lining in this lime kiln. His definition of fire-resistance is as follows: "A brick is fire-resisting when it has proved to be resistant under given conditions, of which the principal feature is technical firing conditions."

Clays vary greatly in their refractoriness, some very calcareous marls fusing at a red heat, whilst high-grade fireclays and china clays have a softening-point above 1800° C.

The refractoriness of a fire-brick or block is greatly reduced if the article is under pressure. Thus, Bleininger and Brown have proposed to value the fire-bricks and refractory clays by loading them with a pressure of 50 lbs. per square inch, raising their temperature to 1350° C. and maintaining it at that temperature

for an hour. A No. 1 grade brick under this treatment will not show any obvious change of shape and will not shrink more than 11 per cent. in the direction in which the pressure is applied.

The plasticity of a clay does not appear to bear any direct relation to its refractoriness, though the more plastic clays resist the action of fluxes better than those which burn to a more open body.

The texture of a clay is important, as the smaller the particles the more easily will the clay fuse, as they enter more quickly into reaction with the fluxes than do the coarser particles.

The use of reducing gases in a furnace in which clay is heated will also make it more fusible, as the iron oxide present is reduced to ferrous oxide, which rapidly attacks the clay, forming a fusible slag.

The refractoriness of a clay is usually tested by forming it into small tetrahedrons of the same shape as Seger cones (fig. 31), but about half the size of those used in ordinary kilns. Special Seger cones of this size may be purchased as standards for testing.

When the material has not sufficient plasticity to be formed into shape a little dextrin may be added to the water used for making it into a paste. These "trials" are then placed side by side with suitable Seger cones on a tile made of bauxite and fire-clay, into which they are pressed sufficiently to make them remain vertical. The clay is then dried and heated until its plasticity is destroyed, after which it is placed in a special furnace and heated until the cones begin to melt. At one time furnaces heated by charcoal or other solid fuel were used for this purpose, but these have been largely superseded by others heated by gas or by electricity. Fig. 32 shows diagrammatically the construction of an electrically-heated furnace supplied by the firm of Dr Seger and E. Cramer, which the author has found extremely convenient.

The true softening-point is usually taken as the temperature required to cause the trial to bend over until its point just touches the base line of the material on which it stands.¹ The number of the Seger cone, which melts under the same conditions as the trials, is used as basis of comparison, or an electrical pyrometer may be used to indicate the temperature. If the cones used have all melted before the test piece, a fresh experiment must be made, using a higher series of cones; if the trials melt before the cones, a lower series of cones must be employed in the next attempt. Owing to the small size of experimental furnaces, great care and some skill is needed to obtain a correct result; the heating must not be too rapid—about 10° C. per minute is a convenient rate of

¹ The Institution of Gas Engineers adopts a different definition (see p. 189).

increase in temperature—the trials and cones must be properly placed so as not to be unevenly heated and not to interfere with each other as they bend over. These conditions will be the more readily fulfilled if, instead of placing cones and trials at the bottom of the crucible, as in the ordinary way, a suggestion of Seger's successors is acted upon, and the cones, etc., are attached to the base block, the crucible being merely used as a cover (fig. 33).



FIG. 31.

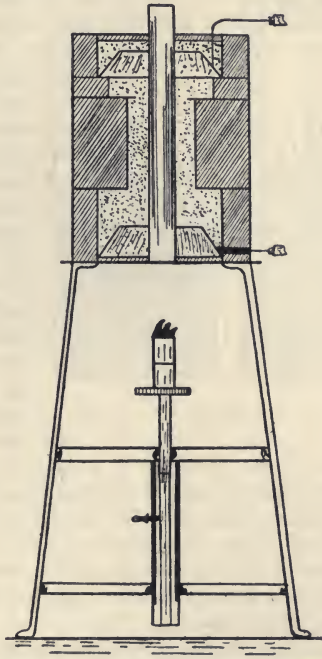


FIG. 32. —Hirsch Electrical Furnace.

When testing clays which undergo great shrinkage on heating, the test pieces are almost certain to fall; in such cases it is best to use trials made of equal parts of the lightly burned and unburned clay. This does not in any way alter the melting-point of the clay, but by diminishing the shrinkage enables the test to be made more speedily and accurately.

Various precautions are necessary with regard to the rate of heating, and, if tests made by different investigators are to be compared, it is essential that they shall all have been carried out

under precisely identical conditions. The various reactions which occur and eventually bring about the bending of the cone have each a speed depending upon the conditions under which they take place. The size of the particles, the porosity of the test piece, and the treatment the material has undergone previous to heating as well as the rate of heating, all exercise an important influence on the softening-point, and, if neglected, may lead to serious errors.

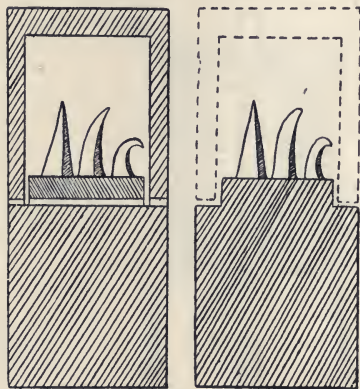


FIG. 33.

For example, the scale of temperatures so frequently used in connection with Seger cones is purely arbitrary, as the indications of the cones do not depend upon temperature alone, but on the rate at which heat has been absorbed by them. Consequently, tests in which an electric pyrometer is used do not necessarily agree with others in which Seger cones are employed. Thus, it not infrequently happens that entirely different results are obtained in a small test

kiln from those obtained in a larger one, as the former is heated far more rapidly, and, if the temperature is "measured" by cones, serious errors may result. Although no definite "law" has yet been formulated, the effect of heat on clay may be said to be proportional to the product of the temperature and the time, or to the product of the rate at which the temperature rises and the duration of the heating.

Clays which do not soften before cone 26 in the foregoing test are considered to be refractory, but Mellor has suggested the substitution of 1500° C. as a minimum softening-point for clays. This is 80° C. lower than the temperature corresponding to Seger cone 26.

The definition of refractoriness adopted by the Institution of Gas Engineers for fire-bricks, blocks, retorts, etc., refers to the temperature at which the angular edges of the material begin to lose their angularity, and so differs from the ordinary measurement of refractoriness¹ (p. 352) in which the material is heated until it

¹ The examination of the sharp angles of a piece of refractory clay as a means of determining its fusibility was suggested by Dr Percy (*Metallurgy*) in 1862.

bends like a Seger cone. The Institution's requirements are met if the test is carried out as follows:—

A piece of the material is moulded or chipped into the form of a Seger cone and is then cemented on to a refractory slab with a mixture of alumina and best china clay, together with Seger cones 28, 30, and 32 (small size). The slab and its contents are then heated in a suitable furnace until cones 28 and 30 fall (if the sample cone falls before these it is of second or inferior grade). The furnace is allowed to cool, and the material under investigation examined. If it exhibits no signs of fusion (loss of angularity), the test should be repeated with cones 31, 32, 33. When cone 32 squats, the sample should be again examined; if it shows signs of fusion the test should be repeated with cones 30, 31, 32. If it still remains unfused higher cones should be used.

A similar method is used for inferior material, cones 26 to 30, or suitable lower ones, being used.

The temperature of the furnace should increase at the rate of about 10° C. per minute. The atmosphere in it must be oxidising.

The standard specification of the Institution of Gas Engineers recognizes two grades of refractory material:—

No. 1 grade, consisting of material which shows no sign of fusion when heated to a temperature of not less than Seger cone 30 (about 1670° C.).

No. 2 grade, consisting of material which shows no sign of fusion when heated to a temperature of not less than Seger cone 26 (about 1580° C.).

An ingenious adaptation of Doelter's electrically heated furnace, recommended by Mellor for the determination of the softening temperature, is shown in fig. 34. In it the piece to be tested is placed in a capsule (which may be of quartz for the less refractory clays), with the hot junction of an electrical pyrometer just below it. The test piece is viewed through a microscope as a dark-ground object, the temperature at which it loses its shape being ascertained from the pyrometer reading. Two observers are necessary—one for the pyrometer and the other for the microscope. No figures relating to refractory clays tested in this manner have been published at the time of writing. Owing to the use of a microscope the amount of fused material produced at what is termed the fusion-point is less with this appliance than when the other methods are used. Consequently this arrangement gives lower results than those ordinarily obtained.

In making a direct determination of the fusing-point of a clay on a small scale great care must be taken to repeat the test several times, as otherwise the results may be far from accurate;

on such a small scale the ordinary errors of experiment are necessarily very large, and in so important a matter as the resisting power of a clay to heat, too much care cannot be taken to obtain an accurate result.

A number of indirect methods of testing the refractoriness of clays have been published, but are now seldom used.

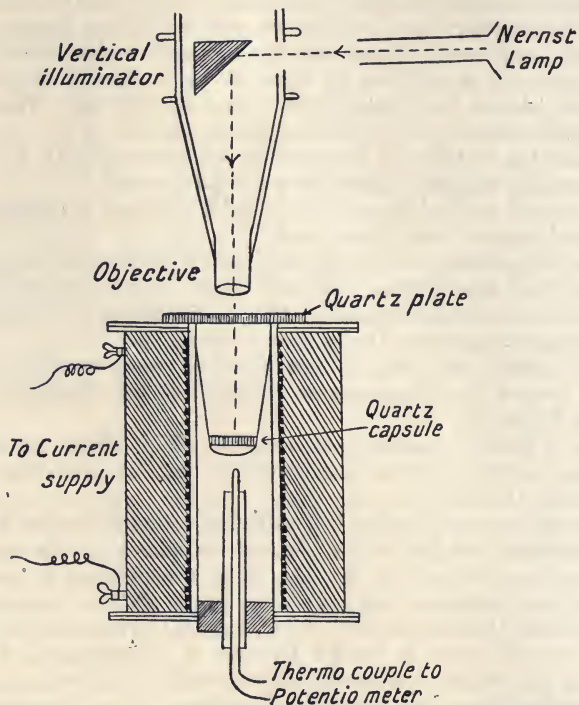


FIG. 34.—Doelter's Apparatus for Determination of Fusing-point.

Many attempts have been made to find a definite relationship between the refractoriness of clays and their composition, but these have been unsuccessful except with the purer clays.

Although the refractoriness of a clay is, to a certain extent, dependent on its composition, it does not at present seem possible to obtain any "factor" which can adequately represent its power in this respect and be deduced from the analysis of the clay. Bischof and Seger both suggested factors of this kind, and

although both are accurate within certain narrow limits, they are not, on the whole, satisfactory.

The most successful attempt to correlate the refractoriness of a clay with its composition is that of Ludwig, who assumed (on a somewhat flimsy foundation) that the fluxes in a clay are in the form of a solid solution with the clay as solvent. He arranged the composition of a clay in the form of a formula with alumina as unity, thus: $x\text{RO} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2$, and by plotting x as ordinates and y as abscissæ, obtained a chart (fig. 35) in which the diagonal

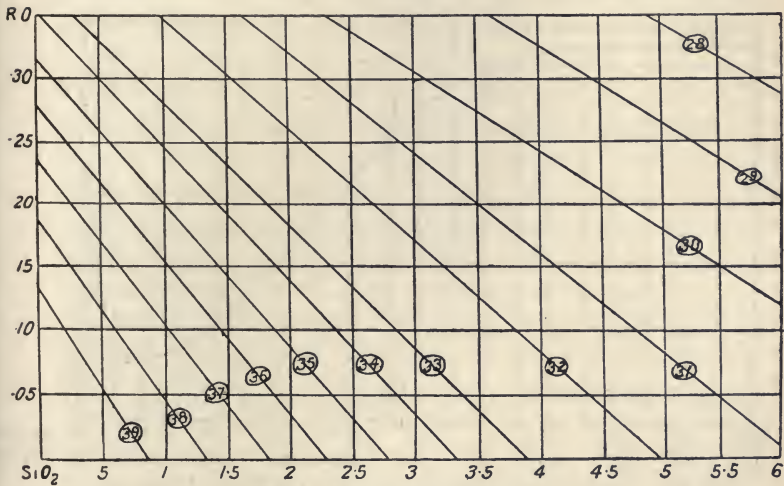


FIG. 35.—Ludwig's Chart.

lines represent the limits of the Seger cones marked thereon, so that the softening-point of a clay is represented in terms of these cones.

This chart, helpful as it is for the more refractory clays, is quite unreliable if the total alkalis exceed 6 per cent., and is in any case only useful for comparison. The reason for its failure in certain cases is that clays are not homogeneous materials and the fluxes are not distributed sufficiently uniformly to admit of their being treated as solid solutions, though the errors in the case of the highest grades of refractory clays are, naturally, small.

The clays which are most noted for their refractory properties are the fireclays; china clay and some ball clays are also highly refractory, but the former is too costly and the latter too plastic

to be used alone. On the addition of a large quantity of grog or chamotte to a ball clay, excellent refractory articles may be made, but this method of manufacture is seldom used in this country, partly because the most available ball clays, whilst highly plastic, are lacking in binding power.

Ganister and various forms of silica are also highly refractory, though not so much as the purest clays. The behaviour of a mixture of china clay and quartz is curious and important in this connection. Seger found that a kaolin used alone had a softening-point corresponding to cone 35, and pure quartz one corresponding

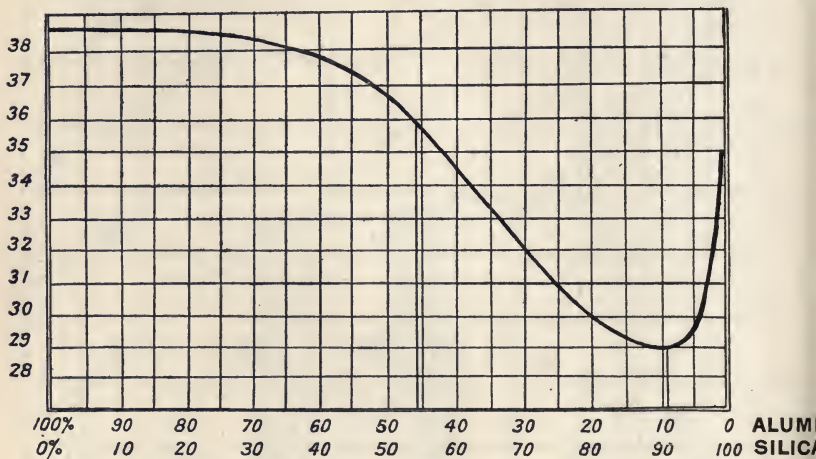


FIG. 36.—Chart showing fusing temperatures of mixtures of Silica and Alumina (Bourry).

to cone 34. If these two substances were mixed together in progressively increasing proportions of silica, the fusibility of the clay gradually increased until a mixture containing 90 per cent. of silica was reached, when the mixture of maximum fusibility (cone 26) was obtained, mixtures richer in silica being more refractory. If pure alumina is substituted for the clay the same phenomenon is observed (fig. 36). This is highly important to users of ganister and other siliceous rocks, as it shows that their refractoriness diminishes rapidly with small amounts of alumina, and that a mixture of such a material and clay containing only 80 per cent. of silica may be even more refractory than one containing 95 per cent. of silica. This fact has not yet been fully appreciated by many manufacturers of silica bricks.

The addition of other materials to a refractory clay usually makes it more fusible, though, if the additions are of coarse sand or grog, they may have little or no effect on the softening-point of the clay, though advantageous in other ways.

Thus Simonis found that in mixtures of kaolin, quartz, and felspar the latter acts as a constant and neutral flux, and in order to determine the softening-point of such a mixture the percentages of kaolin, quartz, and felspar may be represented as k , s , and f , and if k is greater than $\frac{s}{3}$ the "refractory index" will be $R - \frac{s}{3} - f + 60$.

For bodies high in silica, in which $\frac{s}{3}$ is greater than k , the "refractory index" is $\frac{2s}{3} - k - f + 60$. The value of the "refractory index" in terms of cones is given in the accompanying table:—

Refractory index . . .	17·5	22·6	28	33·7	39·2	44·6	50	57·6
Segeer cone . . .	14	15	16	17	18	19	20	26
Refractory index . . .	65	72	80	89	102	114	127	141
Segeer cone . . .	27	28	29	30	31	32	33	34

The effects of impurities in refractory clays have already been described under *Fusibility* (p. 348), *Refractoriness* (p. 351), and in Chap. VIII. (*Impurities*).

Valuable as is the knowledge of the refractoriness *per se* of a clay, there are many considerations which must be borne in mind before the heat-resisting power of a clay under actual conditions of use can be ascertained; particularly when the clay is intended for use in the interior of furnaces (furnace linings), where, in addition to the direct action of the heat, the variations in internal pressure (owing to the expansion and contraction of the mineral by changes in temperature) produce strains which cause far more damage to the clay than the direct action of the heat itself. It is always difficult to ascertain, without actual trial, whether blocks or bricks made of a particular clay will efficiently resist the combined action of heat and pressure; probably the best way is to build a few of the bricks into a furnace lining, to watch them, and to carefully note their behaviour in comparison with bricks of other clay in a similar part of the furnace. The resisting power of fireclay to the action of molten steel and other metals is generally ascertained in a similar manner; experiments on a very small scale are almost, if not entirely, unreliable.

The sizes of the particles, and the porosity or the density of the

material as well as its actual composition, are all important ; and according to the purposes for which it is required, articles made of a refractory clay must be burned to an open or porous mass, a mass with an open interior but a dense surface, or as dense a material as can be produced. No one material can possess all the multifarious characteristics demanded, and users of fire-bricks and other refractory goods must therefore decide which characteristics are of minor and which of major importance.

At present, so little is known as to the physical requirements for refractory articles in certain industries that there is a wide scope for investigation in this direction.

Attempts to increase the refractoriness of clays by the addition of bauxite or other aluminous ores have proved successful in some instances, and Weber has found the addition of corundum to be valuable in some cases where goods are made by his patent casting process (p. 313).

Burned clays behave quite differently from raw ones, as the changes in physical structure and in chemical composition effected by heating clays are numerous and highly important ; the chief value of the goods produced depending upon the choice of a suitable clay and upon its being heated in a suitable manner. In the first place, the clay loses its odour, becomes much harder, and is rougher to the touch. It loses its power of becoming plastic when mixed with water, and is no longer ductile and malleable. In a few cases it may retain its feebly magnetic power. Its electrical conductivity is increased if the temperature has been sufficient to cause vitrification. Vogt found that porcelain crucibles have a sufficient conductivity to allow electrolysis and the removal of some potash.

The colour of clay is also changed, the burned product being white, buff, red, brown, grey, blue, black, or mottled, according to the impurities present in the clay (p. 251).

Clay which has been burned can no longer be broken up into grains of extreme minuteness by simple treatment with water ; it does not slake and will not remain in suspension. Its original lines of cleavage have disappeared, and if the preparation of the clay previous to heating has been suitable, all traces of its original laminated, granular, or shaly structure have gone.

The shape of the particles is no longer of importance, unless some unexpected reactions have taken place, for the heating has converted whatever reversible gels were present into fixed colloids, and has destroyed the semi-permeability and adsorption of the clay.

Burned clay has no binding power, in the sense in which this

term is used in clayworking, nor has it any appreciable elasticity or extensibility.

The behaviour of burned clay when treated with water is entirely different to that of the same clay when raw. It so closely resembles that of a mixture of silica and alumina that it may be assumed that heating to redness destroys the clay molecules, and the character of the product will depend almost entirely on the "impurities" present in the clay.

The porosity is increased if the temperature has not been sufficiently high to cause vitrification. The ability to produce a viscous slip is no longer present, though the burned clay may, itself, form a viscous fluid if heated to a sufficiently high temperature. It is partly on account of this viscosity that no definite melting-point can be found for clays, the difference between the liquid and solid state of the material being due to viscosity and not to a well-defined change of state.

The behaviour of the clay towards acid and alkaline solutions is entirely changed. The action of these on burned clay is seldom appreciable unless the solutions are very strong or the clay insufficiently burned. Vessels of vitrified clay are much used for the storage of strong acids and alkalies, and for the manufacture of corrosive chemicals.

Hydrofluoric acid attacks burned clay, evolving the silica as a gaseous fluoride.

On exposure to the weather, burned clay is not appreciably affected, good bricks being amongst the most durable building materials. Little or no oxidation or reduction occurs in its constituents, and if suitable fireclay is used it can withstand the highest temperatures available, except, perhaps, those of the electric furnace.

Sometimes a **scum** forms on heating clay. This is due to the condensation on it of acid vapours derived from the sulphur in the fuel and carried in the burning gases, which attack any chalk or limestone in the clay and form a sulphate on the surface, or to soluble salts in the clay rising to the surface during the drying, and being converted into a white deposit on burning the clay in a kiln. This latter form of scum is sometimes known as **efflorescence**, and is a troublesome characteristic of some clays. It may often be avoided by adding barium carbonate to the raw clay, which will make any soluble sulphates insoluble. The scum due to condensation-products on the clay can only be prevented by heating the clay with pure air (free from flue-gases) until it is at such a temperature that no condensation-products can form.

A still more troublesome form of efflorescence is that which

appears on the surface of the goods after they have been drawn from the kiln and stored for some time. Such efflorescence is due to external causes, such as piling the goods on a floor formed of ashes, concrete, or mortar, and leaving them exposed to the weather, or in some condition where the floor can absorb moisture. This moisture may be gradually absorbed by the goods, and with it the soluble salts it derives from the mortar, ashes, or concrete. When this moisture reaches the surface of the goods it evaporates, leaving the scum-forming salts on the surface of the goods. Such efflorescence can only be prevented by keeping the burned goods out of contact with ashes, mortar, or concrete, unless they can be kept perfectly dry.

BURNING or FIRING CLAY.—The changes which occur when large quantities of clay are heated—as in the manufacture of bricks, tiles, terra-cotta, pottery, porcelain, etc.—are of such commercial importance as to warrant special description. The chief object of the clayworker is to control these changes so that articles of commercial value will be produced. The effect of heat must, therefore, be regulated, and the reactions which occur must, usually, be stopped before they are really complete, so that the articles may not lose shape or that they may possess certain properties—such as porosity—to the exclusion of others—as vitrification.

The changes are not sharply definable, but occur concurrently and progressively. It is therefore most convenient to consider them in the three stages into which the heating of the clay is commonly divided by those engaged in what is termed firing or burning clay.

These three stages are known technically as (1) the “smoking” or dehydration stage, (2) the “full fire” or oxidation stage (p. 364), and (3) the finishing or vitrification stage (p. 381). Any reactions which occur when clays are heated beyond the stage of complete vitrification are connected with the fusibility or refractoriness of the clays, and have already been described.

The **smoking stage** of firing is so called because a very smouldering fire is used in the kilns, the goods being heated by the “smoke.” During this period any water of formation which has not been previously removed in the drying is driven off. This water forms a vapour or steam, and this “water-smoke” is sometimes stated to have given its name to this stage in the burning. Owing to the emission of this steam, this stage of the firing is also known as **steaming**, and during it the object of the burner is to remove the water as rapidly and completely as possible without damaging the goods.

The removal of this water effects little or no change in the characteristics of the clay, but as the temperature increases to about 450° C. the expulsion of the "chemically combined water" begins,¹ and continues until a bright red heat is reached at about 700° C.

Clays differ greatly in the rate at which they lose this "combined water," and some china clays do not become completely anhydrous until they have been heated to 1030° C., unless the heating is of extremely long duration.

It is a fact, which few clayworkers appreciate, that no matter how much a sample of clay may be dried, it still acts as though it retains a considerable amount of water. In a relatively pure clay, such as ball clay or china clay, about 13 per cent. of water appears to remain,² but ordinary fireclays will contain only about half this amount, and sandy marls and loams may contain even less, though some minerals occurring in commercial clays increase the proportion of this combined water. All clays contain an amount of combined water roughly proportional to the true clay and other hydro-alumino-silicates present, which cannot be removed without heating the clay to redness. Clays which have once lost their combined water can never be made plastic again, as the clay molecule has been decomposed and cannot be re-formed. They may absorb water in their pores, but they never combine with it.

During the removal of this combined water other changes occur. Any pyrite and marcasite present decompose by losing a portion of their sulphur, some carbon dioxide is evolved from the carbonates present, and the carbonaceous matter in the clay commences to burn. When this occurs the second stage of burning has begun. If the clay is removed from the kiln at the end of this first (dehydration) period it is usually dirty grey in colour, very tender, and its form may be destroyed by rubbing with a piece of

¹ This is the generally accepted view, but it is probably more correct to state that at the temperature mentioned the rate at which the combined water is removed is much greater than at a lower temperature. Mellor and Holdcroft have found that there is no temperature below which china clay does not lose water, and the same appears to be true of all clays. At temperatures below 450° C. the rate at which the clay is decomposed is too slow for evolution of the "combined water" to be noticeable except under laboratory conditions.

² It must be remembered that the existence of water, *as such*, in dried clay has not been proved. All that can be said is that on further heating the clay molecule is decomposed and water is one of the products formed. Recent investigations have indicated that clay is not a "hydrated silicate," but an alumino-silicic acid, the oxygen and hydrogen in it being combined as an essential part of the clay molecule and not existing as water (p. 154).

sandstone. The clay has lost its power of becoming plastic on treatment with water, but it has not yet become sufficiently hard and strong to be durable. These desirable characteristics will be gained in the "full fire."

The second, or **full fire stage**, begins immediately after the whole of the water of formation has been driven out of the clay and the kiln has reached a dull heat.

During this stage the temperature rises from 500° C. or a little higher to about 900° or 1000° C., though with refractory clays in which little or no vitrification occurs the temperature may rise to 1350° C. or even higher. It is the most critical part of the burning and the one in which the most errors are made, especially when the temperature is in the neighbourhood of 950° C. (cone 07A). The following are the most important changes which occur in the properties of the clay:—

(1) **Volatilization** of carbon dioxide from the carbonates in the clay, of so much sulphur in the pyrite, marcasite, and other sulphides as was not driven off in the first stage, and of any volatile carbonaceous matter, such as shale oil, which can be distilled completely or destructively in this range of temperature, occurs steadily throughout this stage of firing. The decomposition of the carbonates stretches over most of this period, and as soon as they have been decomposed, reaction between the bases (alkalies, magnesia, and lime) and the clay begins, forming silicates of alkalies, lime, and probably also of alumina. These do not fuse immediately; but at a higher temperature, in the third stage of firing, they effect the final fluxing.

A considerable portion of carbonaceous matter is burned out during this stage; gypsum and other sulphates are partially dissociated at a temperature of about 800° C., but so long as carbon is in the material the expulsion of this sulphur is hindered.

If the heating of the kiln is not too rapid the volatilization which occurs proceeds smoothly and causes no trouble.

(2) **Oxidation** of (a) ferrous carbonate, oxide, and sulphide into ferric compounds which, owing to the high temperature, usually produce red iron oxide if the conditions are favourable for complete oxidation; (b) carbon to carbon dioxide and of its compounds to carbon dioxide and water. The carbonaceous matter present, being both natural to the clay and purposely added in a variety of forms, may burn easily and steadily at a relatively low temperature; or if of a coaly nature, it may produce a sudden rise in the temperature of the kiln, and may cause reduction (p. 367) and so prove very troublesome. Carbonaceous materials, such as coal, sawdust, graphite, are often mixed with the clay. Thus sawdust

is added to form a porous ware, as it burns out and leaves corresponding hollows or pores. Ground graphite and coke are mixed with clay to be used in the formation of crucibles, as they cause a more rapid heating of the metal and enable the mixture of carbon and clay to withstand high temperatures and sudden changes better than clay alone. "Soil," or sifted domestic cinders, is mixed with brick clay around London in order to prevent undue contraction during the drying, and it is also said that the sulphur contained in the "soil" assists in the colouring of the bricks when burnt. Coal dust has been mixed with clay in order to make it more porous, but the gas given off by the coal is disadvantageous. Barley and similar grains have been found useful by Maecler in forming the large pores necessary to prevent scumming in certain kinds of clay. Other waste materials—as naphthalene—have also been employed for this purpose. Except that they differ in the rate at which they burn, all these forms of carbon are oxidised to (gaseous) carbon dioxide during this stage of the burning, providing that the supply of air is sufficient. Otherwise they have a reducing effect on many of the oxides in the clay.

Unless "blue" bricks are required, or there is some other special reason for the use of only a limited supply of air, it is essential that there should be an ample draught in the kiln at this stage. If the temperature rises rapidly without the oxidation of the iron and the carbon in the clay being complete, various discolorations will be produced and slag spots will be formed, and may even cause the clay to lose its shape at too low a temperature. This is particularly the case with shale containing bituminous matter, as the kind of carbonaceous matter present may necessitate the careful regulation of the temperature of oxidation. If the clay contains bituminous carbon, oxidation must proceed at a far lower temperature than when the carbon is similar to that in anthracite, as there is the distillation as well as the burning of the hydrocarbons to consider; as the higher the temperature the more rapidly these hydrocarbons will be evolved, and they may produce a pressure which swells or bursts the ware. In any case, if the heating is too rapid, the gas produced will flash into flame and raise the heat very rapidly, so that the temperature may reach the vitrification or even softening-point, and so spoil the goods. Where the proportion of hydrocarbons is very high, it is advisable to stop firing entirely for some time, the heat of the kiln being kept up by the burning of the carbon in the clay, and in some cases it is even necessary to close the openings in the kiln in order that the combustion may proceed slowly enough to do no harm.

Some brick clays tested by the author on a large scale have required to be kept at a temperature between 800° and 900° C. for 72 hours, and another for 126 hours before all the carbon in them was oxidised, and it is not unusual to find 48 hours' steady heating at this temperature essential. Clays which require more than 50 hours are seldom of much commercial value. They are too costly to burn, except in continuous kilns with twenty or more chambers. In order that the oxygen in the air may penetrate into the clay and so do its work properly, it is essential that the clay shall be sufficiently porous. Clays which are troublesome at this stage (owing to the production of black cores, etc.) must have their porosity increased in some way. The addition of non-plastic material, such as sand, grog, or flint, and a less complete grinding, are the courses usually adopted. Hand-made bricks being more porous than those made by machinery, will oxidise more rapidly. Many shales must be heated with great caution and slowness, as the smallness of their pores makes it difficult for the air to penetrate them and burn the carbon they contain. Dry-pressed bricks are intermediate in this respect.

Orton has shown that to ensure oxidation it is necessary to heat very slowly for a long time before the clay commences to vitrify, as if once this reaction begins it will be impossible to burn out all the carbonaceous matter or to oxidise the iron compounds so as to produce articles of a pleasing colour; and as the pores become closed, the evolution of gases due to the action of the silica on any iron compounds and other salts in the clay cannot escape, and so produce a disagreeable swelling.

Care in the first two stages, and especially when the goods are at a dull red heat, together with sufficient time to permit all the carbonaceous matter to burn away and the iron compounds to become fully oxidised, are the two essentials for success at this portion of the burning. The end of the oxidation period must be ascertained separately for each clay by withdrawing samples at intervals and breaking them open. If they contain black cores of carbonaceous matter the oxidation is incomplete, and the heating must be continued with an ample supply of air, but with a temperature which must never exceed 900° C., and with some clays must be as low as 700° C., until a sample withdrawn from the kiln shows no dark centre on breaking.

The result of heating a brick for various periods is shown in fig. 37, which represents a series of bricks drawn at intervals of six hours each. The illustration shows the section of each brick after fracture, the brick first drawn from the kiln being at the left-hand side of the illustration. This effective method of

demonstrating that the production of cores in bricks may be prevented by sufficiently prolonged heating under suitable conditions was first shown by Orton and Griffiths in their paper on the "Rôle of Iron in Burning Clays."

Failure to complete the oxidation of the carbon present means that as soon as the temperature is high enough the iron will combine with the silica to form ferrous silicate, which vitrifies or fuses suddenly, thus enclosing that portion of the brick still containing carbon. Any carbon dioxide or monoxide forming will cause a pressure which bloats the brick or at least causes the structure of the clay to become vesicular and weak at a temperature far below the proper vitrification temperature, where the iron is present as ferric oxide. Information on the effect of oxidation on the *colour* and *porosity* of clay should be sought under these captions.

(3) Reduction of sulphates to sulphides and the production



FIG. 37.—Showing progressive diminution of dark core on prolonged heating in air.

of slag-like silicates of iron may easily occur with certain clays if they are heated with an insufficient supply of air. Pyrites is particularly troublesome in this respect, as it requires exceptionally careful treatment to secure its oxidation. Indeed, this is seldom complete in clays containing this substance.

The ferric sulphide is dissociated, forming ferrous sulphide, and this, in presence of carbon and some air, forms ferrous oxide. This at once combines with the silica in the clay, if the temperature is sufficiently high, and forms a dark slag.

Sulphates are reduced to sulphides by carbon, and these then undergo the same reactions as pyrites and other sulphides naturally occurring in the clay. In this connection the effect of pyrites in the coal used in heating the clay must not be overlooked. The sulphur dioxide so produced is a powerful reducing agent, and may cause discoloration by its action on the iron oxide in the clay. Sulphur trioxide produced at the same time from the burning fuel may attack the bases in the clay and form sulphates, which may form scum under exclusively oxidising conditions, but which will be destroyed if the conditions are alternately oxidising and reducing.

Carbon cannot be fully burned except in the presence of air in direct contact with its particles, so that if the air supply is deficient, or if for any reason it cannot get to the carbon—as when a clay is dense—the effects of reduction will be observed. As carbon prevents the liberation and expulsion of sulphur from clay, it may be the indirect means of causing the latter to swell as described under *Oxidation*. Carbon also prevents the development of the red colour in a clay at this stage and hinders it at a later one, so that it is essential that reduction should be guarded against as far as possible, by the use of a porous clay and the admission of an ample supply of air if a red colour is desired. In the manufacture of some pottery and porcelain, reducing conditions are necessary to keep the iron in a reduced form, so that the production of a reddish tinge may be avoided. In the manufacture of “blue bricks” a reducing atmosphere is also essential.

If fully oxidised compounds are subjected to reducing conditions (as when a kiln is fired in a smoky condition with carbonaceous matter in the gases or in the clay) they will form ferrous salts which immediately react with the silica present to form a black or blue-grey slag-like mass. This is a serious defect in many articles, but where “blue bricks” are required, the kiln is purposely fired in this manner, as it is on this that the colour of the bricks depends.

When clays contain soluble sulphates (which would form a white scum on the surface) they may be subjected for a time to a smoky atmosphere. This will decompose and reduce the sulphates, and if the temperature is not too high the subsequent oxidation will produce goods of a pleasing colour.

Hearts—dark-coloured or *black cores*—in bricks (fig. 37) are usually the result of reducing conditions in their interior, the pores nearer the surface becoming closed and so preventing access of air to the centre of the bricks. This defect is sometimes attributed to placing the goods in too damp a condition in the kiln, but the only difference made by the presence of this water would be to increase the time needed during the first stage of firing. If no such extension of time is allowed, the effect will be the same as a sudden rise in temperature and the pores will close, and by preventing all the carbonaceous matter being oxidised will produce the effect of a reduction. These cores may be prevented by avoiding reducing conditions (see *Oxidation*). If the clay be alternately heated in an oxidising and a reducing atmosphere, a change of colour, increasing with the number of alternations, is produced. This operation—known as *flashing*—is now frequently employed

in the production of certain classes of goods, and with small kilns and at moderate temperatures it is not difficult to obtain very beautiful effects. The difficulties increase rapidly, however, with an increase in the temperature and size of the kilns. The great point is to secure the complete oxidation of the carbon in the clay (if any be present) at a sufficiently low temperature, so that it cannot combine and so reduce the iron in the clay to such an extent that subsequent oxidation becomes impossible.

Too rapid heating of the kiln at a temperature below 900° C. is the cause of much clay being spoiled, because the carbonaceous matter it contains is decomposed and "set" in such a way that it cannot afterwards be burnt out without spoiling the colour of the goods.

(4) **Porosity**, which is due to the spaces between the particles of clay, increases gradually during the first stage of firing a clay, and reaches a maximum when all the carbonaceous matter has been removed, but before vitrification has commenced. In some clays, with numerous but minute pores, the carbon is never completely expelled, and the porosity of such clays reaches a maximum soon after the commencement of the second stage of firing, at a temperature of about 750° to 850° C.

W. G. Worcester points out that "in a study of all the changes which occur in the burning of a clay there is no single factor that will explain what has taken place so well as a close study of the changes in porosity. These changes enable the rate of vitrification as a whole, the periods of rapid and slow action, and the point where the failure of the mass to retain its shape begins to be traceable, to be studied, and from the porosity temperature curve very safe conclusions may often be drawn as to the suitability of a clay for manufacture so far as its vitrification is concerned."

If the water and carbonaceous matter have been removed from between the particles in the manner already described, a certain amount of pore-space is left (notwithstanding the shrinkage of the clay), and it is this which gives the fired material its porosity or power of **absorption** at this stage. The porosity will therefore depend on the extent to which the clay particles fit into each other and the amount of carbonaceous matter present in the unfired or "green" clay.

As a rule, the purer the clay and the finer it is ground, the less will be its porosity. Overheating the clay will diminish its porosity by causing a partial vitrification of the material, the resultant glassy material filling up some of the interstices formerly occupied by the air.

When other materials are mixed with the clay, with a view of

lessening the contraction, the porosity is also affected according to the nature and proportion of the added ingredients. If these are composed of carbonaceous matter, such as sawdust or coal, the porosity of the fired clay will be much higher than if sand or other non-combustible material had been used. If, on the contrary, the clay had been mixed with a low-melting clay, felspar, Cornish stone, or some other flux, the porosity would be diminished owing to vitrification. As the porosity of the clay gradually diminishes with prolonged heating, its measurement forms one of the most convenient means of determining the point at which the heating should cease in the manufacture of goods from clay.

At the point of maximum porosity a piece of burned clay is usually near its maximum of strength; as the porosity diminishes owing to increasing vitrification, the strength of the material decreases until a point is reached when, on further heating, a sufficient proportion of the mass has become fluid for the clay to lose its shape. This is, however, only true of the intensely hot material. As soon as it is allowed to cool, the fused portion solidifies to a hard glass which binds the remaining particles of material together and forms an intensely strong mass, such as the "blue" engineering bricks of Staffordshire. The clayworker is therefore in a dilemma: if he heats his material sufficiently to produce a considerable amount of vitrification he runs the risk of the ware collapsing in the kiln, whereas if he heats it less strongly the ware will not, when cold, be as strong as similar ware which has been partly vitrified.

The end of the second or "full fire" stage may therefore be defined as being the point at which the porosity of the clay begins to diminish somewhat rapidly, owing to incipient vitrification.

Clays vary so greatly in porosity that it is not possible to state definite limits. It will usually be found, however, that British vitrified bricks absorb from 0.1 to 2 per cent.; white glazed and good red and blue facing bricks, from 5 to 10 per cent.; wire-cut facing bricks, rubbers, and gault bricks 12 to 22 per cent. of their dry weight.

What is usually termed the porosity of clay is really only the **apparent porosity**, as a certain number of pores are always present into which no liquid can penetrate.

To ascertain the **true porosity** these pores must be taken into consideration. Heath and Mellor have shown that

$$\text{True porosity} = 100 \left(1 - \frac{W}{SV} \right),$$

where W equals the weight of the dry test piece, V its volume

including pores, and S its specific gravity in the form of an impalpable powder. The true porosity is seldom determined, the term "porosity" nearly always referring to the apparent porosity. The apparent porosity of fired clay may be measured in various ways, the commonest of which consists in weighing the material, immersing it in water, wiping off the excess of liquid after some time, and re-weighing. The increase in weight is understood to be due to the water "absorbed" by the pores, and the volume of the latter may be calculated from the weight of water thus retained, on the assumption that 1 oz. of water measures $1\frac{3}{4}$ cubic inches, or 1 c.c. of water weighs 1 grm. Although it is usual to express the porosity in a unit of weight, it is more correct to indicate the volume of the pores in relation to the total volume of the test piece. If the article under examination is very large and regular in shape, its volume may be directly calculated (in the case of a brick, by multiplying its length by its breadth and the result by its depth); but if the shape does not permit of this being accurately carried out, the volume of the article may be determined by finding its loss of weight after becoming fully saturated when suspended in water by means of a thread, from one arm of a balance, as in "specific gravity determinations" (p. 291).

Then

$$\text{Porosity} = \frac{\text{weight when soaked with water} - \text{weight when dry} \times 100}{\text{loss of weight when suspended in water by a thread}}$$

If the porosity of unfired clays is to be estimated, some other liquid must be substituted for the water; paraffin is very suitable. The above formula holds in this case also, if the word "liquid" be substituted for "water."

If a piece of burned clay is completely immersed in water the escape of air from its pores is largely prevented by the pressure of the water. It is therefore necessary to exhaust the air by means of a pump and to allow water to enter the vacuum so formed, or to only partially immerse the piece so that the air may escape from the dry portion. Later the immersion may be completed, though the removal of the air is never so complete as when a vacuum pump is used.

The rate of absorption is often interesting as giving some indication of the sizes of the pores. Some burned clays behave very curiously in this respect, as the rate becomes very low for several days and then suddenly rises rapidly, as though some chemical action were going on inside the material. Whilst during the first hour most burned clays imbibe 90 per cent. of the total quantity of water absorbable, and 99 per cent. of it in the first

twenty-four hours, some red hand-made bricks are not completely saturated even after a week's immersion.

The apparent porosity may be determined with much greater accuracy if the volume of the test piece is measured by means of a "volumeter" (Seeger's or Heath and Mellor's, p. 290), and the porosity calculated by multiplying the weight of water absorbed by 100, and dividing by the volume of the test piece.

The porosity of fired clay is very important in certain industries, as it enables it to withstand sudden changes of temperature, to be covered with glaze by "dipping"; and when burned clay goods, such as bricks, are used in the construction of buildings, the porosity of the material enables a certain amount of ventilation to be carried on, while preventing the condensed moisture from the atmosphere from running down the walls of the building. Porous ware is also used as a drying or filtering medium, and for flower-pots. Closely connected with the porosity of fired clay is the extent to which water can penetrate through it. This **permeability** of fired clay is a characteristic of considerable importance, but the ordinary method of estimating it, which determines the speed at which water poured into limited space can be absorbed or can flow through a piece of material, is not very accurate. The evaporation of the water from the open sides of the test piece is a source of large error, as it is practically impossible to estimate its amount.

To reduce this error and the size of the sample to a minimum, so that the test may be applied with accuracy to the small samples which can be fired in a laboratory, Sokoloff has suggested the use of a test piece saturated with water, so that any error which might be due to a "soaking" or absorption-effect might be eliminated. In Sokoloff's method the test pieces are circular discs of 5 cm. (2-inch) thickness, the apparatus used being shown in fig. 39. It consists of a thick-walled tube *a* of a very small diameter, and provided with a scale etched on it. The tube fits into a cylinder *b* by means of a rubber stopper, the under side of this cylinder being fitted with a metallic flange *c*, to which is clamped the test piece *k*, a couple of rubber washers, *i l*, being used to ensure a tight joint. Fig. 38 shows the arrangement on a somewhat larger scale, *d d* being the clamps and *m* a metal washer on which they act.

In the lower part of the cylinder, and above the metal flange, a glass or metal tube *e* is fitted, its upper end being connected to the supply of distilled water *A*. This tube is fitted with a tap *f* and a screw pinchcock *g*, by means of which the stream of water can be regulated with great accuracy. The T-piece *h*

serves to empty the apparatus at the end of a test. The bottle *A* and the tube *a* are closed with cotton-wool plugs. The test is carried out as follows:— The test piece is carefully boiled in water, and is allowed to cool in the same, so that it becomes fully saturated with water. It is then clamped into position in the apparatus, as in fig. 38, and water allowed to flow through the tube *e* until it reaches a given point on the scale of the tube *a* about 40 inches above the test piece, its exact regulation being carried out by means of the pinchcock *g*.

The level of the water in *a* will gradually sink, and the time required for it to sink exactly four inches is noted. The figure so obtained is used as a measure of the permeability of the clay. If the test piece is very impermeable, the upper end of the tube *a* may be connected to an air-pump whereby an increased pressure may be placed on the water in the graduated tube *a*. This is shown in fig. 40, where the pump *c* is connected to a bulb *b* on the top of *a* by means of the tube *o*. The pressure in the apparatus is read on the gauge *n*.

The following precautions are necessary:—

1. The water used must have a

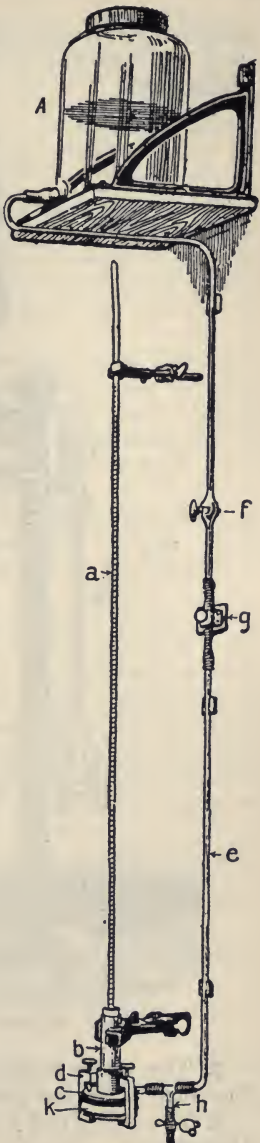


FIG. 39.—Sokoloff's Permeabilimeter.

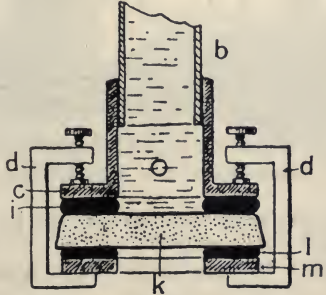


FIG. 38.—Enlarged view of base of fig. 39.

temperature identical with that of the room in which the experiment is carried out, as otherwise the water will expand and give a false result.

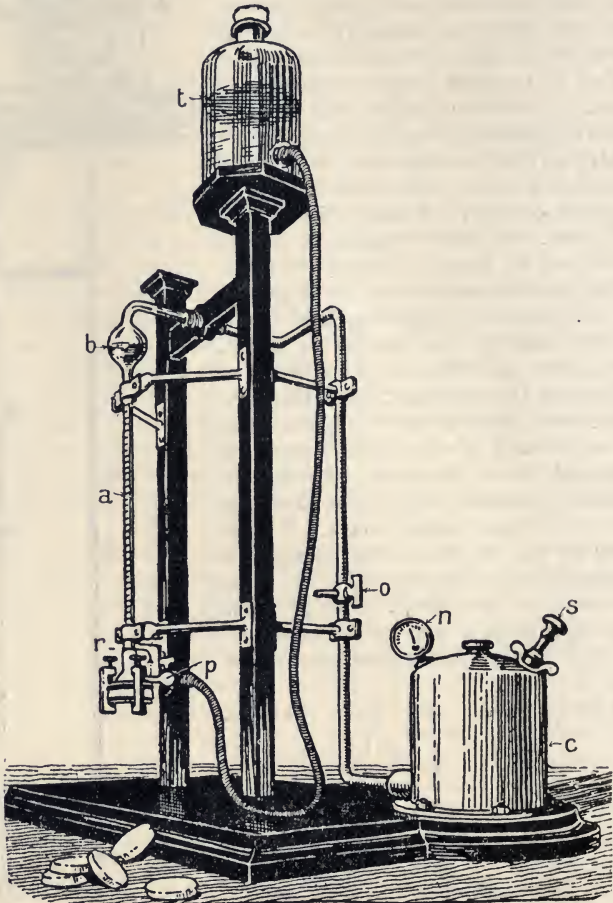


FIG. 40.—Sokoloff's Permeabilimeter for Vitriified Clays.

2. The water must be perfectly clear, so as not to block up the pores in the test piece.

3. The taps *f* and *g* must be completely closed, and must fit properly.

4. It is important that the rubber washer be kept constant in size, and it is essential that its inner diameter shall always expose the same area of clay. A washer with an inner diameter of exactly one inch, when in position, is most convenient. The best results are obtained by using a fairly hard rubber—ordinary “rubber stoppers” being a convenient source from which to cut the rings.

5. The test piece must be sufficiently large in relation to its depth to prevent the water flowing out at the sides, instead of only through its lower face. If much “dew” forms on the sides of the test piece a thinner disc must be used. The results obtained are then very constant, and tests are rapidly and easily made.

By mixing a clay with varying proportions of sand, firing at a definite temperature and plotting the results obtained in terms required for the water to sink exactly four inches, the curves formed indicate the influence of the quantity of sand present on the permeability. To be of value, the test should also be applied to a clay which has been fired at different temperatures.

Sokoloff observed that after repeating the test several times on one sample the disc became slowly impervious, in spite of the greatest care taken to prevent any impurity in the water used from clogging the pores.

(5) Colour changes occurring during the heating of the clay are most noticeable during the second stage of firing. If the clay contained organic matter this will have been partially or completely burned away, leaving the material black or grey with the charred carbon; or white, buff, red, brown, or “blue,” according to the “impurities” present and the method of heating. Thus the colour shown by clay after burning depends upon its composition and the character of the firing conditions, and Seger has therefore divided clays into the following groups:—

(a) Clays high in iron oxide, low in alumina, and free from lime. Red-burning in oxidising gases, but darker if in reducing gases.

(b) Clays high in iron oxide and lime, but low in alumina. Buff-burning.

(c) Clays fairly high in alumina and with a moderate iron oxide content (about 3 per cent. of the latter). Buff-burning.

(d) Clays high in alumina and low in iron. Burning white to light-buff.

There is little or no connection between the colour of a raw clay and that after firing, and the effect of heat on colour can seldom be predicted with certainty. Thus, although clays low in iron usually burn white or buff and those with 5 per cent. or

more of iron generally become red or brown on heating, this is by no means always the case. A clay containing both iron and lime compounds will, at a low heat, burn red owing to the iron oxide present, but at a higher temperature the lime will unite with the iron to form a yellowish or cream-coloured silicate of iron and lime. For this reason red-burning clays are mixed with chalk to make "white" bricks. The conditions of heating also affect the colour; thus, certain clays containing iron compounds will burn red in an oxidising atmosphere, but in the presence of carbon and a limited supply of air a black or "blue" colour will result, the difference being due to the formation of less highly oxidised iron compounds, owing to the reducing atmosphere employed.

Although most red bricks owe their colour to the effects of heat on iron oxide, the mere presence of a large percentage of this oxide will not necessarily produce a good red tint, as so much depends upon the manner in which iron compounds are distributed throughout the clay, the heat-treatment, and the temperature employed. It is seldom that the addition of iron oxide to a clay is satisfactory, even the finest ground material being too coarse to produce a rich uniform tint.

Orton, who has investigated the subject experimentally, states that although presence of iron in a finely divided form is necessary to the production of a buff or red colour, it does not appear to explain all the reactions and colours produced by its aid. The colouring power of iron in the state of granules is practically *nil*, but its presence in this form often causes trouble to the clay-worker through the production of spotted, mottled, and rough, unsightly ware.

As most of the iron compounds present in clay (except the sulphide) form red ferric oxide on heating, it should be possible to obtain an equally red colour from a clay containing iron carbonate as from one in which the iron is present as oxide, but in practice it is found that the carbonate has a greater tendency to granulate, and so produce black or brown specks. The particles of iron sulphide (pyrites), on the contrary, never give a red colour to the clay, but invariably show up as black or slagged spots, owing to the combination of the ferrous oxide with silica, immediately the iron has parted with its sulphur.

Reducing agents such as carbon and sulphur compounds do not, of themselves, affect the colour produced by the iron, but they prevent, or delay, the iron from playing its customary rôle, and consequently may cause untold trouble in the burning, especially with pyritic and bituminous fireclays, as already described

under the caption *Reduction*. Red-burning clays can be made dark or even black by causing reducing conditions to prevail during the last part of the burn.

The oxidation or reduction occurring during the heating of clays containing iron compounds has a far greater effect on the colour than the proportion of iron present, and an error made in the early stages of the firing can seldom be fully repaired later. Thus if the iron oxide has been reduced by the carbon in the clay and has afterwards been apparently fully oxidised, it never assumes its true colour. The change in colour produced by "flashing" has been described under the caption *Reduction*.

Where carbonaceous matter and iron are both present and a strong red colour is desired, it is essential that the clay should be heated very slowly and with an ample supply of air, the time required depending on the size of the pores in the material. The combustion of the carbon and the complete oxidation of the iron must be completed before vitrification is allowed to occur, otherwise the clay will either be black or will contain large black spots.

In clays which are burned at temperatures approaching 1200° C. it is practically impossible to admit of any excess of air, and some amount of reduction always occurs at this temperature. This will not matter much if the clay has been properly oxidised at or below 900° C. On the other hand, it may be generally assumed that if the oxidation is not complete at or near this temperature it never will be finished.

Some clays when heated burn to a peculiar rich glossy brown, owing to the high proportion of manganese they contain. A duller brown is due to iron, possibly with a little manganese, and sufficient fluxes in the clay to cause a slight superficial vitrification.

Seger has shown that the colour of red-burning clays is largely due to—

(a) The quantity of iron oxide contained in the clay.

(b) The other constituents of the clay accompanying the iron. See *Alumina* (p. 258), *Lime* (p. 263), etc.

(c) The composition of the fire-gases during the burning.

(d) The degree of vitrification.

(e) The temperature at which the clay is burned.

Range of Useful Colour.—The range of temperature in which a clay burns to produce coloured ware of commercial value is important. Some clays may be quite useless, so far as colour is concerned, if fired outside this range in order to obtain some other desired characteristic; and as no means of accurately predicting the shade of colour which will be produced is known, actual tests at various temperatures must be made to ascertain the limits of

temperature between which the clay forms a product of pleasing colour.

(6) **Shrinkage** or contraction, though chiefly occurring in the first stage of firing, also occurs during the second on account of the volatility of the combined water, the carbon dioxide, the sulphur, and the combustible material in the clay. This fire shrinkage or kiln shrinkage does not occur regularly, but in a series of short and irregular steps with intermediate quiescent periods, or, occasionally, with periods in which the material expands slightly.

As the shrinkage is very small when once the water and carbonaceous matter have been removed, the main part of all that occurs in the second stage of burning is below 1000° C.

The volume of empty spaces between 600° C. and 800° C. diminishes at first because of the shrinkage, and afterwards because the body diminishes in absolute density above a temperature of about 1000° C. R. Lucas has shown that fire shrinkage takes place without appreciable loss of weight, and his determinations of porosity show that the total hollow space in the apparently dense kaolin bodies is very great, and is reduced on heating. A kaolin which he heated to 1000° C. had a pore-space equal to 39 per cent. of the total volume.

The amount of shrinkage on firing is affected by the formation of sealed pores or gas-bubbles, which are unable to escape from the viscous mass, and may, under certain conditions, cause a *swelling* or increase in volume, instead of a shrinkage. Some clays, if heated too rapidly or with too little air, will swell to such an extent as to make them useless. Carbonaceous matter, accompanied by a considerable amount of flux in a clay, will produce this swelling in a very marked degree (p. 368).

Clays which have an excessive kiln shrinkage must be mixed with non-plastic material, such as sand or grog, which does not contract. Whilst the total shrinkage may be greater with a fat clay than with a lean one, yet the fire shrinkage of the latter may be greater than that of the former, the difference being balanced by the higher-drying shrinkage of the plastic clay. According to Rohland this explains why non-plastic clays such as kaolins, with less pores than a plastic clay, only begin to shrink at high temperatures (*i.e.* in firing).

The proportion of kiln shrinkage may be measured as described on p. 342, or if the cubical shrinkage is required a volumeter (p. 290) may be used.

Though important where articles made of clay have to fit with others, the fire shrinkage of clay during the second stage of burn-

ing is not usually a matter which concerns the clayworker. He pays great attention to the shrinkage during drying, and to the total shrinkage in the kiln, but, except in special cases, does not differentiate the shrinkage in the three stages of firing. It is, however, essential that the heat of the kiln should be regularly distributed, as variations in rate at which different parts are heated will produce strains which may later reveal themselves in the form of cracks. It is for this reason that combustible materials are often added to clay. The pores produced when this is burned out secure a better distribution of the heat through the mass.

The amount of shrinkage occurring when an article is re-heated is a useful indication whether the article has been properly fired and whether it is refractory. Thus the Institution of Gas Engineers' standard specification requires that on re-heating for two hours at Seger cone 12 the linear shrinkage of a fire-brick shall not exceed 1 per cent.

(7) **Warpage** is a term suggested by W. G. Worcester to indicate the amount of warping or deformation of a clay at some stage in its manufacture. It is to be distinguished from fusion only as a matter of degree; and whilst it may occur without any signs of vitrification, it is, in the main, due to the viscous nature of clay both before and during firing.

Worcester has proposed to measure warpage by supporting bars of plastic clay 13 inches by 1 inch by $\frac{1}{2}$ inch on clay knife-edges placed exactly 10 inches apart, firing at different temperatures (from cone 010 to the temperature of overfiring), and noting the amount of sagging at the centre of the bar. Worcester finds that warpage cannot be correlated at all closely to shrinkage, porosity, or other properties of the clay, though frequently a high shrinkage and a low porosity will accompany a high warpage.

(8) The effects of **impurities** in the clay have, to some extent, been previously noted. With the possible exception of the iron, sulphur, and carbon compounds already described, their influence is so much more noticeable in the later stage of firing that they may be conveniently discussed later.

(9) The **specific gravity** of clays usually increases slightly during the second stage of firing, but the change is not very marked, as the few reactions which occur do not appreciably affect the volume of the clay particles so much as they reduce the volume of the mass as a whole.

The specific gravity of a piece of uncrushed clay which has undergone partial vitrification is always lower than that of the same material reduced to fine powder, on account of the viscosity

of the fused portion of the material preventing the gases formed from escaping, and so retaining them as sealed pores not determinable without first crushing the material. Even when highly refractory clays are fired, the specific gravity is always somewhat low, owing to the existence of these sealed cavities.

Until recently, the specific gravity of a clay was considered unimportant, but Purdy has shown it to be invaluable in a study of the changes which occur in the vitrification of clays, particularly with regard to the effect of the sealed cavities just mentioned, the existence of these being unrecognizable by ordinary porosity tests.

Methods of determining the **true specific gravity** and **apparent density** are given on p. 291.

The **apparent density** of clays changes irregularly during the first stages of heating. It begins to diminish as the vitrification proceeds, and reaches a minimum when the mass fuses. This diminution is due to the formation of silicates, which are the least dense when they have been produced at the highest temperature. The simultaneous reduction of the volume and the density of the body then occurs. All natural silicates—felspars, granites, porphyry, etc.—undergo a reduction of density when they are heated to a temperature near that of their fusing-point. The sealed pores in impure clays exercise an appreciable influence.

In heating clays and other materials which lose water at a moderately high temperature, the specific gravity may at first increase, but when this water has been removed, a diminution in specific gravity will be observable. Thus, the absolute density of kaolin before firing is about 2·4, but increases in consequence of the giving off of water to nearly 2·7; then it diminishes again, falling to about 2·5. The apparent density (the weight of the unit volume) starts at 1·6 to 1·7; then it diminishes, at first regularly, until the moment of evaporation of the water, but increases rapidly afterwards, according as the empty spaces disappear. It never becomes equal to the absolute density, because even when a clay appears to be completely vitrified, some empty spaces always remain. If crystallization occurs on cooling, the specific gravity again increases.

The differences between the behaviour of kaolins and less pure clays is largely due to the formation in the latter of vitrified matter and sealed pores.

With clays used for brick and tile manufacture and for coarse pottery, the effect of vitrification is much more noticeable than with the purer china clays and ball clays. Most brick and roofing-tile clays show an irregular but very slight change at first, but on heating to a temperature which varies with the nature of the clay

(cone 02 for red-burning clays, and cone 1 for fireclays) the density drops suddenly and continues to diminish rapidly as the temperature increases. This is due to the formation of sealed pores into which the water used in determining the density cannot enter, and so gives low results. This loss of density indicates a stage of vitrification and of viscosity, with consequent deterioration of structure. The temperature at which this sudden drop in density occurs indicates the "finishing temperature" of the clay; beyond this, the heating can only be carried with a considerable degree of risk of distortion.

According to Purdy and Moore the rate of decrease is proportional to the amount of vitrification, and, as Bleininger has pointed out, the quicker the specific gravity drops when the temperature rises steadily the more rapid must be the process of vitrification, and hence the shorter the range of vitrification—that is, the less suitable the clay would be for most purposes, and *vice versa*. In clay testing the drop in specific gravity during burning is, therefore, a matter to which attention must be paid.

(10) The **volume weight** (p. 289) of a clay at the close of the second stage of firing is markedly less than at the beginning. Measurements of it represent a balance due to the replacement of water and carbonaceous matter by the air, and the shrinkage of material, and are of little value.

Bricks which have been taken from the kiln at the end of the second stage of firing are very soft and friable; in some cases they are so weak that on being placed in water they discolour it and will disfigure white bricks placed beside them. This is not merely a surface discoloration; but sometimes it extends to a depth of $\frac{1}{4}$ inch into the interior. The red colouring matter is iron oxide, which appears to be dissolved colloiddally. It clearly shows the folly of erecting a building coursed with white and red bricks, when both are very absorbent. The question of the solubility of certain ingredients of fired clays has not yet received the attention it deserves; it appears to be closely connected with the gradual decomposition whereby bricks become increasingly porous in use.

The **vitrification stage**, or third period of firing (p. 362), is said to commence as soon as a sufficient amount of material has fused to permit of its presence being detected. The end of this period, in commerce, coincides with the finish of the heating, but for experimental purposes it ends with the partial loss of shape, or even the complete fusion of the mass. The temperature at which it commences may be as low as 700° C., but it is seldom that vitrification can be detected in clays which have not reached a

temperature of 900° C. In some fireclays the vitrification only occurs at so high a temperature as to be commercially negligible, though a certain amount must always be present in order to enable the particles to adhere together. When heated to 1390–1410° C. (cones 13–14) all clays lose their porosity and become dense, but, unless refractory, they also lose their shape owing to partial fusion. With most brick clays there is sufficient vitrification at 1100° to be obvious to the naked eye.

During this stage of firing, oxidation and reduction only occur to a limited extent, though it is often difficult to avoid the latter, as reduction aids vitrification, but spoils the colour; it should, usually, be avoided where possible. The fused portion of the material, which is formed by the heat of the kiln, fills up the pores in the material, forming highly complex silicates, which may remain solid, or may undergo partial fusion, and on cooling form an intensely strong and impervious mass, the strength and impermeability depending on the proportion of fused matter present. If this stage of heating is carried to completion, the porosity of the material disappears, as all the pores have been filled.

With increasing temperature the mass may shrink somewhat, but it frequently swells irregularly. Hard firing will raise the temperature of the clay too quickly to its softening-point, and so will cause the goods to shrink unduly. If a notable proportion of quartz is present, the expansion which the latter undergoes in passing from the density 2·7 to the density 2·2 is added to that of the clay, and it may be that the reduction of the empty spaces is no longer sufficient to hide it. The fact can be easily noticed in fire-bricks rich in silica. Loss of shape is inevitable on excessive heating, and the **finishing-point** may be ascertained by determining the porosity of samples which have been heated to various temperatures, the highest of which is the one where the loss of shape begins, and drawing a curve showing the shrinkage of the clay in relation to the temperature. The point at which the shrinkage begins to diminish rather rapidly may often be taken as the maximum firing temperature for that clay, as the swelling which follows soon afterwards is a sign of the breaking down of the structure of the material. This may also be shown by noting the changes in the density of the clay mass.

As the strength of a porous clay mass can only be increased by filling up some of the pores with fused material, there is no object in continuing the heating when the porosity has become almost constant, and can only be appreciably diminished by so much vitrification as will cause a loss of shape, unless a vitrified article is required.

The **hardness** increases with increasing vitrification.

The vitrification may be caused by the temperature reached being sufficiently high to fuse several of the constituents of the clay, these attacking others in their turn, but it is also due, in clays containing pyrites, to the formation of an easily fusible silicate by the combination of the ferrous oxide from the pyrites with the free silica in the clay. As the temperature at which the pyrites can be completely decomposed is almost the same as that at which the fusible slag is formed, it is almost impossible to produce a red colour from pyrites in clay.

Lime and other basic compounds (except alumina) all react with silica and with clay to form fusible masses, and these with other fluxes are, in most cases, the chief portion of the binding material in the vitrified mass. These silicates may exist in an unfused condition at 800° C., but as soon as their melting-point is reached they fuse and fill up the pores. Their composition has only been partially studied, for they are often complex compounds containing alumina as well as other bases.

Lime compounds usually dissociate and form free lime before the third stage of firing is reached, but though the formation of silicates may occur at the temperature first mentioned, these seldom take part in the vitrification below 1150° C., unless sufficient alkalis are present. Some marls which contain 30 per cent. of chalk fuse completely at this temperature. Hence the effect of various substances on the chemical composition of clays undergoing vitrification can only be stated in general terms.

Iron compounds, in conjunction with carbon, cause serious discoloration, as already explained, if the clay is allowed to vitrify too rapidly and before oxidation is complete. At the highest temperature ordinarily employed in clay works, iron acts as a flux, and its presence in large quantity therefore lowers the refractoriness of a clay.

Sulphur, by its interaction with silica, liberates gases which, if vitrification has commenced, will cause the mass to swell. It should, however, have been removed in the second stage of firing.

Other materials occurring in clay usually aid the vitrification, though silica only does so at very high temperatures, and alumina only when in combination with fluxes, as in felspar.

In this connection it is important to notice that **magnesia** acts far more slowly than lime, and is therefore more valuable in the production of artificial stoneware clays.

If clay containing coarse particles of lime is heated to a temperature sufficient to form a fused silicate, the resulting mass will be strong and durable, but if the lime is not vitrified in this manner

it may "blow" and cause either a disintegration of the mass or may spoil its appearance by forming white spots or hollows on the surface.

In studying the vitrification of clays it is important to remember that a prolonged heating at a given temperature may produce a greater vitrification than a shorter heating at a higher temperature, and that in endeavouring to produce a maximum of vitrification without loss of shape the temperature of the kiln should be kept as constant as possible, or it should rise very slowly. This is known as "soaking the goods in the heat." It is particularly necessary in the production of paving bricks, blue bricks, and engineering bricks generally, and also with stoneware and pottery with a vitrified body. To avoid the use of unnecessary fuel it is usual, where vitrified ware is required, to use a clay rich in fluxes or to add these to a more refractory clay. In fact, the chief purpose in adding fluxes to clay is to increase the vitrification of the mass at a convenient temperature, and to give the goods so dense a texture that they will "ring" when struck. For this purpose it is desirable that the grains of clay and other materials should be very small, as vitrification then takes place more readily. A sufficient number of coarser grains must, however, be left to form a refractory skeleton, which prevents the articles from warping or otherwise losing their shape. It has long been known that the finer the particles the more rapid the vitrification, though, as Goodwin has shown, a certain amount of irregularity in the sizes of the particles will cause them to be packed closer and so may produce the same effect. A coarser texture reduces the speed at which vitrification can occur, but at higher temperatures they may act equally powerfully. This has been proved experimentally by several investigators.

The effect of using wet grog, in place of dry, in fireclays, etc., has been shown by Wilson, Edwards, and Leese to reduce vitrification, as the finer particles of clay are carried by the water into the pores of the grog and so give the effect of a coarser texture than when dry grog is used.

The speed at which vitrification occurs is very important, as, if too rapid, the interval between the end of the second stage of firing and loss of shape is too short. Hence it is necessary to retard vitrification in some cases by the substitution of a different flux or by increasing the sizes of the refractory particles of the clay.

The **colour** usually becomes duller when a clay which has been fully oxidised is heated to vitrification, red clays becoming brown or blackish, and white-burning clays turning a somewhat unpleasant grey. This is often due to part of the iron compounds

present being reduced to the ferrous condition and then forming the blackish slag previously mentioned.

Sometimes the colour of clay which has been heated to incipient fusion is changed during *cooling*. Thus the well-known "flash" or reddish colour on certain fireclays is only produced when the clay is exposed to pure air, whilst still hot enough for some of the iron to be oxidised. If pulled out of the oven whilst at their highest temperature and cooled suddenly, such clays are buff with black spots, but if cooled very slowly with an ample supply of air they become reddish on account of the oxidation of the iron compounds which occurs.

The **strength** of the partially vitrified material will usually depend on the size of the refractory particles and on the extent to which fusion has occurred. As vitrification proceeds the pores in the mass are filled, so that the tensile and crushing strengths of the material, *when cold*, is roughly inversely proportional to the porosity. Thus, in the case of ordinary bricks, those which absorb from 6 to 12 per cent. of water will ordinarily show from 7000 to 15,000 lbs. per square inch of ultimate crushing strength; whilst inferior bricks which absorb one-seventh to one-fourth of their weight of water will average but little more than half these figures. Table XVIII. shows the enormous variations in the crushing strengths of bricks from different sources. In each case any recesses in the samples were filled with cement and the test pieces were bedded between $\frac{3}{8}$ -inch pine boards.

The strength of partly vitrified clay, *when hot*, is the opposite to that just mentioned, being roughly proportionate to the porosity of the material, and inversely to the amount of fused or viscous material present.

The weakness or strength of clays at a high temperature is important in furnace construction, and for this reason Bleinger has proposed that the crushing strength of all fire-bricks at a temperature of 1350° C. should be ascertained (p. 351).

Clays which have been partially vitrified do not yield results of particular interest when subjected to torsion tests, but the **bending moment** is sometimes important.

The resistance to bending may be measured by placing the test piece on two knife edges several inches apart, and loading it in the middle continuously until it breaks, the weight which causes the breaking being noted. If the test piece is corrugated, its surface should be levelled with Portland cement immediately above the knife edges. (*See* p. 333.)

Resistance to **abrasion**, *i.e.* to wear and tear, is an important characteristic to partially vitrified clays used in the manufacture

TABLE XVIII.
CRUSHING STRENGTH OF BRICKS.

District.	Kind of Brick.	Stress in Tons per Square Foot.		
		Cracked slightly.	Cracked generally.	Crushed.
Kent	Hand-made stock	98	118	129
„ (same yard)	Wire-cut stock	147	194	197
„ Crayford	Hand-made stock	187	205	250
Essex	„ „ „	120	165	168
London Market	Hand-made stocks (some unknown)	37	61	63
Bracknell	Hand-made red-facing	164	224	229
Aylesford	Gault	730	880	904
„	„ (another works)	110	230	238
Fletton	Semi-dry process	180	250	250
Leeds	Red engineering (stiff-plastic process)	379	450	460
Suffolk	Wire-cut gault	120	145	160
Sussex (Southwater)	Red-pressed facing	340	409	421
„ (Warnham)	Common red hand-made	187	292	295
Leicester	Wire-cut	255	340	344
„	„ (another firm)	113	302	309
Grantham	„	40	89	92
St Helens, Lancs.	„	210	322	358
Nottingham	Pressed shale	131	162	170
Devonshire	„ (vitrified)	86	389	396
Ruabon	„	350	362	390
„	„ (another firm)	427	596	622
Rugby	Wire-cut	162	181	194
„	„ (another firm)	440	672	679
Staffordshire	Blue	520	780	791
Leeds	Fire clay	168	170	177
Buckley, Cheshire	“Obsidianite”	...	468	792
	Lime sand brick	109	150	158

of paving bricks. It is usually tested by placing a weighed quantity of the material in an iron drum together with large iron balls and rotating the whole for twenty-four or seventy-two hours at a speed of 30 revs. per. min. The iron and coarsely powdered material is then removed and the material re-weighed, the loss being stated as that due to the wear and tear in the “rattler test.” Though useful as a rough guide this test requires to be very carefully standardized before it can be regarded as reliable. In Germany paving bricks and other vitrified clays are sometimes

tested for durability by noting their loss of weight when held for a given time on to the flat surface of a horizontal grinding-stone of compressed emery (fig. 41) which rotates at a definite speed. The same remark as to standardization applies here as to the rattler test described above. A modification of this test, used in France, consists in measuring the extent to which the samples are worn when subjected, under a given load, to the rubbing of a normal sand spread evenly about on a circular cast-iron plate, rotated at a given rate. The usual dimensions of the samples are $2\frac{1}{2} \times 1\frac{1}{2}$ inch base, and a height varying from 4 to 5 inches. The total load on the rubbing surface is usually about 2 lbs. per square inch. The sand used must be sharp and of a definite fineness. The standard "sand" employed for this purpose in France is obtained by pounding and then sifting crushed quartzose Fontainebleau stoneware and retaining that which passes through a No. 50 but is kept entirely back by a No. 200 sieve. One quart of sand per test

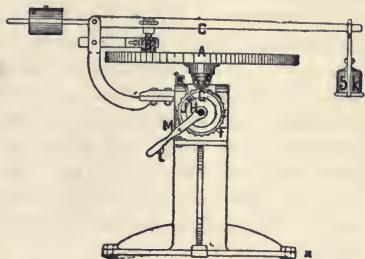


FIG. 41.—Machine for testing Abrasion.

piece and per thousand turns of the disc is used, and the machine has 2000 revolutions per hour, the test piece being subjected to 4000 turns. The losses in height and weight of the test piece should be determined. The same particulars may also be noted in the course of the test after 1000, 2000, and 3000 revolutions of the disc.

The development of heat during vitrification has been studied by Le Chatelier, and others, with a limited amount of success. It is chiefly important as indicating the formation of new chemical compounds, or the decomposition of existing ones. The results obtained, so far, are by no means definite, though—as already mentioned (p. 246)—they indicate the decomposition of the clay itself into a simple mixture of alumina and silica, any impurities present forming a glass-like material. The variety of materials forming this glass is so great and the proportion of each of them is so small and the study of the endo- and exothermal reactions is so complex, that the results are less instructive than when simpler minerals are studied.

For a similar reason, the curves obtained on cooling clays (p. 389) have not, as yet, been applied technically in clayworking, except to a trifling extent.

The **micro-structure** of burned clays affords a valuable indication of the changes which occur during the firing. The material may be examined in the form of (*a*) fragments broken or chipped off larger pieces, (*b*) polished and etched specimens obtained from a fractured portion, or (*c*) as a transparency or thin section.

The fragments—whether plain or polished and etched with very dilute hydrofluoric acid—are examined by reflected light under a low magnifying power, a 1-inch objective being the strongest used for this purpose. The polished specimens are troublesome to prepare and, except under special circumstances, do not produce results very different from those obtained by examining an unpolished fragment.

By reflected light, the coarser and apparently unchanged portions of the clay will readily be observed, and a considerable amount of information as to their proportions, sizes, and nature may be obtained in this manner. These form the bulk of the material, the particles being cemented together by means of a glassy mass so that their edges are not always easy to distinguish, particularly in vitrified clays. Sometimes this cementing material may be removed by etching with very dilute hydrofluoric acid, but in many cases the other constituents are also affected by the acid.

The difficulty of recognizing the various minerals present being so great when the specimen is too thick to be transparent, their identification is chiefly accomplished by the study of specially prepared sections, which are sufficiently thin to be studied as microscopic objects, and Sorby, Glasenapp, Mellor, and others have done valuable work in this connection, particularly on refractory clays and porcelains.

The preparation of these thin slices requires a considerable amount of care and skill, but with the aid of the descriptions given in a good treatise on petrology (such as F. Rutley's *Studies of Rocks*, or Grenville Cole's *Aids in Practical Geology*) it is not really difficult.

Such sections should be mounted on a glass slip and examined (*a*) as transparencies and (*b*) by means of polarised light. In the former case the transparency or opacity and the shape and colour of the materials present will be seen, but owing to the large proportion of semi-transparent fused material some of the crystalline matter will be unobserved. By means of polarised light, however, all the amorphous material is rendered opaque, as light after polarisation by passing between crossed nicols can only travel through substances in a crystalline form. The use of nicols is fully described in the books on petrology just mentioned ;

by their aid it is comparatively easy to determine how much crystalline matter is present in the section, as all the amorphous material will be practically invisible.

The table on pp. 390 and 391 (compiled from information published in the *British Clayworker* by the late G. Harris and others) shows in brief form the micrographic characteristics of the chief minerals occurring in raw clays as well as in those which have been fired to incipient vitrification.

A considerable number of other minerals also occur in clays, or are formed in them on heating; for the identification of these a treatise on petrology or mineralogy must be consulted.

The amount of definitely crystallized matter is usually too small to be observable, the bulk of the material consisting of amorphous grains cemented together by a glassy mass. The proportion of crystals is, however, increased greatly by repeated firings at a high temperature, and in this manner the production of sillimanite (p. 249) has been clearly shown to be due to molecular rearrangement of the clay particles after they have lost their combined water. Other minerals present in crystalline form are rare in the purer clays; in the red-burning and other impure clays they are more frequent, being due to the impurities present; usually, however, they exist in the burned clays in the form of glasses or slags.

The cooling of clays after firing in kilns is a matter requiring considerable care, as the material will crack and disintegrate if its temperature is lowered too rapidly.

Whilst at a red heat, or at a higher temperature, the more fusible portion of the material is in a viscous fluid state, and so long as the temperature remains sufficiently elevated the proportion of fluid will continue to increase, for reasons already given. When, however, the temperature begins to diminish, this material gradually becomes solid, and, under suitable conditions, a portion of it may crystallize.

The more fusible portions of natural clays are so viscous when molten that the proportion of crystalline matter formed is never large, though it may easily be observed under the microscope in the case of the less pure clays, providing that the rate of cooling has been sufficiently low. For many commercial purposes a crystalline structure is a disadvantage, so that care is taken to cool the kilns as rapidly as possible without damaging their contents. In this way supercooling occurs and a glass or slag is produced instead of a crystalline magma.

In investigating the cooling curves of clays and minerals present in them after firing, many difficulties occur on account of

TABLE XIX.

APPEARANCE UNDER THE MICROSCOPE OF SOME MINERALS
OCCURRING IN CLAYS.

Mineral.	Fragment observed by Reflected Light.	Transparency observed by	
		Reflected Light.	Polarised Light.
Quartz .	Irregular, white, crystalline fragments, resembling glass.	Clear, white, crystalline fragments, with minute fissures and sealed pores. (See Plate I.)	Vivid colour changes occur on rotating the specimen slowly. (See Plate II.)
Flint .	Irregular, bluish fragments.	Colourless and translucent, sometimes glassy.	Opaque or with minute crystals.
Felspar .	White opaque, irregular fragments or, occasionally, crystals (see p. 15).	Opaque, white (<i>sometimes</i> translucent or, if crystalline, transparent). Crystallites not uncommon. It is seldom possible to determine the nature of the felspar in fired clays.	The unaltered crystals may be readily seen, but much felspar in a partially fused state may be present and remain undetected. (See Plates I. and II.)
Mica .	Characteristic, thin, shining scales.	The darker micas are usually yellow or brown and show close parallel lines, the fragments having ragged edges.	Using one nicol only, the mineral changes from dark to light on rotating the sample (= dichroism). With two nicols little change is noticed on rotation, except in yellows and browns.
Iron oxides .	Brown or blue-black areas, or films on other grains, particularly on quartz.	Opaque.	Opaque.
Pyrites .	Yellow, brassy particles, often cubical.	Opaque.	Opaque.

TABLE XIX.—*continued.*

Mineral.	Fragment observed by Reflected Light.	Transparency observed by	
		Reflected Light.	Polarised Light.
Calcite .	Dirty white grains, partially transparent. In burned clay forms opaque white grains.	Opaque unless very pure.	Frequently opaque, but if pure is transparent to polarised light.
Chalk .	White, opaque.	Opaque.	Opaque.
Selenite .	Minute specks or "tears" of whitish powder. In larger fragments it may resemble ice. In burned clays it is an opaque white powder.	Opaque unless very pure, when it may form transparent needles. In burned clays it is opaque.	If crystalline it is transparent, otherwise opaque. In burned clays it is always opaque.
Gypsum .	White, opaque fragments.	Opaque.	Opaque.
Sillimanite .	Whitish, translucent needles or rhombic crystals. Sillimanite is scarcely affected by dilute hydrofluoric acid and so may be separated from much amorphous matter.	Translucent or transparent rhombic crystals.	Translucent or transparent rhombic crystals.
Tourmaline.	Colourless to black rhombohedral crystals, with unequal ends.	Semi-opaque crystals, usually brown in colour. (See Plate I.)	The paler specimens polarise light. Strikingly dichroic (see Mica, above).
Kaolinite .	Whitish grains or hexagonal crystalline plates.	Transparent hexagonal plates.	Translucent flat plates.
Clay .	Opaque grains varying in colour according to impurities.	Opaque grains, which usually appear to have a sponge-like structure under the highest magnifying powers.	Opaque.

the presence of so much unfused material. It is, therefore, almost impossible to employ direct methods for ascertaining the proximate composition of such materials.

When a fused material composed of a single substance is cooled slowly it solidifies at a definite rate, and the time-temperature curve is a straight line or a simple curve. If a mixture of two substances which do not form solid solutions with each other is cooled, the solidifying point of each is lowered, and the portion of the mixture which has the lowest solidifying point is termed the *eutectic*. If, under the conditions of cooling, the composition of the material is intermediate between that of the first substance and the eutectic, the mixture will begin to solidify at a temperature below that of the freezing-point of the first substance and above that of the eutectic, and will tend to deposit crystals of the first substance. As these crystals separate, the composition of the remaining material approaches more and more closely to that of the eutectic, and when the latter is reached the remainder of the material becomes solid without any further reduction in temperature.

If the two substances can react on each other to form several different compounds more than one eutectic is formed. Thus Day and Shepherd found that mixtures of lime and silica have three distinct eutectic points when the fused mass is cooled slowly. The first separation occurs when the mixture is cooled to a temperature of 2015° C., when, if the material contains 32.5 per cent. of silica and 67.5 per cent. of lime, olivine (Ca_2SiO_4) and free lime are formed. As the cooling progresses the lime-content of the fluid is reduced, and at 1430° C.—when the melt contains 46 per cent. of silica and 54 per cent. of lime—a second eutectic point is reached and a mixture of olivine (Ca_2SiO_4) and pseudo-wollastonite (CaSiO_3) is deposited. On still further cooling, a third eutectic is reached at 1417° C., the fluid containing 63 per cent. of silica and 37 per cent. of lime, and the eutectic mixture consisting of pseudo-wollastonite (CaSiO_3) and tridymite (SiO_2). At 800° C. the latter is slowly converted into quartz.

Similar investigations with mixtures of alumina and lime, alumina and silica and lime, alumina and silica, by Shepherd, Rankine and Wright, and others, have produced similar results, the most interesting compounds being sillimanite, andalusite, and kyanite (p. 249), the two latter being converted into the former at a temperature of about 1300° C.

These results all indicate that fused silicates—when pure—obey the ordinary laws of solution and crystallization, though the phenomena are complicated by viscosity and other disturbing

factors. In the case of burned clays the proportion of fused material is usually so small that the eutectics cannot be readily isolated, and its viscosity is so great that glasses rather than crystalline eutectics are formed.

The effect of **repeated heating** on clays depends upon the temperature used. If this is sufficient to cause vitrification, each succeeding heating will increase the amount of vitrified matter and may produce clearly definable crystals on cooling. If a fire-clay is heated repeatedly the same phenomena will occur, but to a less noticeable extent, on account of its greater refractoriness. The crystals when formed are bedded in a mass of unfused or surfused material, and their composition is not easy to ascertain. Sillimanite may, however, be more easily detected, as it is not dissolved on treating the material with cold hydrofluoric acid. On the assumption that (1) contraction can be used as a measure for the progress of heterogeneous solutions of clay, etc., in the molten fluxes of the body; (2) the change of contraction during firing is proportional to the square of the contraction which has yet to take place, the effect of repeated heating at 1130° to 1150° (cone 01 to 1) has been shown by Mellor to follow approximately the law for bimolecular reactions, so that if x = the observed contraction after any number of firings t , a = the maximum contraction after an indefinitely large number of firings, and k is a constant dependent on the nature of the material and the conditions of heating,

$$x = \frac{a^2kt}{1 + akt}.$$

The contraction at the end of any firing may be calculated from this equation.

As the speed of reaction between the particles slackens after each time of heating, though never entirely ceasing, it will be found that when clay is heated to a higher temperature than that at which it is to be used the subsequent contraction will usually be negligible. If, on the contrary, the clay has been insufficiently heated before use it may shrink so much as to cause serious damage. It is this fact that has led to so extensive a use of silica in place of fireclay for lining certain furnaces.

The repeated heating of clays is also accompanied by numerous other obscure yet important phenomena. Thus the loss of alkalis which occurs is one reason why chamotte (p. 152) is preferable to raw clay in the manufacture of refractory goods. Having been heated intensely before use and again when made up into articles, it loses sufficient alkali in the double heating to

produce a superior product. Mellor has found that a piece of Staffordshire sagger-marl heated seven times to nearly 1200° C. lost nearly 22 per cent. of the total alkalis present, and the author has ascertained that a similar but slightly larger loss occurs on heating Newcastle fireclay three times to Seger cone 9 for twelve hours at a time. Some of the less fusible red-burning clays lose iron oxide on being repeatedly heated to 1300° C.

It is well known that bricks in furnaces and other places where they are repeatedly exposed to high temperatures soon become **brittle**. Mellor attributes this to the formation of crystals irregularly distributed, and to the local contractions which occur when the vitreous substance crystallizes. To some extent crystallization may be prevented by rapid cooling to 800° C. or a little lower, when the clay can withstand this treatment.

The **susceptibility** of fired clay to sudden changes in temperature is important, particularly in the manufacture of refractory goods. Many clays disintegrate if they are cooled too rapidly, and great care is therefore necessary in this process. Clays which are dense after firing usually suffer most from rapid cooling, and, consequently, many manufacturers add sawdust and other combustible materials to the clay so as to increase its porosity in the kiln. To a large extent this has the desired effect, though articles made of very siliceous clay (ganister) or of comparatively pure silica (silica bricks) are always extremely sensitive to rapid cooling.

The **specific heat** of clay is very low (about 0.2) and does not change materially during firing. Its **conductivity** is very slightly increased, but seldom exceeds 0.0035 calorie per cm. per second per degree C., and averaging only .0025 calorie. Clay is at all times a bad conductor of heat, but it has a higher power of radiation; hence articles placed in clay boxes (saggers) may be heated intensely in spite of the low conductivity of the saggers.

CHAPTER X.

PROSPECTING, MINING, AND QUARRYING.

THE searcher for clays is greatly handicapped unless he has a good knowledge of geology at his disposal and some knowledge of the natural appearance of the clays of which he is in search. Many clays change colour very quickly on exposure, and others are so hard as to be mistaken for rocks of entirely different composition. In most cases, however, the plasticity developed when a little of the crushed material is carefully kneaded with water

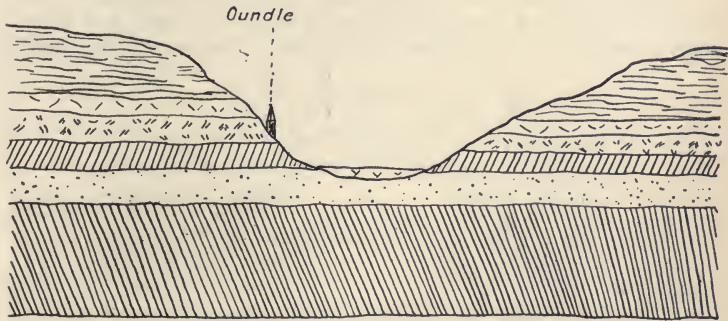


FIG. 42.—Valley in Horizontal Strata. (*Harris.*)

will prevent the prospector from carrying away large quantities of useless rock. A small bottle of hydrochloric acid will enable him to distinguish clays rich in lime and therefore of doubtful value for any purpose but cement making.

The clay deposits in Great Britain are roughly divisible into those at or near the surface and those occurring at a considerable depth. The former are usually recognized without serious diffi-

culty; the latter can only be examined where they rise to the surface or are brought up by means of a pit shaft.

The maps of the Geological Survey, or the more portable *Geological Atlas*, published by E. Stanford, are invaluable for indicating the general disposition of the larger areas of clay, but for a more detailed study it is necessary to examine the deposit itself.

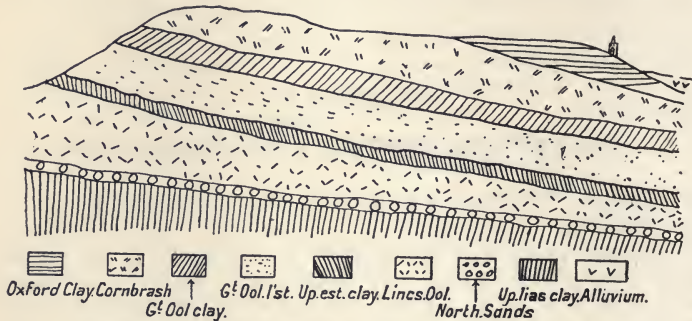


FIG. 43.—Inclined Strata in Lincolnshire. (Harris.)

The sides of hills and valleys and railway cuttings often offer special facilities for the study of portions of clay beds not otherwise accessible, and the direction in which the strata lie should

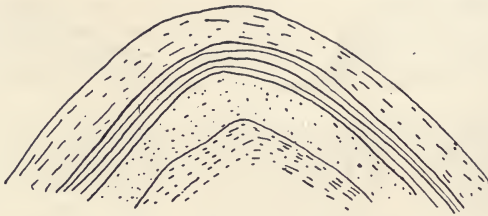


FIG. 44.—Anticline of Folded Beds.

be carefully noticed. If they are horizontal (fig. 42), the material composing them may extend over a considerable area; but if they are inclined (fig. 43), an outcrop may occur which renders one portion of the deposit very accessible, whilst the remainder would be increasingly costly to obtain. In some instances a saddleback or anticline (fig. 44) occurs, and special care is needed if a clayworks is situate on such a site, lest by working too far in one direction the clay should be "lost."

Faults¹ (figs. 45 and 47), fissures, fractures, slips, hitches, etc., caused by volcanic and other action, frequently cause trouble in prospecting for and in obtaining clay, and must be carefully studied, their direction being recorded on a map drawn to a sufficiently large scale. In several brickyards large masses of rock have apparently cut right through the clay deposit, and a considerable amount of skill is often required in order to overcome the difficulties such intrusions may cause.

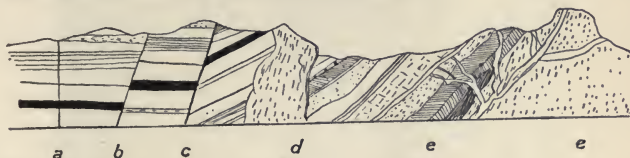


FIG. 45.—Various Formations, showing Faults at *b* and *c*. (*Ramsay*.)

Although some clays occur at the surface, most deposits are covered with an overburden or calow (figs. 43, 46) ranging in depth from a few inches to many feet, and as surface indications always require confirmation before they can be relied upon, owing to strata thinning out unexpectedly, etc., it is usually necessary to make a considerable number of boreholes, or pits, before the depth,

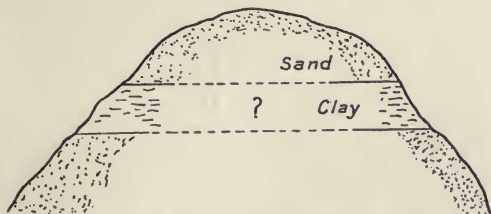


FIG. 46.—Clay Outcrops on Hill. (*Ries*.)

area, and even location of a given clay can be reliably ascertained. In some districts, as in Dorset, the clays occur at a depth of a hundred feet or more and present considerable difficulties in prospecting, on account of the tenacity with which the boring tool and clay adhere, as well as of the irregularity of the clay beds.

The area in which the clay is supposed to occur, or that portion of it which it is proposed to prospect, should be carefully mapped

¹ A *fault* is a displacement running through a series of rocks by which the beds on one side are raised or lowered in reference to the beds on the other side. It is not necessarily straight along the outcrop at the surface, and in an exposure the plane of faulting is often overgrown or partially hidden.

both horizontally and vertically, the vertical sections being prepared from contour lines, or from actual measurements of the hills and depressions. This gives a better mental picture of the actual site than does a map with the contour lines marked upon it.

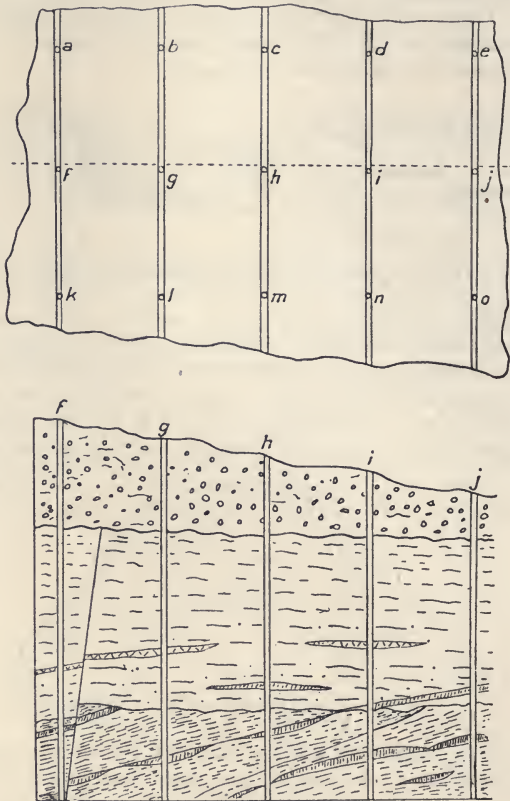


FIG. 47.—Survey of Deposit near Cardiff.

The probable depth from the surface of the ground and the direction of the clay strata, together with any surface indications of clay, sand, rock, etc., should be indicated on the map and sectional drawings, so far as they are ascertainable, and a definite scheme of boring arranged. It is desirable to divide the area to be examined into a considerable number of equal parts (fig. 47)

and to make a boring in the centre of each ; but as it would prove costly if a very large number of borings were to be made, some discretion must be used as to which portions shall be left untested. It is seldom that less than five borings should be made in a single site, and these should usually be distributed fairly equally over the

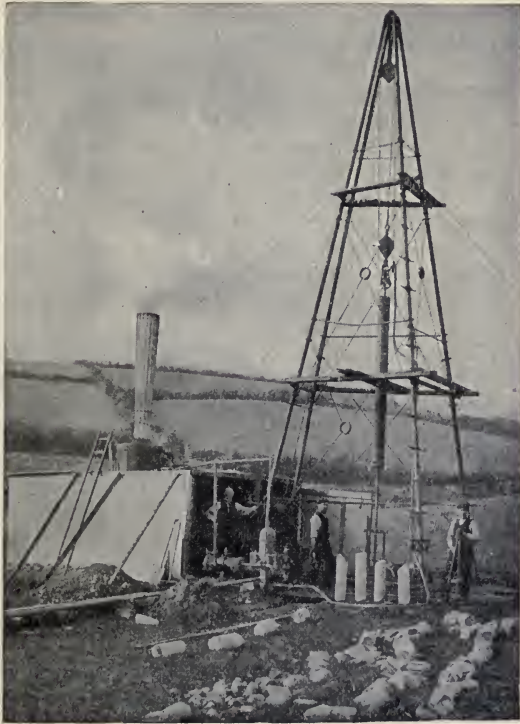


FIG. 48.—Boring by Duke & Ockenden's "Dando" Rotary Driller, showing cores produced.

whole area in which clay is likely to occur. As the results of the borings are obtained they should be marked on the drawings, the spaces between the borings being filled in as accurately as circumstances permit, as in the lower part of fig. 47.

If the clay is presumed to be within 20 or 30 feet of the surface, a series of wells may be dug by an ordinary labourer with a spade, but for greater depths boring tools (fig. 48) should be used. As

these latter are costly, require some skill in use, and are only wanted temporarily, it is better to employ a firm of professional borers, who will do the work for a definite price. In any case the boring should be conducted so as to produce "cores" (Plate IX.) of the material, an auger drill being unsuitable where it is desired to examine the material.

The examination of the material obtained by boring is by no means easy, as, in the first place, the passage of the tool may cause some amount of admixture of different strata and so produce an incorrect sample, particularly with lean clays. As any report on the analysis and other properties of the material must be based on these samples, it is absolutely essential that they should be as correct a representation of the various deposits as is possible. Too much care cannot be taken to ensure accuracy in this respect. If the total length of the cores withdrawn does not agree closely with the depth to which the boring tool is sunk, seriously erroneous conclusions may be drawn.

It is unfortunate that the nomenclature commonly employed in plotting boring records is far from conveying an exact idea as to the nature of the strata. The following special terms are in common use, but their meanings vary with different borers:—

Faikes or *fakes*—shaly sandstones or shales.

Blaes or *blaize*—dark, bituminous shales.

Hard pan—consolidated marl or friable material.

Peldon—hard rock, usually siliceous.

Whin or *whinstone*—any igneous rock, but usually applied to Trappean rocks (p. 12) and not to granite.

Grey whinstone—hard sandstone.

Killas—argillaceous schist (p. 48).

The nature of the *tests* applied to the samples depends chiefly on the purpose for which they are required. An ultimate chemical analysis is of little value at this preliminary stage, and more useful information will be obtained from—

- (a) The percentage of material which will not pass through a No. 100 sieve when the sample is mixed with water and washed on the sieve until all the plastic portion has been removed;
- (b) The nature of this residue material;
- (c) The percentage of soluble salts in the sample;
- (d) The behaviour of the sample when made into a paste with water, and when dried and burned at various temperatures up to complete vitrification.
- (e) For some purposes other characteristics indicated in Chap. IX. must also be ascertained and examined.



Cores from various parts of England, including New Red Sandstone, Old Red Sandstone, Carboniferous Limestone, Permian, Granite, etc. The crescent shape piece on left-hand side is a core from Wealden Rock showing the irregular cutting of an original *Percussion* tool which had bored the well out of the perpendicular and re-bored by "Dando" Driller.

(By courtesy of Messrs. Duke & Ockenden, Ltd.)

[To face p. 400.

A particularly useful tabular form for this purpose, which has been used for some years by the author, a modification of which has recently been published by W. G. Worcester, is shown on p. 402.

Before finally deciding to work a clay deposit, tests should always be made, on a reasonably large scale, at least a ton of the material being made into the articles it is proposed to manufacture, as otherwise it is difficult to gain reliable information as to the most suitable methods of working and to discover difficulties in treatment which cannot be shown in smaller samples. Preliminary tests on a small scale, if properly carried out, are the best means of saving costs in prospecting and should always precede larger tests, but the latter should never be omitted if the former give favourable indications as to the value of the material. Neglect of this precaution has involved the waste of enormous sums of money by prospectors and capitalists.

As the success or failure of the enterprise may eventually depend upon the accuracy with which the prospection and tests have been made and the reliability of the indications given, it is wise to place the whole of the investigation in the hands of an expert¹ in clayworking. This is the more necessary as, even when the nature, situation, and extent of the clay deposit are known, there are several highly important matters—such as the planning of the mine or quarry, precautions against flooding and the disposal of the overburden—to be considered.

The location of the site relative to the market for the product is a further factor requiring consideration, as it has not infrequently happened in the history of brick and tile manufacture that a firm have suffered many inconveniences due to unsuitable location, when a little more knowledge of the disposition of the clay deposit they use would have saved them much trouble and have materially reduced their cost of manufacture.

The **valuation** of a clay deposit must be based upon (1) its size ; (2) its location ; (3) the cost of bringing the material to the place where it will be used (*e.g.*, to the surface, or on to the railway or boat) ; and (4) the rate at which it will be obtained. The last factor is specially important to the purchaser, as the present value of a clay deposit, portions of which cannot be used for some years, is necessarily different from what it would be if the whole deposit were to be used in a single year. Thus, if the present value in pounds = C , the rate of interest for similar investments

¹ Brickmakers, potters, machinery manufacturers, and public analysts have neither the skill nor facilities for carrying out such investigations. A specially trained man with a proper equipment should be employed.

TABLE XX.
SUMMARY OF TESTS ON A SAMPLE OF CLAY.

No.	Locality.	Formation.	Date.
Behaviour on Burning.			
Properties in the Raw State.	Property.	Rate of Change in Burning.	Opinion on the burned material with regard to the given property, within the range of useful colour and texture.
Percentage of water needed to make properly plastic = per cent. (Normal is about 20 per cent.)	Oxidation . . . Reduction . . . Colours obtainable Range of useful colour . . .	Rapid or slow ? " " " ... Between cone and .	
Shrinkage on drying, in inches per linear foot.	Hardness . . . Porosity . . .	= No. on Mohs' scale. per cent. { Extinguished at cone .	
Kiln shrinkage in inches per linear foot.	True specific gravity Apparent density Indicates good structure to cone .	
Cross-breaking strain in dried condition (in lbs. per square inch).	Shrinkage . . .	{ Rapid or slow ? Regular or spasmodic ? Produce chart of temperature - shrinkage and temperature - specific gravity changes.	
Results of analysis, washing tests, microscopical examination, percentage of soluble salts, etc.	Warping . . . Underfired . . . Overfired . . . Softening - point (fusibility) .	{ Chiefly between cone and . At cone . Colour : Uses : At cone . What change in colour ? Any other effects ? Cone = ° C.	
Final Opinion and Remarks :			

(usually taken as 4 per cent.) = r , the number of years required to work out the deposit = k , the value of the clay to be removed annually or the royalty paid per annum = V pounds sterling, then

$$k = 1 + \frac{r}{100};$$

and

$$C = \frac{100 V(k^n - 1)}{rk^n}.$$

For practical purposes this may be simplified into the following table, in which the first column shows the duration of the clay deposit and the second and third the number of times the yearly royalty or the value of the clay removed annually (V), which is equivalent to the total present value of the deposit.

TABLE XXI.
VALUATION OF CLAY BED.

Duration in Years.	Present Value.	
	Interest at 4 per cent.	Interest at 5 per cent.
10	8.11 V	7.72 V
15	11.11 V	10.39 V
20	13.58 V	12.46 V
25	15.62 V	14.10 V
50	21.48 V	18.13 V
100	24.50 V	19.85 V
200	25.00 V	20.00 V

If R = the royalty in pence per ton, and T = the average number of tons to be removed annually,

$$V = \frac{RT}{240}.$$

It will be noticed that the rise in value after fifty years is very small, and may usually be neglected. Indeed, few clayworkers would give more than sixteen times the value of the clay removed annually.

Clays are usually worked by means of (a) *quarries* or open workings, commonly termed *holes*; (b) *drifts* or *tunnels*; (c) *pits*;

and (*d*) *mines*. The distinctions between these are well known, and need not be described in further detail. The special methods used in mining china clay in Cornwall are described on p. 160.

In getting clay it is very important, if possible, to get natural drainage, so as to avoid the necessity of pumping out water in the wet season.

In *Quarries* the material is usually dug with spades, with or without a previous loosening with picks, or wedges, or by blasting; but where the amount required is sufficiently large, steam navvies or electrically operated excavators will be found far more economical. When plastic clay is being dug, a curved spade (fig. 49) is often used, the depth of clay taken out by each spadeful being termed a *spit*. With highly plastic clays the spade must be lubricated by repeatedly dipping it in water. Ball clays are cut into blocks in this manner and are not "dug." Shales are blasted or pickaxed, and are shovelled into waggons. As each digger works horizontally, he forms a series of steps (see figs. 50 and 51 and the central portion of Plate VIII.), and when the working is sufficiently deep it is necessary to erect gantries or platforms on which the clay can be thrown as it is dug, or to use cranes and buckets for raising the clay to the surface.



FIG. 49. Hence in the majority of brickworks the clay-hole is intermediate in shape between a quarry and a pit.

Usually clay beds are so distinctly stratified and are so shallow that it is necessary to work on a series of different levels, the materials from each of these being kept separate or mixed in predetermined proportions. In the Isle of Wight, and in some districts on the mainland, the beds are so steeply inclined that small pits are the only available means of working.

Drifts or tunnels are only used where a deep-lying bed crops out on the side of a hill¹ and the useless material above it is so extensive that it would be unprofitable to remove the overburden. If this overburden is of a rocky nature it may form a natural roof to the tunnel, but if "timbering" or wooden roofing has to be specially erected the cost of obtaining the clay is greatly increased. Fireclays are frequently worked by drifts, but for clays of less value it is seldom profitable.

¹ Such an outcrop is termed a *bassett*.

Shallow mines are used in localities where the clay is sufficiently near the surface. A mine of this description is shown in Plate V., the method of working being outlined on pp. 133 and 137.

Deep-mine methods, such as are employed for coal, are only used when a clay is very valuable, or when other deposits are being worked. Thus, many fireclays are associated with coal and are brought to the surface of the ground in order to facilitate the getting of the latter. These large heaps of fireclay are usually valuable when they have been exposed to the weather for a few years, but they require to be carefully examined, as the material forming them, being originally regarded as "rubbish," is often very variable in composition. In Nottinghamshire and Yorkshire

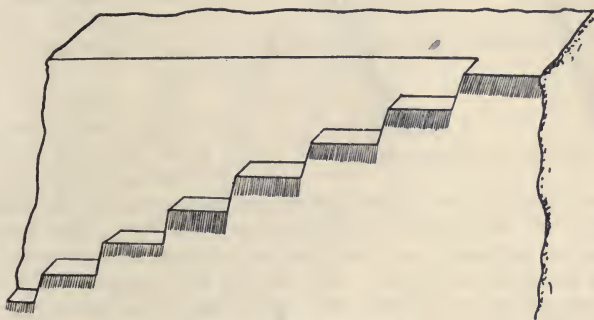


FIG. 50.—Step-quarrying.

they are particularly abundant, and are largely used by clay-workers for the manufacture of bricks and drain-pipes.

Precautions.—The methods adopted in deep-mine working are so numerous and require such skilled labour, that several treatises have been written upon them by mining engineers, and to these the interested reader may refer. In working clay by pits or quarrying, numerous other precautions are required, descriptions of which are not so generally available, and the most important may, therefore, be mentioned here.

Clay is very liable to become softened by rain and to slip, and in obtaining it care must be taken to allow for this. For instance, it is very unwise to allow the material to project above the workmen's heads unless there is expert evidence to show that the overhanging material is perfectly safe; and quite apart from any direct or indirect legislation on the subject, it is invariably better to work in a series of steps or terraces (figs. 50 and 51), the overburden being first removed by means of spades

or a steam navvy. Where drainage is good and a sufficient water supply is at hand, stripping on a large scale may be carried on by hydraulic means. In this way 1200 cubic yards of top soil have been removed in ten hours by two men using a $\frac{1}{2}$ -inch nozzle and water under a pressure of 80 lbs. per square inch. Its disposal is largely dependent upon its nature, but is

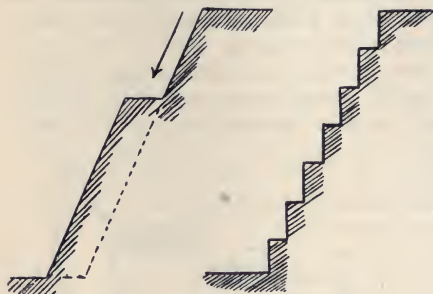


FIG. 51.—Step-quarrying.

usually tipped into any convenient hollow, or even into the worked-out portion of the pit or quarry. If the latter plan is adopted, care must be taken that it is not tipped on to clay which may be required later.

The depth of each "step" will depend upon that of the clay stratum, but should seldom exceed 6 feet, unless special arrangements are in existence whereby all likelihood of slipping is prevented. The simplest method of securing safe working is to keep the material well within its angle of repose. This differs with different clays, but, as a general rule, the angle the upper part of the face of the clay makes with the ground-level should not exceed the following limits:—

TABLE XXII.

ANGLES OF REPOSE OF CLAY.

Depth of Face.	Angle.
3 to 12 feet	75°
12 to 30 ,,	60°
Above 30 ,,	45°

These angles may readily be measured by inserting a rod vertically in the face of the deposit so that the top of the rod is at the ground level. If the horizontal distance from the top of the rod to the face is one-quarter the height of the rod, the angle is 75°; if one-half the height of the rod, the angle is 60°; and if equal to the height of the rod, the angle is 45° (fig. 52).

When **blasting** is necessary, all the directions advised by the makers of the explosive should be carefully followed, as these materials vary greatly in the manner in which they can be most safely and advantageously used. The requirements of the various Acts of Parliament relating thereto must also be observed.

Some firms waste a considerable amount of explosive by placing the hole into which the charge is placed in the wrong position,

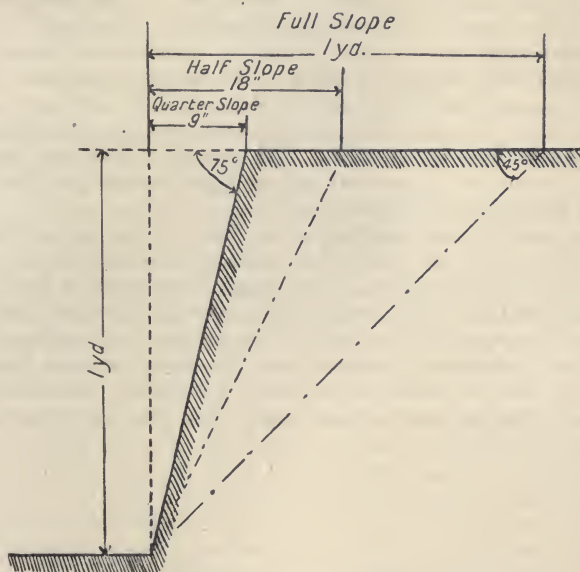


FIG. 52.—Angles of Safety.

or by boring it at an unsuitable angle. The most efficient depth and angle varies slightly with different kinds of clay or rock. For most materials a distance of 6 feet from the sloping face, a depth of 12 feet, and an angle of 75° (*i.e.* the bottom of the hole should be 9 feet from the face) are satisfactory. The correct angle can always be ensured if a triangular wooden "rest," one side of which stands on the ground and the other is properly sloped, is used by the borer as a gauge.

The clay which has been obtained is conveyed to the works in trucks or waggons, the size of which varies with the gradients over which they have to pass. For very steep gradients very small

waggon, each holding about 5 cwts., are usually hauled from the quarry by an endless chain, but in drifts and for longer distances a single haulage rope or a "main and tail" system are employed. Clay which is obtained from pits must usually be raised to the ground-level by a steam-driven lift or hoist, but simple hand-driven hoisting gear of the familiar "winch and bucket" type are used in some works, where the output required is small or fuel difficult to obtain. These arrangements are described in detail, with illustrations, in the author's *Modern Brickmaking*. Useful suggestions will also be found in the author's *Clayworker's Handbook*.

The **drainage** of a clay pit is a matter which should really have attention before the clay working is commenced, but if this is not possible, a complete scheme should be arranged as early as possible in each case in order that the excessive pumping necessary in some works may be avoided. The drainage of a clay site is, however, the work of a consulting engineer or other specialist, and cannot be described in detail here.

Sometimes the men working at the face do not quarry the clay to the best advantage; they may also get in each other's way or fail to bring the clay down in a manner convenient to the fillers. A clay deposit of variable composition must be watched very carefully, or "economical" methods of winning it will cause such a mixture of materials to be sent from the quarry or mine that the good clay will be spoiled and rendered worthless. In some yards it is only with the most patient and continuous supervision that this can be avoided.

CHAPTER XI.

THE PURIFICATION AND PREPARATION OF CLAYS.

ACCORDING to the purposes for which they are used, clays must be prepared or purified, as they can seldom be used in the state in which they are first obtained.

The chief processes of purification are briefly outlined below.

Hand-picking is one of the most primitive means of removing the coarser impurities from clay, yet with certain materials (such as fireclays) it is the only method at present available. It requires a keen-sighted, conscientious man with a temperament specially suited for this very tedious work. It is useless to set boys to this task, as they cannot be expected to take the necessary trouble.

Washing consists in mixing the material with sufficient water, or in making a slip or slurry of such a density that only the finer particles remain in suspension, the coarser particles sinking to the bottom. A wash-mill¹ is used for this purpose, and consists of a brickwork well in the centre of which is a pillar carrying an arrangement of rotating arms and stirrers or harrows. These may be driven by horse-power, or, more economically, by an engine. The clayey material is fed into the mill together with a suitable quantity of water, and the two are churned up together by the action of the harrows. If the material is troublesome to break up, a spiked roller may replace one of the harrows.

When the materials are judged to be sufficiently mixed the mill is stopped and the slurry run off through a grating in the side, the stones and much of the sand remaining behind. Some mills are made continuous in action, a supply of material and water being constantly fed into them and the slurry being run out at a definite rate. For many purposes this latter type is

¹ Illustrations of the plant described in this chapter are given in the author's *Modern Brickmaking*, published by Messrs Scott, Greenwood & Son, London, E.C.

convenient, but it does not produce so clean a clay as those which work intermittently, though it has a much larger output.

The slurry is run off into settling tanks, where the clay sinks to the bottom and the water is run off as soon as it is sufficiently clear. The clay, in the form of a stiff paste, is allowed to dry until sufficiently stiff to bear the weight of a man. It is then dug out and sent away.

If used on the works situated close to the settling tanks or "wash-backs," it is sent away in the form of a stiff paste, but if to be despatched by rail it is usually cut into blocks or balls (Plate X.) and placed in sheds to dry.

A modification of this method used for china clay and designed to affect a more complete separation of impurities is described on p. 166.

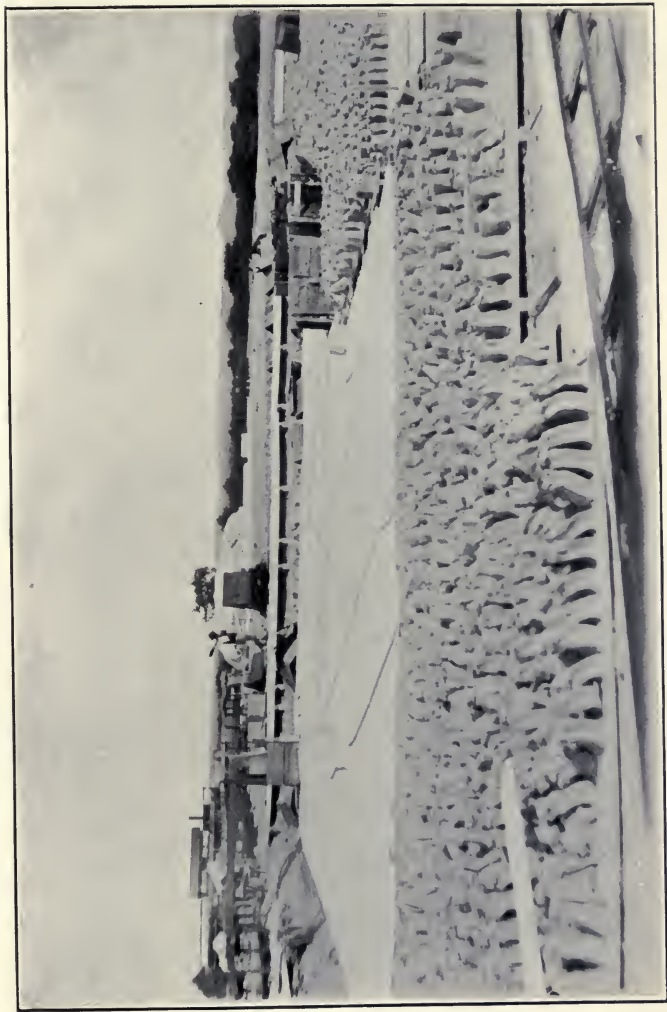
No process capable of being used on a commercial scale has yet been devised for the complete purification of clay; a careful washing, followed by the passage of the slurry through long troughs in which the speed of flow is carefully regulated, is the most efficient process yet devised.

Clay cleaning is a term used by brickmakers and others to indicate a means of separating clay from its coarsest impurities, and particularly from limestones. When it is desired to remove sand from clay the mixture must be treated in a wash-mill as just described. For the removal of only coarse impurities, however, the production of a slip and the drying subsequently necessary make the use of a wash-mill unnecessarily expensive.

The principle used in all clay-cleaning appliances is the production of a soft paste, which is forced through a series of perforations of such a size that the undesirable material is retained. It is obvious that only the coarsest particles can be removed in this manner, as it is impracticable to have perforations smaller than $\frac{1}{2}$ inch in diameter, and $\frac{1}{8}$ -inch perforations are more frequently employed.

Various types of clay cleaner are on the market, particularly on the Continent, where they are much used in preparing a useful "clay" from drift deposits. One¹ which has been proved successful with some of the boulder clays of Great Britain is a form of pug-mill with a perforated barrel, in which water and clay are mixed together by means of blades and the soft paste so formed is carried forward by the propelling action of the blades, aided by a screw conveyor. As the end of the machine is closed the only exit for the material are the perforations in the circumference of the barrel, and from these the clay exudes in thick threads. The

¹ See footnote on previous page.



Wash Pond at Messrs. Pike Bros., Wareham.

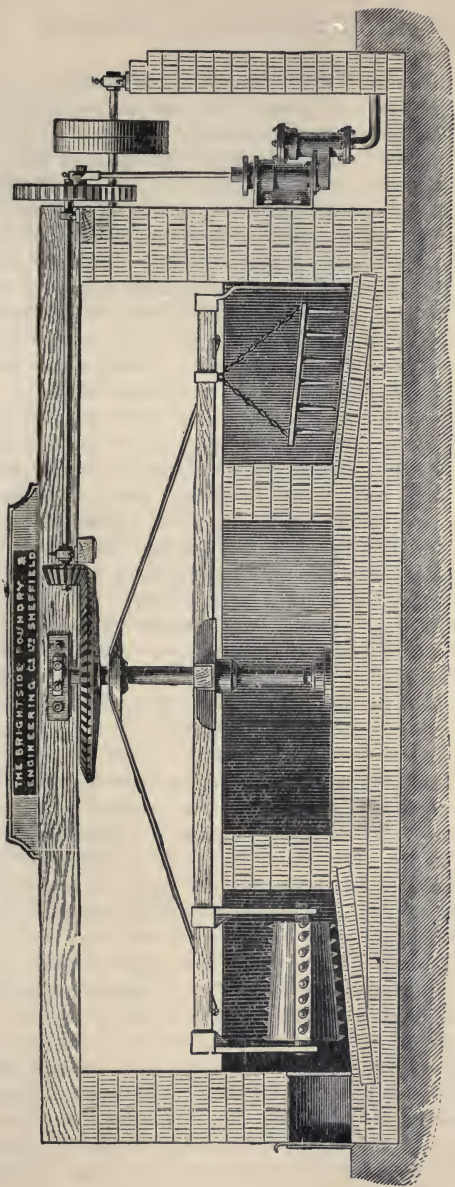


FIG. 53.—Sectional View of Wash-mill.

stones being unable to pass through these openings, accumulate within the barrel and are passed out at intervals by opening a small vent at the end of the machine.

In order to obtain a satisfactory cleaning of the clay it is necessary that the material which it is desired to remove should not be less than $\frac{1}{8}$ inch in diameter, and that stones more than 3 inches diameter should have been previously picked out by hand, as they cause unnecessary damage to the blades.

Various modifications of this arrangement are in use, but need not be described here, as all such appliances are at the best only capable of being used where bricks or similar articles are to be made from a material which is of such a composition that—without purification—it can scarcely be designated as clay.

Weathering—described in an earlier chapter—is a well-known means of purifying certain clays. Its chief action consists in the oxidation of certain iron compounds which are thereby rendered harmless, and in the leaching out of soluble impurities, some of which may have been formed by exposure. An indirect advantage of weathering clays containing nodules of pyrites is that these become rusty red on exposure and so may more easily be recognized, picked out, and thrown away.

Air separation has proved very successful in the removal of impurities from the more valuable clays. These must be dried thoroughly—usually by artificial heat—and are then placed in a combined ball mill and air-separator. The finer material is thus separated from the coarser particles, the grinding being stopped as soon as the fine material becomes too much contaminated with impurities. This process of purification depends upon the relative speeds at which the (soft) clay and the (harder) impurities will be reduced to powder of a given fineness; consequently the most satisfactory results are obtained when a definite quantity of material is placed in the mill and any residue remaining after a certain length of time is removed and discarded. The process is not used on a large scale in this country, but the author has often found it useful in carrying out experimental purifications where it was undesirable to wash the material. Ries has stated that it is being used successfully in the United States.

The **preparation** of clays for the market or for use in various industries can only be described briefly here. Each industry has methods specially adapted to its needs, and as, in many cases, the works are situated close to the clay deposits, the plant used for the preparation of the clay is commonly regarded as an integral portion of that used in the manufacture of the various articles made.

The following six methods of preparation indicate, shortly, the chief operations involved:—

(a) **Drying** may be “natural,” *i.e.* in rough sheds or even in the open air, or “artificial,” *i.e.* by the application of heat. Both these methods are advantageous wherever clays are very tenacious and sticky, and as a source of dry material for use in wet weather when that obtained direct from the pit contains too much water to be used. Clays which are despatched by rail (as ball clay) or which have been washed (as china clay) are usually air-dried in this manner, though artificial heat is frequently employed to hasten the removal of the water.

Bleining has discovered, what has long been known to several users of London clay, that highly plastic clays, if heated to a temperature somewhat higher than is necessary to dry them, may be made much easier to manipulate. The temperature most suitable for this purpose is below 200° C., the clay to be treated being passed through a slightly inclined drum with open ends and provided with blades to prevent the clay caking unduly. Care is required to prevent the clay from becoming overheated, or it will lose its plasticity completely and will then be useless. Quite apart from this, the use of a rotary drum for drying clay is often very economical, as it enables the consistency of the material to be kept more uniform, and greatly reduces the cost of grinding.

The artificial drying of clays is not so simple an operation as would be thought at first sight, because the temperature must not, usually, exceed 110° C., though with very sticky clays it may be as high as 200° C. without being detrimental. For small outputs the process generally employed consists in placing the clays on iron floors, or on refractory slabs, consisting of a system of flues heated by steam, or by fires beneath them. The thickness of the plates or slabs should be regulated so that the heat transmitted should be uniform at all points on the floor and that the temperature should not exceed the limit previously noted. The clay is spread in a layer 6 to 9 inches thick, and is turned over from time to time in order to hasten the drying and to avoid overheating. A large quantity of heat escapes to the chimney, and the surface occupied by the apparatus is fairly considerable, so that it can only be employed for small outputs. This method is not adapted for dealing with large quantities, on account of the amount of transport labour it involves.

For larger outputs more economical dryers must be used, those with shaft furnaces or inclined rotary drums into which the clay is introduced in the upper part, and passes out below in a dry state in a continuous manner, being preferred.

(b) **Weathering** is a very important means of preparing clay and making it more easy to manipulate. It has already been described fully on pp. 32 and 411.

(c) **Crushing** is necessary in order to break up large masses of clay or to reduce the stony material in them to powder. Many types of crushing machines are employed; descriptions of those most frequently used will be found in the author's *Modern Brick-making* (see p. 409).

It should be remembered that any impurities present in a clay are not removed by the crushing appliances, but are reduced to powder of varying fineness and become a part of the clay-mixture. In many cases such materials are advantageous (as when a highly plastic clay is mixed with crushed sandstone in the manufacture of bricks), but care must be taken that stones of an undesirable nature (such as limestone) are removed previously by means of a clay cleaner (p. 410) or by washing (p. 409).

(d) Making a plastic paste from a dry clay is one of the most important portions of the preparation of the material. It consists, briefly, in mixing the crushed clay with a suitable amount of water in a mixer or pug-mill, the amount of treatment required being dependent upon the nature of the clay. Full descriptions of the machinery required for this process will be found in the author's *Modern Brickmaking*, in Bourry's *Treatise on the Ceramic Industries*, and in other works¹ dealing with the manufacture of bricks, tiles, pottery, and other clay products.

In some purely agricultural districts a light alluvial deposit is often made into a plastic paste suitable for brickmaking by moistening the clay and turning it over repeatedly with a spade until it is as uniform as this crude process permits. For the manufacture of crucibles and some other articles the mass obtained in this way is carefully trodden by the naked feet of workmen employed for the purpose, it being claimed that the ordinary mixing machinery does not effect so thorough an incorporation of the materials. Experiments made by the author have failed to show any difference between properly pugged paste and that which has been produced by treading as above described.

(e) **Slip-making** is equally important in the preparation of clay for potters' use. It consists in mixing the material with about its own weight of water, either in a wooden tub or tank by hand, if the quantity is small; or in a specially constructed blunger, if larger quantities are needed. The precautions which must be observed will be found in treatises on pottery manufacture.¹

¹ A fairly complete Bibliography of books on clayworking is given in the author's *Clayworker's Handbook*.

(f) **Burning clay** as a means of preparation is only used in the manufacture of chamotte or grog, which is used as a convenient form of non-plastic clay in the manufacture of many refractory articles. As the material must usually be of uniform colour if it is to fetch a good price, it is necessary to burn it under such conditions that it is out of contact with fuel or flame. The most suitable kilns for the purpose are of the shaft type, such as are used for burning lime, but heated by gas.

For less important work the clay may be roughly shaped into bricks, and these may be burned in a brick kiln. If a still cheaper quality of burned clay is required, ordinary broken fire-bricks may be employed, though they are by no means so satisfactory as some users suppose.

The temperature at which the grog is burned should be higher than any to which it will be subjected in use, so that careful management of the kilns is essential.

The burned clay used by farmers is produced by putting alternate layers of coal or peat and clay in a limekiln and igniting it by a small fire beneath. Some clays are sufficiently burned by making a heap of brushwood and small faggots, covering this with the clay, and setting the wood on fire.

CHAPTER XII.

THE LEGAL POSITION OF CLAYS.

THE position of clay in the legislature is complex and often anomalous, and depends entirely upon whether it is or is not a "mineral" in the legal acceptance of this word. As there is apparently no legal definition of the term "clay," J. W. Gregory has defined a mineral as "any constituent of the earth's crust which has a value of its own apart from its value as soil or as a support, including any material obtained from the crust of the earth which, if of organic origin, has been fossilized or essentially altered, and is used as a source of metals, fuels, or other materials of economic value."

This definition, which has been considered by its author in connection with various legal decisions with respect to clay as a "reserved mineral," may be taken as the most recent scientific definition which does not exceed the limits of the chief legal pronouncements on the subject.

Although with two gaps of sixteen years and thirteen years respectively the question of how far clay is a mineral has been continuously fought in the law courts since 1872, the decisions and expressions of various judges are, at first sight, very confusing, and in some respects are by no means final.

They refer chiefly to section 77 of the Railways Clauses Consolidation Act 1845, in which occurs the expression "mines of coal, ironstone, slate, or other minerals." This expression is, according to Lord Macnaghten (*Great Western Railway v. Carpella United Clay Co. and Viscount Clifden*, 1910), beyond the possibility of doubt equivalent to the expression "mines and minerals" in common use with conveyancers, and that "such mines, or, in other words, all mines and minerals not expressly purchased by a railway company that purchases land within or under which minerals may be found, may, in case the company has not agreed to pay compensation, be worked by the owner,

lessee, or occupier thereof complying with the statutory provisions applicable to the case, even though such working may interfere with the use of the railway, and absolutely destroy the surface. The only condition to which the working is made subject is that it must 'be done in a manner proper and necessary for the beneficial working' of the mines, 'and according to the usual manner of working such mines in the district where the same are situate.' Such being the law as explained in this House, the only question open on this appeal is a question of fact."

"This question of fact may be most conveniently expressed in the form of an answer to the query, 'Is the particular clay under consideration a mineral?' The reply depends upon the nature and situation of the clay."

China Clay.—The case of *Hext v. Gill*, in 1872 (Law Reports, 7 Chancery 712) decided that china clay was a mineral in a voluntary sale, grant, or contract, and the case of the Great Western Railway, in 1908, decided that china clay was a mineral in a compulsory sale under the Railways Clauses Consolidation Act of 1845. Thus china clay is always and everywhere a mineral, and can be "reserved and worked by the owner, sold separately, or used to obtain compensation from the purchaser of the land."

Fireclay remains to some extent uncertain, though in the Scotch Court of Session, in the case of the Caledonian Railway Company *v. Glenboig Union Fireclay Company*, Lord Skerrington held that fireclay was a mineral within the meaning of the Act. In this case the fireclay was worked by underground mining, and in a report of the decision there occurred these words: "It was enough to say that the fireclay in dispute did not, in his Lordship's opinion, form part of the subsoil. Should a question hereafter arise as to the same fireclay at the outcrop, or as to a bed of fireclay forming the ordinary subsoil, of a district, different considerations might apply."

In some statutes fireclay in conjunction with coal, etc., is specifically stated to be a mineral.

Indeed, as the Attorney-General remarked in the House of Commons on the 22nd September 1909, "there has been in the Courts considerable diversity of opinion, and there may be some difficulty in applying the term mineral to clay."

Common Clay or Brick Clay.—The tendency of recent decisions of the Court is to regard the situation of a stratum next the soil as a determining factor in ruling whether or not it is a mineral.

Thus Staffordshire brick clay, lying from 6 inches under the surface, down to 300 or 400 feet deep, was held not to be a mineral. The judge in that case (*Great Western Railway v. Blades*,

1901) not only referred back to another case, that of the Glasgow Corporation *v.* Fairie, decided in 1888, but commented thereon as follows: "It is impossible to read the speeches without seeing that it may well be that within that decision *the same clay may be a mineral in one district and not in another.*"

In the case of the North British Railway *v.* Turners Ltd. in 1903, the clay "subsoil" extended to a depth of some 100 feet, but at no depth was any compensation allowed for it as a "reserved mineral."

Since 1898, however, no common brick clay has been held to be a "mineral" under the Railways Clauses Consolidation Act of 1845, and the highest legal tribunals of this country have consistently refused to allow owners of common brick clay to obtain compensation for it as a "reserved mineral" from railway companies.

It is important to note that although common brick clay has never yet been held by a court of law to be a mineral, no court has ever held that it is never a mineral, and in the cases cited all the judges have been most careful to make it clear that, except in connection with railways, they did not in any way impugn the long-standing presumption that clay is, generally speaking, a mineral. The result is that there are decisions that show when common brick clay is *not* a mineral, yet it cannot be ascertained when, if ever, it is a mineral, as the decision in *Hext v. Gill* (1872), wherein Lord Justice Mellish defined as mineral "every substance which can be got from underneath the surface of the earth for the purpose of profit," has not been followed in more recent decisions.

Taxation of Clays.—In the Finance Act of 1909, whereby minerals are subject to taxation, there is a proviso (in section 20, subsection 5) that mineral rights duty, reversion duty and increment duty (section 22, subsection 8) "shall not be charged in respect of common brick clay, common brick earth, or sand, chalk, limestone, or gravel."

It is therefore clear that this duty is chargeable on all china clay, but never on common brick clay. "Fireclay" has not, at present, been definitely decided. A leading counsel's opinion, according to the *British Clayworker*, is that, if refractory, it may be taxed as a mineral, but not otherwise. That is to say, certain non-refractory shales associated with coal and therefore liable to be confused with fireclay are exempt. The same authority has stated that marls,—being a mixture of chalk and clay—are likewise exempt.

Output of Clays.—Table XXIII. is taken from the General Report on Mines and Quarries to H.M. Government, and shows the output of clays and shales in the United Kingdom in 1910, as compared with 1909. The corresponding figures for coal and iron-ore are also included.

TABLE XXIII.

Description of Material.	Mines.		Quarries.*	Total Output, 1910.	Total Output, 1909.
	Coal Mines Act.	Metalliferous Mines Act.			
	Tons.	Tons.			
Alum shale . . .	6,674	6,674	9,120
Bauxite	3,792	..	3,792	9,500
Clays and shale . . .	2,919,181	113,022	11,058,117	14,090,320	14,067,810
Coal . . .	264,417,588	..	15,440	264,433,028	263,774,312
Gravel and sand	12,323	2,187,529	2,199,852	2,104,837
Ochre, umber, etc.	6,339	10,176	16,515	16,313
Oil shale . . .	3,130,280	3,130,280	2,987,057†
Sandstone . . .	125,153	134,044	4,127,084	4,386,281	4,600,084
Slate and slate slabs	99,514	316,810	416,324	402,184
Iron-ore . . .	7,979,750	1,851,351	5,394,914	15,226,015	14,804,382

* Exclusive of the product of most of the quarries of less than 20 feet deep, but including the product of all open workings for iron-ore and ochre.

† Average yield of ammonium sulphate is 43 lbs. per ton of shale.

The above table only gives a faint idea of the extent and importance of the industries dependent on British clays, shales, and sands, but it is the most accurate one available for the raw materials at the time of writing.

Tabulated Analyses.—There are few analytical figures so misleading as those published respecting various kinds of clays, as they create an impression that they are typical of the materials mentioned, when in reality this is far from being the case. Yet, as some indication of the ultimate composition of certain groups of clays is occasionally required, the figures in Table XXIV. are given, on the distinct understanding that materials yielding results notably different may still, with truth, bear the same names. In each case the analyses have been made during the past nine years by the author, or under his immediate supervision, and the figures for each clay are the average of at least ten different samples taken at different times.

The figures relate to the clays themselves and not to the composition of the beds, as a whole, which may bear the same names.

No really satisfactory figures can be given for "brick clays," as the materials used for this purpose vary too much to enable a fair average to be obtained. For the same reason, fractional figures have, in most cases, been omitted.

TABLE XXIV.

District.	Clay.	Silica.	Alumina.	Iron Oxides.	Lime.	Magnesia.	Alkalies.	Water, etc.
St Austell . . .	China clay	46	39	...	0·5	...	0·5	14
Scotland, Elgin . . .	" China clay "	39	38	...	1	1	1	20
Dorset . . .	Ball clay	49	32	2	0·5	...	3	13·5
" . . .	Stoneware ball clay	70	7	2	0·5	...	1	7·5
Devonshire . . .	Ball clay	48	36	0·5	1	...	1	13·5
" . . .	Stoneware ball clay	76	16	2	0·5	...	1·5	4
Burton . . .	Stoneware clay	57	29	2	0·5	...	2	9·5
Thames Basin . . .	London clay	51	28	1·5	0·5	...	1	19
Reading . . .	Mottled clay
Hull . . .	Alluvial	51	21	7	6	4	2	9
Banks of Thames . . .	"	60	11	8	8	3	0·5	9·5
Portsmouth . . .	"	59	18	3	10	...	1	9
Medway . . .	Blue gault	44	15	6	15	2	0·5	17·5
" . . .	Mud	70	12	9	2	...	2	5
Warwickshire . . .	Blue Lias	37	15	4	19	3	0·5	21·5
Ruabon . . .	Red-burning	63	20	6	5	6
Fletton . . .	Oxford clay	62	14	1	2	...	2	9
Accrington . . .	Red-burning shale	62	24	7	1	3	1	2
Stourbridge . . .	Fireclay	65	22	2	0·5	...	0·5	10
Scotland, Kilmarnock . . .	"	52	28	1·5	0·5	0·5	1·5	16
" Glenboig . . .	"	62	28	2	0·5	0·5	0·5	6·5
Northumberland . . .	"	60	28	2	1	...	2	7
Chester . . .	"	59	28	3	0·5	0·5	...	9
Leeds . . .	"	71	20	1·5	0·5	...	1	6
Halifax . . .	"	79	19	0·5	0·5	0·5	0·5	...
South Midlands . . .	"	59	28	2	1·5	0·5	1	8
Teign Valley . . .	"	77	17	2	4
Turton Moor . . .	"	59	29	1	1	10
Dowlais . . .	"	57	17	11·5	3	...	0·5	11
Shropshire . . .	"	59	27	1	0·5	...	0·5	12
Sheffield . . .	Ganister	89	4	3	3	...	1	...
Glamorganshire . . .	Dinas	98	1	1
Cambridgeshire . . .	Marl	17	7	...	74	...	0·5	1·5
Petersfield, Hants . . .	"	27	2	3	53	15
Nottingham . . .	Permian red marl	66	15	7	2	...	1	9
Derbyshire . . .	{ Limestone Pocket clay }	81	11	1	1	...	2	4
Harefield . . .	Brick earth	59	20	3	3	6	1	8
Arundel . . .	"	63	8	4	19	1	2	3
Staffordshire . . .	Blue burning	46	38	1	1	14
" . . .	Sagger marl	62	29	3	1	5
Shrewsbury . . .	Shale	40	14	3	15	6	...	22
Buckley, Cheshire . . .	Obsidianite	79	15	3·5	0·5	1	...	1
Wiltshire . . .	Kimeridge clay	54	23	8	5	...	2	8
Dorset . . .	"	39	21	3	18	...	2	17
Worcestershire . . .	Keuper marls	54	20	5	5	5	2	9
Shropshire, Broseley . . .	Red-burning from Coal Measures	60	22	8	2	8
" . . .	Wenlock shale	48	22	2	8	1	2	17

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