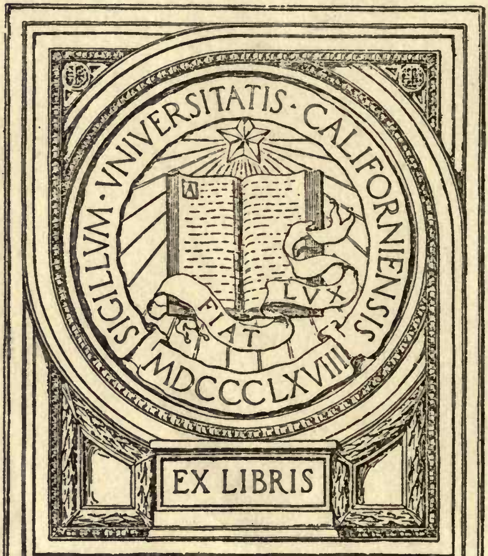
INDUSTRIAL CHEMISTRY

BEING A SERIES OF VOLUMES GIVING
A COMPREHENSIVE SURVEY OF

THE CHEMICAL INDUSTRIES



AGRIC. DEPT. Plant Nutrition

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SILICA AND THE SILICATES

BY

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GENERAL PREFACE

THE rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument.

Each book will be divided into sections instead of chapters, and the sections will deal with separate branches of the subject in the manner of a special article or monograph. An attempt will, in fact, be made to get away from the orthodox textbook manner, not only to make the treatment original, but also to appeal to the very large class of readers already possessing good textbooks, of which there are quite sufficient. The books should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to the large standard works for fuller details on special points if required.

To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary textbooks, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger textbooks when they wish to refresh their memories in regard to branches of the subject with which they are not immediately concerned.

The volume will also serve as a guide to the standard literature of the subject, and prove of value to the consultant, so that, having obtained a comprehensive view of the whole industry, he can go at once to the proper authorities for more elaborate information on special points, and thus save a couple of days spent in hunting through the libraries of scientific societies.

As far as this country is concerned, it is believed that the general scheme of this series of handbooks is unique, and it is confidently hoped that it will supply mental munitions for the coming industrial war. I have been fortunate in securing writers for the different volumes who are specially connected with the several departments of Industrial Chemistry, and trust that the whole series will contribute to the further development of applied chemistry throughout the Empire.

SAMUEL RIDEAL.

AUTHOR'S PREFACE

An apology is due to the public, the publishers, and the general editor, for the delay in the appearance of this volume, but it is hoped that the additional notices of recent work (which it was in consequence possible to include) may in some measure compensate for the extra time of waiting. When the work was undertaken, it was realized that the task in hand was no light one, but its magnitude far exceeded all expectations. The vast amount of material which was gradually accumulated rendered it necessary to consider carefully whether (in order to keep the book within moderate limits) every section should be treated in little more than bald outline, so as to deal in a more or less uniform fashion with the various branches falling within the wide scope of the general scheme, or whether it might not be more useful to deal very briefly indeed with some portions so that more space could be devoted to certain selected subjects of special interest. It was eventually decided to adopt the latter alternative, though it was inevitable that the selection should be arbitrary, having regard more particularly to the great amount of research work accomplished during the last few years, especially in connection with glass and refractory materials. Section IV. (Ceramic Industries) presented an exceptionally difficult problem in this connection. Clay refractories and silica refractories have received special consideration, and other refractories have been dealt with briefly in view of their importance, though they do not strictly fall within the scope of the treatise.

No previous English author appears to have attempted to cover the same range of subjects within the limits of a single volume, and in the French treatise of Le Chatelier bearing the same title, and the German book of similar scope by Drs. W. and D. Asch, the treatment is on entirely different lines, though the former furnished many valuable hints and suggestions. Those who seek fuller information on specific topics than is contained in the present volume will, it is confidently anticipated, find ample references to the best available literature. At the same time, it is hoped that this book in itself may have some value in meeting a want, quite apart from such references. After due deliberation, it was decided to select illustrations as far as practicable from apparatus and appliances actually put on the market, so that reliance might be placed on their suitability for their purpose, and thanks are due to the various firms who have supplied them. It does not necessarily follow that any particular contrivance is adapted only for the purpose for which it happens to be used as an illustration. Thus, grinding apparatus of different types will be found illustrated in connection with the grinding of cement, but most (if not all) would be equally available for grinding other materials of approximately the same degree of hardness.

Every care has been taken to avoid inaccurate or ambiguous statements, and the hope is entertained that as far as it goes the book may provide a thoroughly reliable guide to the important industries concerned.

The Author desires to acknowledge valuable suggestions and references supplied by the general editor.

JAMES A. AUDLEY.

HANLEY,
February, 1921.

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LIST OF ILLUSTRATIONS

ERRATA

Page 14, line 19, *for* "and in glass manufacture for cutting glass," *read* "and for cutting glass in its manufacture."

Page 118, line 19, *for* "Powdered crystalline silicon carbide," *read* "Powdered silicon carbide."

Page 146, *add*, after inscription to Fig. 8, "(Bradley Pulverizer Co.)."

Page 152, line 11, *for* "sieves," *read* "sleeves."

Page 153, 5 lines from bottom, *for* "consistent with age," *read* "consistent with increasing age."

Page 154, line 28, *for* "loss of ignition," *read* "loss on ignition."

Page 157, line 26, *for* "alumina-silicic" *read* "alumino-silicic."

Page 158, line 25, *for* "perfectly," *read* "imperfectly."

Page 172, line 12, *for* "Coarser," *read* "Coarse."

SILICA
AND THE SILICATES

SECTION I.—SILICA

SILICA is an oxide of the non-metallic element silicon, which is itself an unfamiliar substance, though its compounds occur very abundantly in nature. Silicon is never found in the free state. It is known in three modifications:

1. **Amorphous Silicon,** first obtained by Berzelius (1823) by heating dry silico-fluoride of potassium or sodium with an equal weight of metallic potassium or sodium respectively. It has since been obtained by the action of heated potassium, sodium, or aluminium, on silicon chloride vapour; by the action of heated sodium on gaseous silicon fluoride; by heating silica with magnesium powder (or with aluminium), mixed with magnesia so that the action may not proceed too violently; by sparking liquid silicon hydride; and by electrolysis of a fused mixture of potassium fluoride and potassium silico-fluoride; also by other methods.

Amorphous silicon is a brown or maroon-coloured powder, with a specific gravity of 2·35; it readily fuses and volatilizes in the electric furnace, dissolves in many molten metals (silver, iron, aluminium, etc.), readily absorbs gases and water vapour, which can only be expelled at a red heat. It is attacked by hot water in glass vessels, but is not affected by concentrated hydrofluoric acid at 100°. It oxidizes superficially in air, but when heated readily burns to form silica.

2. **Graphitoidal Silicon.**—This was obtained by Berzelius by heating amorphous silicon in a platinum crucible. Other methods are the action of heat on a mixture of

aluminium with potassium silico-fluoride, and the fusion with aluminium and cryolite of the product obtained by heating magnesium with finely-powdered sand; on treating the first of these products with hydrochloric acid and then with hydrofluoric acid, the graphitoidal silicon is left in the form of hexagonal tables with curved edges; treatment of the second product with water and acids leaves black glistening spangles of graphitoidal silicon. Still another method is by fusing aluminium with leadless glass and cryolite.

Graphitoidal silicon is not readily oxidized, and is not attacked by acids except by a mixture of hydrofluoric and nitric acids, though it is soluble in strong potash or soda. It reduces many metallic oxides.

3. **Crystalline or Adamantine Silicon.**—This is obtained in dark steel-grey globules, sometimes giving double six-sided pyramids, by heating amorphous silicon, in a platinum crucible lined with lime, to a temperature between the melting points of steel and cast iron. It is also obtained by passing silicon chloride vapour over fused aluminium in an atmosphere of hydrogen; the aluminium becomes saturated with silicon, and afterwards the excess of silicon separates in large dark iron-grey needles, reddish by reflected light and iridescent. The form is derived from a rhombic octahedron, the crystals often have curved faces, and they can cut glass. Another method is heating to redness in a clay crucible a mixture of potassium silico-fluoride and sodium and zinc; on removing the zinc as far as possible by melting out, then treating in turn with hydrochloric and boiling nitric acid, the crystalline silica remains in the form of long needles. The most convenient method of preparation is by heating aluminium with potassium silico-fluoride, and purifying the product.

Crystalline silicon is less reactive than the amorphous. If finely divided it is attacked by boiling water.

Still another modification of silicon was obtained by Moissan and Siemens, along with ordinary crystalline silicon, by dissolving silicon in molten silver. This modification differs from the others in being readily attacked by hydrofluoric acid. Its specific gravity is 2·42.

Silicon has received no important industrial application, but Le Roy recommends it for use in electrical heating in place of metal and carbon resistances. The resistance of a silicon rod, 10 cms. long, and of 40 sq. mm. cross section, is 200 ohms, as compared with 0·15 ohm for a similar carbon rod. (1)

Silica as a Constituent of the Earth's Solid Crust.—The importance of silica as a terrestrial substance may be judged from the fact that in the combined and uncombined condition it has been estimated by F. W. Clarke to form close on 60 per cent. of the earth's crust, the estimate being based on careful consideration of very numerous analyses of the solid rocks (including loose materials) occurring in all parts of the world, and calculated to a depth of 10 miles below the sea level. (5)

As might be expected, much of this material is available for various industrial purposes.

The silica sometimes occurs in anhydrous condition, and sometimes hydrated.

Anhydrous silica presents more variations than any other known substance. Some varieties are crystalline, and some are amorphous. The varieties of crystalline anhydrous silica fall into two groups, with a mean specific gravity of about 2·6 and about 2·3 respectively. Each of these varieties when heated undergoes reversible transformations called inversions, giving new varieties which are stable only between certain limits of temperature.

Silica easily assumes the vitreous amorphous state, and communicates it to mixtures which it forms with different silicates to produce ordinary glasses; this property is possessed in so high a degree by no other mineral substance. Boric acid exists well in the vitreous state, but, as its anhydrous crystalline state is unknown, it is not available (like silica) for studying the passage from the solid amorphous state to the crystalline state.

Hydrated silica shows indefinite variation in its water content with the condition of the surrounding medium. It has the property of giving with water so-called colloidal solutions, in which it is not certain whether the gelatinous masses are really hydrated chemically or are rather constituted of extremely fine anhydrous silica forming a paste with the water.

The industrial importance of silica may be gathered from the extensive use of silicious materials for construction purposes. Sand for mortar is nearly pure silica, and sandstones have been largely used for road pavements and for buildings. The cathedral of Strassburg is an important example of a sandstone structure.

Many silicates—in some cases associated with silica itself—receive useful applications. Granite, being very resistant to ordinary atmospheric influences, is used for footways, uprights of windows, and other constructions. In like manner porphyry, petrosilex, and other silicious materials, including trap rocks, make good road metal. Slates and schists are used for roofing. Volcanic lavas, either by excavation or by grinding and shaping, followed by heating to restore the condition of consolidation, supply excellent acid-proof utensils for chemical works. Clay, shaped and burned, gives articles much used for construction. Other important classes of silicates provide ceramic products, glass goods, cements, slags, and other industrially-useful materials.

Anhydrous Protoxide of Silicon (SiO), is said to be obtained as a chestnut-brown powder, very light, by distilling in an electric furnace a mixture of silica and carbon (the latter being insufficient to fully reduce the silica), and condensing the resulting vapours in a metallic chamber out of contact with air. The specific gravity is 2·24; it is less readily soluble in hydrofluoric acid than silica. The powder is prepared industrially by Potter's process (as above, German patent 189833, Eng. patent 1279/06), and sold under the name of *Monox*, and is used as a pigment in oil painting. It takes a much greater weight of oil than other pigments—up to four times its weight as compared with an equal weight for light pigments like ochres and one-fourth the weight for heavy pigments like minium (red lead). The composition of the brown powder approaches that of the protoxide, but it may possibly be an intimate mixture of silicon and silica. (1) and (2)

Silicones and **Leucones** are compounds of silicon with oxygen and hydrogen, having properties quite different from those of silica and silicon.

Silicone is obtained by the action of cold concentrated hydrochloric acid on a calcium silicide rich in calcium. It forms transparent yellow lamellæ, which bleach in light, giving off hydrogen, and becoming transformed into leucone. Heated in a vacuum, it is completely decomposed, giving off more hydrogen, and leaving a brownish-black mass, which is regarded as a mixture of silicon and silica. Heated in contact with air, it inflames, giving silica, slightly coloured by a little silicon. It is not attacked by cold acids, except hydrofluoric acid, which dissolves it quickly. Alkaline solutions also dissolve it quickly, giving off hydrogen, and forming a soluble alkaline silicate. The formula of silicone seems to be $Si_2H_2O_2$ or $Si_2O.H_2O$, according to Wöhler, but other formulæ have been assigned to it.

Leucones are white substances of varied composition, with properties quite similar to those of silicone, viz. transforming into silica by direct oxidation, dividing into two when heated not in contact with air, liberating hydrogen at first, then silicon. Leucones corresponding to $SiO.H_2O$ and $Si_2O_3.H_2O$ are known, their properties being identical. Here, also, other formulæ have been suggested.

Several other compounds of silicon with hydrogen and oxygen are known, but they possess only theoretical interest.

Silica exists in three principal varieties, all represented by the formula SiO_2:

1. **High Specific Gravity Crystallized Silica,** including quartz and chalcedony. Quartz has specific gravity 2·65, with characteristic crystalline form. Chalcedony has specific gravity 2·56, and occurs in compact masses with conchoidal fracture; its microcrystalline structure is only

recognizable by examination of thin sections under the polarizing microscope.

2. **Low Specific Gravity Crystallized Silica,** including tridymite and cristobalite. Tridymite has specific gravity 2·28, and it is found as very small crystalline lamellæ in all volcanic rocks. Cristobalite, crystallized in pseudocubes, and having specific gravity 2·33, is of very rare occurrence, in certain volcanic soils of Mexico—it was first identified in specimens from San Cristobal, whence its name. It is formed when quartz or chalcedony is heated to a high temperature for a time insufficient to produce definite transformation into tridymite. This variety is especially characterized by extremely irregular expansion.

3. **Amorphous Silica,** including vitreous silica and the calcined silica of laboratories. Vitreous silica is obtained by fusion of any other variety of silica. Calcined silica results from dehydration of hydrated silica by heating. It is a white powder, and very light.

4. **Hydrated Silica** has no definite composition or crystalline form. It consists of translucid, gelatinous masses, or bundles of more or less soft clots, which have none of the characters of ordinary hydrated acids. Hydrated silica is prepared by the action of an acid on silicates in the presence of water. The liberated silica assumes three different forms. On pouring slowly a solution of sodium silicate into concentrated hydrochloric acid, no precipitate is formed, the silica remaining in a state of *colloidal solution.* If the acid be poured into the sodium silicate solution, it forms very voluminous *gelatinous clots* of hydrated silica. The action of a weaker acid like formic acid, on sodium silicate, or of a stronger acid on more resistant silicates like certain natural zeolites, gives a much more granular-looking and less voluminous silica. The action of boiling hydrochloric acid on still more resistant silicates, like glauconite, leaves a silica skeleton with the exact shape and dimensions of the original mineral grains. In like manner chrysotile on boiling with dilute acids produces silica which is brilliantly white and fibrous like the mineral; even after heating to

redness it still retains the flexibility of silk; serpentine and magnesian silicates generally, yield fibrous and not gelatinous silica. Even when prompt and abundant precipitation of silica occurs, a certain quantity always remains in the state of colloidal solution.

Calcined Silica is obtained by adding hydrochloric acid to solution of sodium silicate, evaporating to dryness, taking up by acidulated water, and filtering, the insoluble deposit being well washed, then dried and ignited.

In order to obtain chemically pure silica, silicon fluoride is decomposed by water.

Chemical Function of Silica.—Silica gives definite salts with bases. Simple silicates of protoxides generally correspond to $SiO_2.MO$ or $SiO_2.2MO$, and these salts may be anhydrous or hydrated, but no silicates of sesquioxides are known with the oxygen in base and acid having the same ratios (1 : 2 and 2 : 2).

Action of Bases on Silica.—As an acid body, silica combines with bases, by direct action or by double decomposition, to form metallic silicates. Freshly precipitated hydrated silica dissolves almost instantaneously in alkaline solutions. Calcined precipitated silica scarcely dissolves in the cold, but rapidly on boiling. Quartz and flint—even in very fine powder—are scarcely attacked by boiling solutions.

Flint is dissolved easily at 200° C. by alkaline solutions under pressure, this being one of the *industrial processes* for making *sodium silicate.*

Silica combines less easily with alkaline earthy bases, because of the insolubility of the resulting silicates. This reaction is utilized in the *hydraulic products industry*, where certain varieties of silica combine with lime and cause hardening of the mass. Even ground quartz combines with lime in the presence of water under pressure, at about 150° to 200° C. On that reaction the *manufacture of sand-lime bricks* depends.

Combination of every variety of silica is effected just as readily in the dry way, if the temperature be above the fusing point of the silicates formed. This combination is produced partially at lower temperatures with very finely divided materials mixed very uniformly. The reaction is greatly facilitated in this case by the presence of fusible compounds serving as solvents, as in the case of lime by the presence of aluminous and ferruginous compounds. On this property is based the manufacture of all the ordinary *hydraulic products*, viz. hydraulic limes and cement, constituted essentially by silicates of lime, and burned at temperatures much below the fusing point of these compounds, which exceeds 2000° C.

Action of Alkaline Salts.—Silica is the weakest inorganic acid, and its heat of combination being lower than that of all the other acids, its substitution for any one of them absorbs heat. This reaction, like all endothermic reactions, will become the more complete as the temperature is raised. Volatilization of the displaced acid favours the reaction.

At ordinary temperatures all alkaline and alkaline earthy silicates are immediately decomposed by all acids, including even the weakest, like carbonic acid. On boiling, hydrated silica, and even calcined precipitated silica, dissolves in concentrated solutions of alkaline carbonates, the carbon dioxide being continually carried away by water vapour. The reaction is favoured by concentration of the solution *of* carbonate of soda, and also by increase of the total mass of carbonate with reference to the total weight of silica to be dissolved. At a little above 100° C. the alkaline nitrates begin to be decomposed by silica. At a red heat the displacement of carbonic acid by any variety of silica (even quartz sand) is instantaneous.

The alkaline sulphates begin to be decomposed above a bright red heat, but even at 1400° C. decomposition is not complete. This reaction is utilized in the *manufacture* of *glass*, a little carbon being often added to make the decomposition of the sulphate more complete, and to avoid leaving in the glass too much of that salt, which in crystallizing on cooling might give rise to white opaque spots.

At a red heat silica reacts also on sodium chloride in the presence of water vapour, thus: $SiO_2+2NaCl+H_2O = SiO_2.Na_2O+2HCl$. This reaction is applied in the *ceramic industry* for *salt-glazing stoneware.*

Acids in general do not act on silica, excepting hydrofluoric and phosphoric acids.

Action of Hydrofluoric Acid on Silica.—Hydrofluoric acid acts on silica from ordinary temperatures upwards, very rapidly on precipitated silica (whether calcined or not), and more slowly on crystallized silica. The reaction gives in the dry way silicon fluoride (gas), and in the wet way hydrofluosilicic acid:

$$SiO_2+4HF=SiF_4+2H_2O$$
$$SiO_2+6HF=SiF_4.2HF+2H_2O$$

The first reaction is only possible in presence of excess of gaseous hydrofluoric acid to oppose the inverse reaction of silicon fluoride on water (tending to reproduce silica and hydrofluoric acid). This property of hydrofluoric acid is utilized in chemical analysis to verify the purity of silica, which should volatilize completely with excess of hydrofluoric acid. Hydrofluoric acid is also used in analysis for silicates in which it is only proposed to determine bases, much time being saved in this way.

This property of hydrofluoric acid is also used for etching glass surfaces, and in the manufacture of cast iron for cleaning cast pieces, which often retain on their surface silica and silicates from the moulding sand.

In laboratories the limited action of hydrofluoric acid on large crystals of quartz causes corrosion figures to appear.

Action of Phosphoric Acid on Silica.—Phosphoric acid combines with silica to form a crystallized compound: $P_2O_5.SiO_2$, exactly as if silica were a base. This phosphate of silica occurs in four distinct allotropic forms, differing in crystalline form and chemical properties. Two of them, prepared at low temperature, are more or less rapidly attacked by water. Two others, prepared at higher temperature, are unaffected by water and even by hydrofluoric acid. This last property is imparted to silicious glasses when phosphoric acid is introduced.

These phosphates of silica are prepared from 5 parts hydrated silica (obtained from decomposition of silicon fluoride by water) mixed with 100 parts of trihydrated phosphoric acid, $P_2O_5.3H_2O$. The mixture heated to 260° C. gives at first a transparent mass, all the silica being in solution, but this solution is not very stable, and would in time allow the second phosphate of silica to crystallize. The mass taken up again by alcohol leaves hexagonal prisms, macles, showing energetic double refraction and changeable by water. Still warming slowly the clear solution prepared at 260° C., it soon grows muddy, and at about 360° C. it deposits numerous crystalline lamellæ, producing a felting in the whole liquid. These lamellæ are hexagonal, have very weak double refraction, and much resemble tridymite (a low specific gravity form of crystallized silica). But melted silver nitrate gives with them yellow phosphate of silver. This variety is decomposed by water much more slowly than the preceding.

The same solution made at 260° C., then heated suddenly up to 700° or 800° C., remains at first clear, but if maintained at this temperature it causes gradual deposition of octahedral crystals, completely isotropic, of phosphate of silica. Water does not affect this variety. The density is 3·41, and it melts at 1400° C., giving a vitreous mass which does not devitrify on cooling.

A solution less concentrated in silica than the preceding, heated between 900° and 1000° C., gives no octahedra, but clinorhombic prisms, which act on polarized light, but are not affected by water.

Starting from metaphosphoric acid, $P_2O_5.H_2O$, and adding pure silica (from silicon fluoride), octahedral phosphate can be prepared.

Calcined silica and crystallized silica do not seem to be attacked in the same conditions, up to 300° C., but at a higher temperature all the varieties of silica are attacked by phosphoric acid. (1)

Action of Reducing Agents on Silica.—Carbon has no action on silica below 1200° C., but in the electric furnace reduction begins at 1450° C., according to the equations:

$$SiO_2+2C=Si+2CO$$
$$SiO_2+3C=SiC+2CO$$

Silica can be reduced still more easily by heating with certain metals, as potassium, magnesium, or aluminium, which reduce it to silicon. Aluminium is sometimes employed in the *preparation of silicon*. By throwing into a heated crucible (at 800° C.) a mixture of aluminium and finely divided silica, a violent reaction produces a mixture of brown silicon and alumina. On adding potassium silicofluoride to the mixture, and using excess of aluminium, a metallic melted bottom is obtained, which after the action of hydrochloric acid leaves crystals of silicon (soluble in the melted aluminium, recrystallizing on cooling).

The presence of certain metals—copper, silver, iron, platinum—favours partial reduction of silica by carbon through absorption of the silica. On heating of cast iron (consisting mainly of iron and carbon) in silica crucibles, it takes up from the walls of the crucibles several per cent. of silicon. The same reaction takes place in blast furnaces at the expense of the silica of the slags; it is more complete the higher the temperature, and the less basic the slags. Grey cast iron includes normally 1 to 2 per cent. of silicon which has been thus reduced. (1)

Quartz is by far the commonest variety of silica, and indeed the commonest of all minerals. It occurs in various forms and under different conditions, mostly in grains or in extensive masses of a white or grey colour. Sometimes quartz occurs of a red, brown, yellow, blue, green, or even black colour. The transparent colourless crystals known as rock crystal (or simply crystal) are practically pure silica. Impure quartz may be almost opaque. Crystals up to 20 inches in diameter have been found in Brazil and Madagascar, whereas grains of quartz in sand are often less than $\frac{1}{25}$ in. in diameter. Naples museum has an aggregate of quartz crystals weighing about a ton.

Quartz possesses in a very marked degree circular polarization.

It also possesses the special property of *piezo-electricity*; it can transform mechanical energy into electrical energy, and conversely, and this fact has been applied by Curie in the construction of an electrometer of high precision.

The thermal expansion of quartz is quite abnormal, as it is with all the other varieties of crystallized silica.

Crystalline Symmetry of Quartz.—Most quartz crystals have six faces (opposite faces being parallel) of a hexagonal prism, with a hexagonal pyramid at one end or at each end. The prism is sometimes absent, the two pyramids meeting at their bases. The faces are often very unequal as regards size, making the crystals look distorted, though the angles between corresponding faces remain the same. The prism faces have parallel striations, which are horizontal when the prism is placed in a vertical position, and which serve to distinguish quartz from other minerals of similar form. Rather rarely, one end of the quartz crystal is terminated by a plane (instead of a pyramid). In some specimens the terminal hexagonal pyramid is replaced by a trihedral one. The hexagonal pyramid is really made up of two sets of faces, the alternate faces forming either set agreeing with one another, but showing differences from those of the second set. One set of three faces has striæ, the other set being smooth and sometimes slightly convex. The corrosion figures (produced by action of dilute hydrofluoric acid) always show a marked difference between adjacent faces of the pyramid. These corrosion figures show lines perpendicular to the axis of the crystal (and parallel to the base of the triangular face of the pyramid) on three of the faces, whereas on the other three faces the lines are inclined.

The symmetry of quartz crystals is, in fact, only ternary, and not hexagonal. One rhombohedron, generally better developed than the other, is said to belong to the *direct* form (with corrosion striæ perpendicular to the axis), and the other to the *inverse* form. The two forms of rhombohedron are distinguished as *right* and *left*, according to the direction in which they cause rotation of the plane of polarized light. Occasionally small trapezoidal faces are found replacing the corners between the prism and pyramid faces.

Inclusions.—Liquid inclusions in quartz are water or liquid CO_2, both being sometimes included in a bubble. Generally a little nitrogen is present with the CO_2.

Coloration.—Quartz crystals are sometimes coloured and opaque. At other times different minerals are visible in the interior of transparent quartz crystals.

Fracture.—Quartz crystals show no cleavage along definite planes, but break in the manner of glass with a bright conchoidal fracture, and small fragments have sharp splintery edges. Sometimes fractured surfaces show a minute rippled marking resembling finger-prints.

Specific Gravity is never less than 2·65 for quartz. The mean specific gravity of quartz at 0° may be taken as 2·6507. The volume of the inclusions never reaches 0·1 per cent. of that of the crystal, and cannot affect more than the third decimal.

Expansion on Heating.—A knowledge of the anomalies is very important for the application of silica to making refractory products. At low temperatures (below 100° C.) the coefficient of expansion has been found to be nearly twice as great perpendicular to the axis as parallel to the axis. Below 570° C. the values obtained for coefficients of expansion are practically the same as those for the low temperatures.

At 570° C. there is a sudden expansion, from 1·0068 and 1·0116 of 0·0034 and 0·00547 respectively. Above 570°, after this sudden and reversible modification, the expansion is changed into a slow contraction. This behaviour is applied in the manufacture of silica bricks by heating the quartz to redness before submitting it to crushing. In like manner, the ancients are said to have used fire to facilitate the cutting of roads in the granitic rocks of the Alps, which include a large proportion of quartz. It also explains difficulties met with in earthenware manufacture in trying to secure agreement between bodies and glazes. The body always includes quartz (or other form of crystalline silica) in some quantity, and owing to irregularity of expansion it is impossible to find a glass capable of agreeing perfectly with the body. In porcelain the body has become partly vitreous, and the silica has assumed the amorphous state. In hard porcelain the coefficient of expansion is nearly constant up to 1000° C.

Hardness.—Quartz is No. 7 on the hardness scale of Mohs, and is harder than most minerals, including all the commoner ones. It also scratches glass. Certain industrial applications of quartz depend on its hardness.

Sandstone formed of grains of quartzose sand serves to make millstones to use for grinding and for cutting hard bodies. In minor industries these millstones are used for sharpening tools, and in glass manufacture for cutting glass. Quartzose sand is largely used as abrasive powder, not so hard as emery, but much less costly; it is largely used for polishing. A jet of sand propelled by compressed air (sand blast) has received numerous industrial applications.

Compact sandstones and quartzose rocks make excellent building materials. Crushed quartzites are very good for the manufacture of concrete. A suitable crusher and pulverizer made by the Patent Lightning Crusher Co. is shown in Fig. 1, p. 15.

Specific Heat of quartz exhibits peculiarities. About 600°, during transformation, there is absorption of heat (5 calorie-grms. per grm. of substance). At higher temperatures the specific heat tends to diminish, contrary to all other bodies (except certain silicates). (1)

Circular Polarization of light by quartz is exceptionally distinct.

The double plate of quartz is formed of two semicircular halves (one dextro-rotatory and the other lævo-rotatory) cut perpendicular to the prism edges, joined along a vertical diameter. The thickness of the plate is 3·75 mm., enough to turn the plane of polarization of yellow rays through an angle of 90°. If the principal section of the analyser be perpendicular to the primitive plane of polarization the two halves of the extraordinary image will show the transition tint, and will thus have an identical coloration as if there had been only a single plate. A very small rotation of the analyser will cause one plate to change to red, the other to blue, and so accentuate the difference.

In order to determine the position of the plane of polarization, the principal section of the analyser has only to be turned until the tints of the two halves of the extraordinary image become identical, when this principal section will be strictly perpendicular to the plane of polarization.

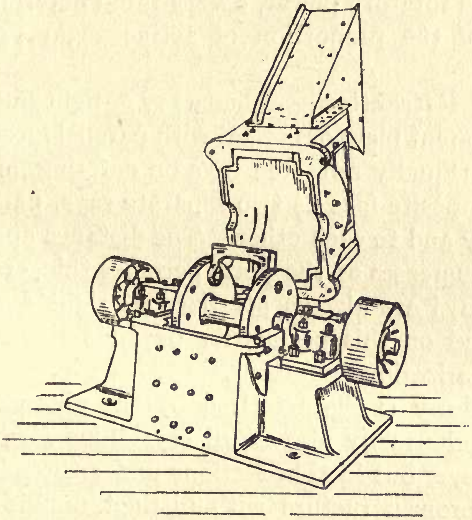

FIG. 1.—Crusher and pulverizer.

Circular polarization by other substances can be detected with the aid of the same apparatus. The effect of another substance placed in front of the double plate is added to that of one-half of the plate and subtracted from the other, and the result being the same as for a difference in thickness of the two plates, identical tints cannot be obtained for the two halves of the image. On restoring equality by means of a compensator, the rotatory power of the substance introduced is measured. The compensator comprises two plates with parallel faces, one right, the other left. One plate has fixed dimensions, but the thickness of the other can be varied—as by using two bevelled plates, of which one can slide over the other while keeping the two external faces always parallel. (1) and (2)

Saccharimeters are instruments for measuring the rotatory power of certain sugar solutions, etc. By measurement of this rotatory power, a very rapid determination can be made of the proportion of active sugar present in a solution.

Double Refraction.—When a ray of light falls obliquely on a transparent plate or crystal with parallel faces, it divides into two unequally refracted rays on entering, and emerges from the opposite face as two separate rays, parallel to the incident ray and to each other. The distance apart of these two rays increases as the plate becomes thicker. The two emerging rays are always polarized at right angles to one another, and on this peculiarity depends the construction of most polarization apparatus.

Chalcedony is characterized by the absence of transparency, and usually also of all crystalline form visible to the naked eye, but in thin sections under the microscope it shows a fibrous structure with distinct double refraction. The *density* is usually between 2·55 and 2·58 (that of quartz being 2·65). The *expansion* is quite similar to that of quartz, and presents the same anomaly towards 600°. The varieties of silica included in chalcedony are generally impure; they include small quantities of water, and seem to be transitional between hydrated silica and quartzose silica. Crystals of quartz are, in fact, often found on one face of a mass of chalcedony, and hydrated silica on the other face. Chalcedony often occurs as concretionary masses, formed in more or less regular beds, and sometimes distinguished by the variety of colorations, like certain agates.

Not only chalcedony, but all terrestrial rocks include small quantities of water of which the state is not fully elucidated. It may be simply lodged in voids between the fibres. Chalcedony is not absolutely compact. The transition from chalcedony to opal seems to be continuous, so that the last would be constituted by crystalline elements too fine to be discernible even under the microscope. Chalcedony often surrounds foreign materials in the rock in which it occurs, notably fossils. Everything indicates that these agglomerations of silica are formed in the wet way and at low temperature, which is not generally the case for the other varieties of silica. Quartz is often formed above 600° C., as its corrosion figures prove, and other varieties of silica with low density at temperatures higher still. (1)

Action of Heat on Chalcedony.—Chalcedony begins to lose its water between 100° and 200° C. Too rapid heating may cause rupture with explosion, as happens with all materials having very fine pores impregnated with water, such as slate and porcelain biscuit. This shivering arises from inability of the water vapour to escape quickly enough through the pores, and so the internal pressure increases very rapidly. This dehydration can be effected without shivering, not only for chalcedonic material like flint, but for slate or moist unglazed porcelain, on heating these bodies to 200°, a temperature at which the vapour pressure is not great as compared with the mechanical strength of the solid bodies which imprison it. The water vapour is disengaged slowly—sometimes for several hours—and afterwards the temperature can be raised rapidly without any risk.

In further raising the temperature of chalcedony, ruptures by shivering are again produced towards 600°, from exactly the same cause as the shivering of ordinary quartz at the same temperature. After this transformation the material loses its translucency, becomes whitish, and takes a permanent increase of volume, With further gradual rise of temperature this swelling increases regularly until 1000° C., and perhaps higher. The permanent expansion produced at 1000° C. corresponds to a linear elongation varying according to the sample from 0·5 in the case of fossil woods to 4 per cent. for agates. Successive heatings of the same specimens do not cause new permanent expansions so long as the temperature of the first heating is not exceeded, but the sudden and reversible change at about 600° C. always recurs.

This expansion, and the loss of transparency which accompanies it, seem to result from the formation of innumerable fissures. The calcined samples have, in fact, become porous and capable of absorbing liquids. Their absolute specific gravities have not diminished, but the apparent volume has increased.

When heated at 1400° C. in the porcelain oven, chalcedony is completely transformed into a variety of silica of specific gravity about 2·3. It is the same transformation that quartz suffers, but is produced more rapidly with chalcedony. (1)

The more important varieties of quartz may be grouped as follows (slightly modified from L. J. Spencer) : (2)

A. Crystallized quartz with vitreous lustre.
B. Quartz with enclosures of other minerals.
C. Chalcedony or cryptocrystalline quartz.
    1. With waxy lustre.
    2. Compact varieties with dull lustre.

Not included in these are a few varieties which are rocks rather than minerals: sand, sandstone, quartzite, vein-quartz, oilstone, whetstone, etc.

Group A includes rock-crystal, amethyst, citrine, cairngorm and smoky quartz, rose quartz, milk quartz, sapphire quartz, and prase. The name *crystal* or *rock-crystal*—from the Greek *krustallos*, "clear ice"—originated in the ancient belief that the mineral, which seems cold to the touch and commonly occurs in rocks among Alpine glaciers, was really congealed water. It has been used from a very early period for making ornaments, carved vases, etc., sometimes finely engraved, and lenses or globes were applied for kindling fire and other heating purposes. Ladies were provided with crystal balls to cool their hands in hot weather. Rock crystal is still used as a cheap gem-stone or ornamental stone, and for making spectacle lenses, though in some directions largely replaced by glass, and it is also carved into seals, paper weights, and spheres for crystal-gazing, etc. Locally it often receives such names as Bristol diamond, Cornish diamond, Isle of Wight diamond, etc. The "pebble" for lenses comes chiefly from Brazil and Madagascar. The finest rock-crystal in Great Britain occurs in Cornwall and about Snowdon. (See below.)

Amethyst is a violet or purple transparent quartz used as a gem-stone. The name is from the Greek *amethustos*, "not drunken," because of the ancient belief that wearing it prevented intoxication. Heating has the effect of changing the colour of amethyst to yellow, and much of the yellow quartz of jewellery is said to be produced in this way from amethyst. The origin of the colour in amethyst is not known, though manganese is sometimes stated to be the cause. Amethyst is composed of irregularly alternating lamellæ of right-handed and left-handed quartz, and often gives on this account a minute rippled fracture suggesting finger prints. *Citrine* includes yellow varieties of quartz, called by jewellers "occidental topaz," "Spanish topaz," "Scotch topaz," etc. These yellow varieties are sometimes included in the term *cairngorm* (from the name of a peak of the Grampians in Banffshire), which also includes the brown *smoky quartz.* The latter becomes yellow on heating, but the yellowish-brown colour can be restored by the action of radium. Smoky quartz sometimes shows the same striated structure as amethyst, and some mineralogists include with the latter all varieties showing such structure, irrespective of their colour. The brown colour of smoky quartz is sometimes deep enough to make the stone seem almost black, and it is then sometimes termed *morion.* *Rose quartz* has a pale rose-red colour, but is never found in the form of crystals bounded by faces. *Milk quartz* is white, with milky opalescence. Other white varieties include the *potato-stone* from Clifton (Bristol), which is hollow and lined with crystals, and *cotterite,* an Irish quartz with a peculiar pearly lustre ; potato-stone, however, belongs rather to the agate group, the quartz crystals only lining the interior. *Sapphire quartz* is blue, and *prase* of a leek-green colour.

Group B includes avanturine-quartz, cat's-eye, tiger-eye, hair-stone, needlestone, eisenkiesel, etc. *Avanturine-quartz* (or *aventurine-quartz*) is spangled throughout with minute yellow scales of mica, etc. ; it is found in Spain, and is used for ornaments, like other members of this group. *Cat's-eye quartz* exhibits opalescence due to enclosed fibres of a mineral resembling asbestos. *Tiger-eye* has a golden yellow colour, and consists of quartz and limonite (hydrated oxide of iron) ; this ferruginous quartz has the finely fibrous structure of the crocidolite from which it was derived, with a silky lustre and considerable hardness ; similar specimens retaining the indigo blue colour of the crocidolite are known as *hawk's-eye*. *Hair-stone, needle-stone,* etc., enclose needles of rutile, actinolite, etc. *Eisenkiesel, iron flint,* or *ferruginous quartz,* encloses iron oxide and hydroxides, which give it a yellow or red colour.

Group C 1 includes agate, onyx, sardonyx, sard, carnelian, chrysoprase, plasma, bloodstone or heliotrope, etc.

Agate is a natural mixture of crystalline, cryptocrystalline, and colloidal silica, but consists mainly of chalcedony. The name is derived from the river Achates (now the Drillo) in Sicily, where it was first found. In most agates the silicious material occurs in regular layers, so that a section gives a banded appearance, and such stones are sometimes termed banded agate, riband agate, and striped agate. This zoned structure generally arises from silicious matter being deposited from solution in successive layers within cavities formed by escaping vapour in eruptive rocks or old lavas. Sometimes such deposition has taken place in fissures, and sometimes in cavities of stratified rocks, as in the potato-stones mentioned in connection with Group A. The analysis of an agate gave 98·8 per cent. silica, 0·53 per cent. ferric oxide, 0·62 lime, and 0·2 water. Deposition of silica in forms very similar to those of certain agates, has been effected artificially. The cavities in rocks may contain various minerals resulting from decomposition of the constituents of the rock. The first deposit—forming the " skin " of the agate—is generally a dark green earthy mineral, delessite (a hydrated silicate of aluminium, iron, and magnesium), or celadonite, or chlorophæite, other hydrated silicates rich in iron, probably produced by the decomposition of the augite in the rock. Subsequent deposits often fill the cavity more or less completely, and from the commonly almond-shaped kernels of mineral the rock is said to be *amygdaloidal*. This shape is due to elongation, by the flow of viscous lava, of the original bubbles of gas or steam. When the mineral kernel is hollow it forms a geode (or cavity lined with crystals), but when nearly filled with alternating layers of chalcedony, jasper, quartz, and other forms of silica they constitute true agates. The green skin outside an agate is often browned by the formation of limonite (hydrated oxide of iron) from the green mineral. The largest and finest agates come chiefly from Brazil and Uruguay, mostly as pebbles from the beds of rivers. The " Scotch pebbles " used as ornamental stones, found chiefly in Perthshire and Forfarshire, similarly occur in river beds, but also in pebble drifts on the land, having in both cases been set free by disintegration of the rocks. Agates also occur in Northumberland, in Somerset (Mendip Hills and near Bristol), and about Lichfield (Staffordshire). They resist the action of air and water, as well as mechanical influences such as abrasive action, better than most minerals. In ordinary agates the successive layers are variously curved; in *fortification agate* they run in zigzag lines; when sections show concentric circles (due to stalactitic or stalagmitic growth) the stone is called *ring agate* or *eye-agate*, and a Mexican agate showing only a single eye is called " cyclops." *Moss agate* consists of chalcedony enclosing filaments, etc. (mostly green, but sometimes red or brown), suggestive of vegetable growths. A variety of agate known as *Mocha stone* consists of white or brown chalcedony with black or brown dendritic or arborescent markings due to infiltration of oxides of manganese and iron. Imitation Mocha stone has been produced artificially at Oberstein.

Agate-working has long been practised in the neighbourhood of Oberstein (on the river Nahe, a tributary of the Rhine). Agates were formerly obtained in the district, but they are mostly imported from Brazil and Uruguay. Waldkirch, like Oberstein in the Black Forest, has also been the scene of some agate-working.

Most commercial agate is artificially stained, the Brazilian agates being easily coloured, much more so than the German stones. For a dark brown, or black colour the stone is kept for some time in a sugary solution, or in olive oil, at a moderate temperature. The agate is then washed, and digested for a short time in sulphuric acid, which carbonizes the sugar or oil in the pores. If stained too dark, the colour may be "drawn" or lightened by the action of nitric acid. Some layers of chalcedony are practically impermeable and remain uncoloured, so that usually alternate light and dark bands are obtained. Agate may be stained red or brown to simulate carnelian or sardonyx, by means of ferric oxide, either formed in the stone by simply heating, or by heating after the artificial introduction of the solution of a salt of iron (such as ferrous sulphate). A blue colour in imitation of lapis lazuli is produced by first using ferrous sulphate and afterwards a solution of potassium ferrocyanide or ferricyanide. A green colour, like chrysoprase, is given by salts of nickel or of chromium, and a yellow tint is produced by hydrochloric acid.

Among the purposes for which agate is used are the knife-edges of delicate balances, small mortars and pestles, burnishers and writing styles, umbrella-handles, paper-knives, trinket boxes, seals, brooches, beads, and other small ornaments, etc. Most of them have been cut and polished in the Oberstein district, from South American agates.

Onyx is a variety of chalcedonic silica differing from agate only in the straightness and parallelism of its differently coloured layers, it is thus suitable for engraving as cameos. The alternate bands of colour are usually white and black or white and red. Most of the onyx with strong colour differences are now coloured artificially in the same way as agates. **Sardonyx** is much used for seals and cameos, and usually consists of a layer each of sard or carnelian and milk-white chalcedony, sometimes several such alternating layers. The sardonyx is thus simply an onyx with bands of sard or carnelian, though in the latter case it would be more correctly called a "carnelian onyx." Imitations of sardonyx have been made by cementing together two or three stones, but most of the modern sardonyx is cut from South American agate, coloured artificially as mentioned in connection with agate. **Sard** is a reddish-brown or yellowish-brown chalcedony, much used as a gem-stone (for cameos, etc.) by the ancients. Some kinds of sard greatly resemble carnelian, but are usually rather harder and tougher, with duller and more hornlike fracture. Both are chalcedonic quartz coloured with iron oxide. The colour of sard ranges from golden, orange-red, and hyacinthine to a dark brown (almost black). **Carnelian** or **cornelian** is a yellowish-red or orange coloured chalcedony, much valued for engraving; its fracture has a peculiar waxy lustre, distinct from that of sard. It is imitated by staining agate. **Chrysoprase** is merely a pale green (apple green) chalcedony, and **plasma** is a darker green variety (leek-green or grass-green). **Heliotrope** is a dark green chalcedony, with sometimes bright red spots, streaks, and splashes, when it is called **bloodstone**; the red colour is due to hæmatite, which is itself sometimes called bloodstone. Bloodstone is used for seals, knife-handles, and various small ornaments. It is found in the Isle of Rum.

Certain rare varieties called lutecite, quartzine, and pseudo-chalcedonite, present slight differences of structure from chalcedony, which can only be ascertained by the aid of the microscope.

Group C 2 includes jasper, flint, Lydian stone, and buhrstone, etc.

Jasper is a coloured mixture of silica and clay, with iron oxide and hydroxide, and is a compact opaque mineral with a dull earthy fracture, though it takes a good polish.

The colours are chiefly brown, red, yellow, and green The impurities present with the silica sometimes amount to 20 per cent. Jasper is cut and polished as an ornamental stone, and was highly prized by the ancients. *Egyptian jasper*, which occurs as nodules and pebbles in the Nile Valley, resembles a brown flint with dark zones and cloudings. *Banded jasper* is a striped variety, like the red and green "riband jasper" of the Ural Mountains.

Flint is a dark grey or dark brown variety of chalcedonic silica, and when pure shows no structure to the unaided eye. Though individual flints look dark and opaque, thin plates or edges of splinters are pale yellow and translucent. It is harder than steel, and its specific gravity is about 2·6. It is brittle, and when hammered it readily breaks up into powder consisting of angular grains. The fracture is conchoidal, so the blows of a hammer detach flakes with convex, slightly undulating surfaces. At the point of impact is produced a bulb of percussion—a somewhat elevated conical mark—which distinguishes flints thus shaped from such as have been split by the action of frost and other weather agencies. Flint often contains 98 per cent. of silica, sometimes 99 or only 96, and also contains a little organic material, to which the dark colour seems to be due, as it becomes white when calcined, but with duller lustre. In microscope sections flint appears very finely crystalline, and colloidal or amorphous silica may also be present; according to Dr. J. W. Mellor, the flints used in pottery manufacture have about 1½ per cent. of colloidal silica. Sponge spicules and microscopic and larger shells, often occur in flints. Flint occurs chiefly in the upper chalk, either as irregular nodules or as tabular masses. The white crust on the outside of a chalk flint contains a considerable proportion of calcium carbonate, the other constituents being practically the same as in the black core.

Flint is often used for building purposes, and as a road material. To prehistoric man flint served many of the purposes for which steel is now used, especially for making weapons and other implements. When struck with steel or with iron pyrites, flint gives sparks; hence the once universal employment of flint and steel with tinder, and the use of gun flints in the locks of old firearms. The shaping of gun flints survived till recent times at Brandon, in Suffolk, about thirty men being thus employed in 1870. When heated and thrown into cold water, flint can be easily pulverized; the white powder so obtained is used in pottery manufacture and to some extent for glass making. About 30,000 tons of flint per annum are obtained from chalk pits in the South of England, and a similar quantity is imported for the manufacture of pottery.

Chert or **hornstone** is a coarser and less homogeneous substance of the same nature and approximately the same composition as flint, but it usually contains more oxide of iron and lime. Its colour is grey, black, or brown, and it commonly occurs in limestone (particularly the carboniferous limestone) in the same way as flint occurs in chalk. Chert is extensively worked from carboniferous limestone quarries in Flintshire and Denbighshire, Derbyshire, and at Reeth in Swaledale (Yorkshire). It is used in connection with potteries for paving the flint mills.

Lydian Stone, Lydite, or **Flinty Slate,** also called **basanite,** is a black or grey cherty material, hard and close-grained, which has been used as a touchstone for testing the quality of gold. The metal is rubbed on a polished surface of the stone, and the resulting streak is compared with standard streaks of alloys of known composition, and also tested with acid. Another use of Lydian stone is as a hone-stone. Most Lydian stone has a schistose structure, and may be regarded as a hornstone slate. The Lydian stone of Devonshire and east Cornwall is a fine-grained, indurated, carbonaceous shale. In Sweden, Lydian stone is made into ornaments.

Buhrstone or **Burrstone** is a hard tough material consisting of chalcedonic silica with a cellular texture, particularly suitable for use as millstones for grinding corn, paints, etc. It is white, grey, or creamy in colour. The best stones are found in the woods of Meudon, Marly, etc., about Paris, and it forms the best building stone in that neighbourhood. The cellular spaces represent the casts of fossil shells, etc.

Silicified wood is a comparatively rare form of chalcedony, and shows the microscopic details of vegetable structure. Tree trunks over a yard in diameter have been found.

Sand is an accumulation of grains of mineral matter derived from the disintegration of rocks. When rocks or minerals are broken up by either natural or artificial agencies, the products may be gravels, sands, and muds or clays, according to the size of the constituent particles. When many of the particles are as large as peas (or larger) the product is a gravel, and when the material forms an impalpable powder owing to the extreme fineness of the particles (about $\frac{1}{1000}$ in. across), it is a mud or clay; intermediate grades constitute sands, which may vary greatly both as regards size of grains and the nature of the component minerals. Sands which have been sorted out by gentle currents of water, or by steadily blowing winds across smooth arid lands, may be uniform. Natural sands are mostly formed by the action of the air, rain, frost, heat, plants, and other agencies in breaking up the surfaces of rocks, but volcanic sands (consisting of fine particles of lava) were produced by explosions of steam in the craters of active volcanoes. A few sands are artificial, like the crushed tailings formed in the extraction of metals from their ores. Quartz is the most abundant rock-forming mineral, and its hardness, want of cleavage, and chemical properties enable it to offer a strong resistance to both mechanical and chemical action; it survives after the destruction and dispersal of the accompanying minerals, and accordingly sands are generally silicious. Much of the earth's surface is covered by sand. Fertile soils are very often sandy, though in most soils sand is mixed with clay or stones, and such soils should be described rather as loams than sands. Wind-blown sands are found in the interior of deserts, or form sand-dunes about the coast. The grains of desert sand are usually much more rounded than those of water-borne sand. The abrasive power of blown sand is utilized in the *sand-blast,* a process in which glass or stone may be quickly engraved or cut by the action of a jet of sand driven with high velocity by steam or compressed air.

Besides quartz, sands often contain a little felspar, but felspar, though very common in rocks, splits up easily and then decomposes to form mica and kaolin; the two last-named are washed away by water and are deposited as muds or clays. Mica is often mixed with the quartz and felspar in sands; though it is much softer than felspar, it is much more resistant to decomposition, but may become very finely divided. Sands also contain such hard and resistant, common rock-forming minerals as garnet, tourmaline, zircon, rutile, and anatase. Of less common occurrence in sands are topaz, staurolite, kyanite, andalusite, chlorite, iron oxides, biotite, hornblende, and augite; in the coarser sands are often small particles of chert, felsite, and other fine-grained rocks. Shore sands and river sands, which have not been carried far often contain soft or readily decomposable minerals. Thus sands about the Lizard in Cornwall are rich in olivine, augite, enstatite, tremolite, and chromite. Sands near volcanic islands may contain considerable quantities of minerals like biotite, hornblende, augite, and zeolites. Marine sands nearly always contain either plant remains or bits of calcareous shells. Shell sands often occur which consist almost entirely of shell fragments. Coral sands consist of coral fragments, mixed with broken skeletons of calcareous algæ, sponge-spicules, etc. Green sands owe their colour to dark-green rounded grains of glauconite. Many sands are coloured yellow or brown by hydrated ferric oxide. Gem-sands (and gravels) occur in Ceylon, Burma, Brazil, South Africa, etc., and, as the name implies, contain precious stones such as the diamond, ruby, spinel, chrysoberyl, and tourmaline, with often garnets and zircons. Gold and platinum, etc., also occur in sands, and so does tinstone as "stream tin." By a special washing process the heavier minerals may be separated from sands. (2) and (3)

In the use of sand for filtration of water on a large scale, the bed of filtering material consists of layers of graded sand and gravel. At the bottom is placed a layer of gravel about a foot thick, the size of the pebbles, and fragments ranging progressively from about an inch at the bottom to about $\frac{1}{8}$ in. at the top. Above the gravel is a layer of fine sand, usually several feet in thickness. The main purpose of the coarser material is simply to support the fine sand, which forms the bulk of the filtering bed, and is the real filtering agent. The sand generally used has a grain size of 0·2 to 0·4 mm., the average being about 0·3 mm. or a little more. The rate of filtration depends on the size of grain of the sand, the thickness of the bed, the head of water, and the degree of turbidity of the water. The suspended material in the descending water is arrested by the top layers of sand, rarely penetrating more than a few inches. As the filtering bed gets clogged with accumulated material, the water is allowed to sink through the sand, the top layer of which is then scraped off to expose fresh material. At intervals clean sand is supplied to keep the bed up to an effective thickness. Sometimes, especially when filtration is aided by vacuum pressure, the surface of the sand is protected by a network of iron or wood, so that the deposit may be shovelled away without greatly disturbing the sand.

Sands are put to many uses. Silicious sands practically free from iron are used for making glass. Sand is also used for making mortar, sand-lime bricks, and artificial stone. Another important use is for polishing and scouring, both for domestic and manufacturing purposes. "Bath bricks" are made from the sand of the river Parrett (near Bridgwater). Large quantities of sand are used in foundries for moulding purposes, the best moulding sands containing a little clay. Further applications of sand are for brick-making, and for filtering water. The sand-blast has been alluded to. A minor application is the use of desert sand (with well-rounded grains) in hour-glasses.

Sandstone is a consolidated sand rock, consisting of sand grains united by a cementing material. When the cement is weak, the friable material is termed *sand-rock*. The size of the particles in sandstones varies greatly, and may be regular or irregular. Coarse sandstones, called *grits*, connect sandstones with conglomerates (composed of pebbles cemented together), and fine-grained sandstones usually contain some mud or clay, and pass very gradually into sandy shales and clay rocks. Certain very impure brown or grey sandstones are called *greywackes*.

Sandstones contain the same minerals as sands, the commonest of them being quartz, with often a considerable amount of felspar, and usually some white mica as well. Other minerals often present in sandstones, sometimes in notable quantity, are chlorite, clayey matter, calcite, and iron oxides; whilst garnet, tourmaline, zircon, epidote, rutile, and anatase, are also often present, but with rare exceptions only in small quantities. Silicious sandstones consist almost entirely of silica, some ganisters, etc., containing as much as 99 per cent. of silica. Felspathic sandstones or arkoses, which contain notable amounts of felspar, are less durable than silicious sandstones. Micaceous sandstones have mica flakes arranged along planes of bedding. Argillaceous or clayey sandstones are mixtures of sand and clay. Ferruginous sandstones are brown or reddish, due to the presence of ferric oxide (hæmatite) or hydroxide (limonite), the latter brownish yellow and the former reddish, which form thin coatings around each quartz grain. Impure sandstones usually consist mainly of quartz with a considerable admixture of other minerals.

The consolidation of the sand may result either from pressure or from deposition of mineral matter between the grains. The cementing material is often fine chalcedonic silica, sometimes in such small amount that even with a microscope its presence is not easily detected; some cherty sandstones contain more chalcedony, and also rounded dark green grains of glauconite, and such green sandstones belong to the greensand formation. Silicious sandstones are very hard and durable, but difficult to work. Calcareous sandstone, in which the sand grains are cemented by calcium carbonate (calcite), may readily be worked as a freestone, but tends to become disintegrated by weathering. In Fontainebleau sandstone, Kentish Rag, Spilsby sandstone, etc., the calcite is in large crystalline masses which on broken surfaces show plane cleavages mottled with small rounded sand grains; the Fontainebleau sandstone has rather large crystals with external rhombohedral faces. Argillaceous sandstone, which contains fine clayey material, has been consolidated by pressure, but remains comparatively soft, and is easily broken up by weathering, etc. In ferruginous sandstone the iron oxide or hydroxide generally forms only a thin pellicle about each grain, but in some cases they are more abundant. In micaceous sandstones the mica scales often facilitate splitting along bedding planes, as in Yorkshire flagstone. The felspar grains in felspathic sandstones are either crystalline or partly decomposed to form kaolin, as in much of the English millstone grit, which was produced by disintegration of granitic rocks. Other cementing materials, found only in certain localities, are dolomite, barytes, fluorite, and calcium phosphate (or phosphate of lime). (2) and (3)

The colour of sandstone is mostly due to impurity, pure silicious and calcareous sandstones being white, creamy, or pale yellow from small amounts of iron oxides. Black colour arises from coal or manganese dioxide, red from hæmatite, yellow from limonite, and dark green from glauconite. Grey is often due to fragments of shale, etc., but in many sandstones bluish and greyish tints are referred to the presence of ferrous carbonate, finely-divided iron pyrites, or even iron phosphate.

Sandstones are much used as building stones, and are also used for grindstones and millstones. Very pure silicious sandstones (such as ganisters) are used for lining furnaces, hearths, etc. Sandstones, being porous, absorb water freely, and so often form important sources of water supply (as the water stones of the Midland Trias in England). Some sandstones are so impregnated with metallic compounds that they form useful ores: among others occurring in this way are carbonates of copper, sulphide and carbonate of lead, cobalt and manganese ores, metallic copper, etc.

Quartzite is a sandstone formed by deposition of crystalline quartz between the grains. As compared with ordinary sandstones, quartzites are solid quartz rocks free from pores, and have a smooth fracture, the break passing through the sand grains; in ordinary sandstones the fracture passes through the cementing material, exposing rounded faces of the grains, and so giving the broken surface a rough or granular appearance. Quartzites are too hard and splintery to be at all largely used as building stones, but are much used for roads, though in spite of their hardness they are readily crushed to powder if not well embedded in the road surface; quartzite of Emborough (near Bristol) and of Cherbourg is thus used for roads.

Oilstone is a fine-grained hone-stone used with oil for sharpening edged tools. An oilstone from Whittle Hill in Charnwood Forest (Leicestershire) is a fine-grained, silicious slaty rock. Welsh oilstone is a somewhat similar material from near Llyn Idwal in North Wales. A famous oilstone comes from Asia Minor. In Arkansas (U.S.A.) is found a bluish-white fine-grained oilstone used for delicate instruments. This and the opaque white Washita oilstone, found by the Washita River, Arkansas, are called *novaculite*. Their material is 99·5 per cent. chalcedonic silica.

Whetstone.—Very fine whetstones for sharpening edged tools are made from novaculite (named from novacula, a razor). The sharpening quality is attributed to the presence of disseminated crystalline silica, or, in some varieties, to minute garnet or rutile crystals. The rock itself has to be cut with diamond dust. Some of the pure white novaculite seems to be a silicious deposit from hot springs, other varieties being fine-grained altered schists. "Chocolate whetstone" is mica-schist from New Hampshire, and "Hindostan whetstone" is from Indiana. "German razor hones" are formed of a fine-grained argillaceous rock found in slate near Ratisbon. The Scotch "Water-of-Ayr stone" or "snake stone" is used for rubbing down the surfaces of other stones and of copper-plates, and "Tam o' Shanter hones" are used as ordinary whetstones. Coarse whetstones for scythes have long been worked near Blackdown in Devonshire under the name of "Devonshire batts"; they are made from silicious concretions embedded in sand. Similar stones for scythes have been worked at Benzlewood, near Stourton (Wiltshire).

CRYSTALLIZED SILICA OF LOW SPECIFIC GRAVITY.

Several varieties of crystallized silica with specific gravity between 2·25 and 2·35 are known They occur in very small crystals—perhaps none as much as 5 mm.—often only observable in compact rocks by the microscope. All these varieties of silica are, like the calcined silica of laboratories, easily soluble in concentrated boiling solutions of sodium carbonate.

Tridymite has a specific gravity 2·28. It possesses a rather complex crystalline constitution, but extremely constant so that it is easy to recognize. It was described by von Rath as hexagonal, but Schuster and von Lasaulx showed that it was not uniaxial, so it is only pseudo-hexagonal. Its crystals are made up by the union of three orthorhombic individuals—whence the name, meaning three twins. The network of tridymite presents great analogies with that of the cube. Groupings are observed under the constant angle of 70° 36′, which is very near the 70° 32′ of the regular octahedron. The hexagonal appearance is found in the trachytes of Mont Dore. The ordinary appearance of the twin, as met with in silicious refractory products, is different.

Optical Properties of Tridymite.—The mean index of refraction for the D ray is 1·4775. Double refraction is weaker than for quartz, the colour does not go beyond grey.

Merian found that a comparatively small rise of temperature causes in tridymite a reversible dimorphic transformation, which renders it positively uniaxial, and it is then strictly hexagonal. Mallard showed that this transformation takes place at 130 ± 5. This transformation of tridymite explains the hexagonal form of its crystals. They are always produced at temperatures above 130°; at the moment of their formation they have taken the hexagonal form, and on cooling have kept this geometrical form, in spite of the internal transformation of their network. The transformation at 130° is accompanied by an abrupt change in the linear dimensions. This sudden change of dimensions is notably less than that of quartz. The melting point of tridymite is 1670° C., as recently determined by Ferguson and Merwin.

Several varieties of tridymite occur, one of which is found in meteorites. Tridymite is met with exclusively in volcanic rocks and their recesses; or in the refractory products of works (as steel works or glass works), and then only formed at high temperatures. It is one of the essential elements of all volcanic lavas, but in recent lavas only occurs in microscopic crystals, distinguishable especially by their twinned arrangement. In ancient volcanic rocks (andesites and trachytes) it is sometimes found in crystals up to 2 or 3 mm. in size, as in Auvergne. Lavas produced artificially (by M. Lévy and Fouqué) also contained tridymite crystals, but smaller.

In fragments of granite rocks or sand carried away by the lava stream, and heated by it, the quartz is partly or wholly transformed into tridymite.

The original material of silica bricks is quartz with a small percentage of lime. The temperature is about 1600° C., where the transformation into tridymite takes place.

Cristobalite.—Von Rath discovered in the trachyte of San Cristobal (Mexico), along with tridymite, small white octahedral crystals of silica. Mallard showed that the angle of the octahedron is 70° 21′, very near that of the regular octahedron. The specific gravity is 2·34, and its melting point is 1710° ± 10° C., as recently determined by Ferguson and Merwin.

Like tridymite, cristobalite is not altered by heating to a high temperature. Its crystals are in reality quadratic, but appear pseudocubic by the grouping of three quadratic crystals having for bases the three faces of the cube. Each of these is negative uniaxial. The birefringence (double refraction) is even lower than that of tridymite.

At 175° C. cristobalite undergoes reversible dimorphic transformation, and above this temperature its birefringence disappears completely. It becomes cubic, which explains the octahedral form of its crystals, produced certainly at a high temperature. It thus differs from tridymite both by its birefringence and by its point of transformation 400° higher.

Cristobalite occurs also at Mayen (Prussia), as pointed out by Lacroix.

By heating in a platinum crucible for five hours in an autoclave a solution of colloidal silica with a little boron fluoride, Chroustschoff obtained colourless, transparent, and perfectly isotropic crystals of silica (99·78 per cent. SiO_2) with specific gravity 2·41 and index of refraction 1·48. Like cristobalite, the crystals were isotropic above 170°, and feebly birefringent at ordinary temperatures, and indeed can hardly be regarded as distinct from cristobalite.

By heating quartz—or still better chalcedony (or flint)—to a very high temperature, but not high enough to cause formation of tridymite, a product is obtained which must be considered as identical with cristobalite. This is characterized by abnormal expansion, with sudden increase of linear dimensions at about 210° C., amounting to 1 per cent. Quartz in crystals is not appreciably changed after 24 hours in a porcelain oven at 1400° C., whereas the same quartz finely ground (to pass a 200-mesh sieve) is completely transformed by the same heating. The presence of lime in contact with the silica promotes this change, whilst alkalies give amorphous silica instead.

The production of this cristobalite explains many irregularities and accidents of manufacture, as the cracking of fine faience (earthenware), and also supplies a reason for certain manufacturing processes which were developed empirically. These will come in for further consideration later.

Small crystals of quartz were first produced artificially in 1851 by De Sénarmont on heating gelatinous silica to 350° C. in a sealed glass tube, and in 1857 (along with wollastonite crystals) by Daubrée by simply heating pure water in ordinary glass tubes (enclosed in iron tubes) at 320° C. for several months. In 1879 Friedel obtained them more readily at a higher temperature, and using a little potash solution instead of acid with the precipitated silica. In 1883 Chroustschoff obtained small quartz crystals from gelatinous silica with a little boron fluoride by heating to about 300° C., whilst at lower or higher temperatures other varieties of silica were obtained.

In 1878 Hautefeuille first produced quartz crystals in the dry way by dissolving silica in certain melted salts. When the temperature of the fused material exceeded a certain limit, only crystals of low specific gravity forms of silica were obtained. In 1906, Day and Shepherd produced distinct crystals of quartz by heating silica to 700° C. and lower with 80 parts potassium chloride and 20 parts lithium chloride.

Tridymite has never been produced artificially in the wet way, but has easily been obtained in very imperfect crystals by the prolonged heating of silicious glasses, as when Fouqué and M. Lévy reproduced volcanic lavas.

In 1869, G. Rose first announced the production of tridymite, but, according to Le Chatelier, that may have been a phosphate of silica, which closely resembles tridymite, but was not identified until later by Hautefeuille. (1)

The production of tridymite was also reported by Hautefeuille and Parmentier, and by Day and Shepherd; here, too, Le Chatelier considers that more recent researches of Lacroix indicate that cristobalite rather than tridymite was obtained. When fluxes are used a low specific gravity form of crystalline silica is certainly obtained between

800° and 1000° C., but whether tridymite or cristobalite seems doubtful.

Herschkowitsch showed that vitreous silica is devitrified towards 1300° C., and the specific gravity of 2·33 for the resulting confused crystalline material seems to indicate the formation of cristobalite.

Regions of Stability.—Quartz is stable at low temperatures, and at 300° and 700° C. (at which it is produced in the wet and dry ways respectively). It is possible that chalcedony may be the stable form under some conditions rather than quartz. When heated rapidly, quartz reaches its softening point without being transformed. When maintained near 1500° C. for a long time, quartz becomes completely transformed into tridymite, and at much lower temperatures if finely powdered, as previously mentioned. The upper limit of stability of quartz is, in fact, only about 800° C., at which temperature transformation takes place, whilst the product changes back into quartz at 750° C. at atmospheric pressure. Increased pressure raises the temperature of transformation.

Tridymite is the stable variety of silica above 1500° C. (and near the fusing point). The lower limit of temperature for stability of tridymite is not known. It was stated to coincide with the upper limit of quartz, but Lacroix showed that Day and Shepherd had obtained cristobalite and not tridymite.

Le Chatelier's experiments showed that the low specific gravity silica obtained in laboratory experiments, by heating between 1200° and 1400° C. bricks made of fine sand, possessed neither the same expansion properties nor the same transformation point as tridymite, but rather agrees with cristobalite. There is apparently an interval of temperature between the region of stability of quartz and that of tridymite.

Le Chatelier observes that if cristobalite has its own zone of stability it should occur more frequently in nature, at least in volcanic or metamorphic districts. Its very weak double refraction renders its observation rather difficult when isolated crystals do not occur in the geodes.

Notwithstanding doubtful points, these reciprocal transformations of silica play an important part in geological phenomena, and in certain operations in ceramics.

Hydrated Silica.—The proportion of water usually lies between 3 and 12 per cent. and varies—even in the same sample—with external temperature conditions and hygroscopic state. These hydrates of variable composition are not crystallized, but occur in gelatinous masses or in clots without showing any geometrical form or any action on polarized light. (Certain zeolites, hydrated silicates in very fine crystals, also possess a content of water varying with atmospheric conditions.)

Hydrated silica gives so-called colloidal solutions, which easily freeze into jellies. Artificial hydrated silica has been shown to contain a variable quantity of water, like the natural material.

Coagulation of Hydrated Silica.—The mechanism is as follows :—At a given moment the homogeneous material is divided into pure water and silica retaining less water than before. One of the liquids is resolved into small independent drops, and the other forms a network uniting the first ; the second becomes more or less solid and makes the mass pasty. This second portion is often separated into isolated clots which remain suspended in a continuous mass of water. A jelly or *gel* consists of a continuous mass of the semi-solid material with isolated little drops of pure water in the middle of it.

The gel contracts progressively, causing the water to ooze. The water, beginning with $SiO_2.300H_2O$, is, by dripping a long time on a glass plate sheltered from evaporation, reduced to less than $SiO_2.100H_2O$. By compression between porous bricks, under a pressure of 0·5 kg. per sq. cm., more water is expelled, reducing to about $SiO_2.20H_2O$. The tension of water vapour exercised by the material remains invariable all this time, and is equal to that of pure water.

Desiccation goes on slowly when drained gels are exposed to the atmosphere at definite vapour tension below that of pure water.

According to Le Chatelier, the only plausible hypothesis is that silica does not form hydrates, but always exists in the anhydrous state, even in "hydrated" silica. Other acids, also, as chromic acid, do not form hydrates in presence of water.

The existence in gelatinous silica of a material as hard as anhydrous silica should make it applicable for polishing metals, etc., a deduction which has been confirmed experimentally.

Natural hydrated silica includes the varieties of opal.

Opal is a natural colloidal silica, commonly occurring in nodular and stalactitic forms in cracks and cavities of volcanic rocks. The name comes from Latin *opalus*, "a precious stone." Its hardness is about 6 (5·5 to 6·5), and its specific gravity ranges from 1·9 to 2·3. The proportion of water usually varies from about 2·5 per cent. to 11 or 12 per cent. Unlike quartz, opal is almost entirely soluble in hot solution of caustic alkali. Opal is normally isotropic, like other non-crystalline minerals, but many varieties, especially of noble opal, are strongly birefringent, probably owing to strain set up by unequal contraction in different directions during solidification of the originally gelatinous material. The index of refraction for the middle part of the spectrum is 1·437 to 1·455.

When heated, opal loses water, cracks, becomes pearly, and often preserves its original coloration. Certain opals heated in concentrated sulphuric acid blacken like jet, keeping still coloured reflections; they include a little carbonaceous matter. A Hungarian noble opal with less than 1 per cent. of impurities contained in the natural state 11 per cent. of water, and after desiccation at 16° and 100° the water was 9 and 4·7 per cent. respectively; these two last correspond to $3SiO_2.H_2O$ and $6SiO_2.H_2O$ respectively, and are proportions found rather often in other varieties of hydrated silica.

Hyalite (from Greek *hualos*, "glass,") *glassy opal*, or *water-opal*, sometimes called "Müller's glass," is a colourless transparent variety of opal with little water. It is found chiefly at a few places in Bohemia, Mexico, and Colorado, U.S.A.

Semi-opal includes the dull, opaque varieties, which are generally more or less impure.

Common Opal is a name applied to any opal which has not a sufficient display of colour for ornamental purposes, including milk-opal, wax-opal or resin-opal, agate-opal, prase-opal, jasper-opal, rose-opal, etc., the appearance of which is suggestive of the stone or other substance forming part of the name. Common opal is often found in the vesicular lavas of County Antrim and the West of Scotland, etc.

Fire Opal, sometimes called "girasol," is found chiefly in Mexico, and has a brilliant orange or hyacinthine-red colour, which gives it some value in jewellery.

Noble Opal or **Precious Opal** is unique in its brilliant flashes of iridescent colours by reflected light. This play of colour has been ascribed to the presence, within the substance of the opal, of numerous microscopic fissures or pores or delicate striæ, but H. Behrens attributes the effect to very thin lamellæ of opaline silica (or foreign matter) having a different refractive index from that of the matrix. In the variety called by jewellers "harlequin opal," the colours flash from small angular surfaces, forming a sort of brilliant mosaic. In other varieties the colours are distributed in broad bands or comparatively large irregular patches. The finest opals occur in Hungary, along with common opal, in an altered andesite. Slabs of the matrix, or "mother-of-opal," enclosing brilliant particles of opal, are polished as ornamental stones. Precious opal is also found in Honduras, Mexico, Queensland, and New South Wales. Opals are usually cut with convex surface, but when too thin for this, as is often the case in Queensland, the opal is used for inlaid work, or is carved into cameos with the dark-brown ferruginous matrix forming an effective background. The "root-of-opal" consists of opal disseminated through the matrix. The matrix penetrated by veins and spots of opal, and perhaps heightened in colour by artificial treatment, has been termed "black opal," but true *black opal*, enclosing patches of manganese oxide and showing a brilliant play of colours, occurs in New South Wales.

Menilite or **Liver Opal** is a grey or brown opaque opal occurring as nodules of a special lenticular form about Paris, especially at Menilmontant.

Hydrophane is a porous opal which is opaque and dead white when dry, but which becomes more or less transparent when immersed in water, and sometimes gives a play of colours. A fine variety from Colorado has been sold in America as "magic stone." *Tabaschir* is a similar silicious and concretionary matter deposited in the nodes of bamboos.

Cacholong is another kind of porous opal, with somewhat pearly lustre. It occurs at the Giant's Causeway (Antrim), etc. (4).

Wood Opal or **Lithoxylon** is simply *silicified wood* or *resinite* which has been fossilized with opaline silica. It appears similar to that formed from chalcedony, and only differs in the larger water content. In cut and polished specimens the woody structure produces a pleasing effect, and the material is therefore used in slabs as an ornamental stone.

Besides the compact forms of opal, loose and friable forms of opaline silica occur as silicious sinter or geyserite, kieselguhr, etc.

Geyserite or **Silicious Sinter** is opaline silica deposited by spontaneous evaporation from hot springs (geysers) in Iceland, New Zealand, and the Yellowstone National Park (Wyoming, U.S.A.). It is fibrous and mammillated, opaque in mass, but composed of small transparent globules imprisoned in an apparently gelatinous paste, and includes a high proportion of water.

Fiorite or **Pearl Sinter** is opaline silica with a rather pearly lustre, from the hot springs of Santa Fiora (Tuscany).

Pealite is a variety with an exceptionally small proportion of water, from the Yellowstone Park.

When very loose in texture, silicious sinter is often called *silicious tuff*.

Kieselguhr, Diatomite, Diatomaceous Earth, Infusorial Earth, Tripoli (or **Tripolite**), **Randanite,** is made up of the minute silicious shelly remains of diatoms and radiolarians (but especially the former), which accumulated at the bottoms of ancient lakes, often forming extensive deposits, usually of a white or greyish colour. The purest varieties consist of 88 per cent. silica, 10 per cent. water, and 2 per cent. basic oxides. Salvétat found in randanite from Auvergne that the water content varied with desiccation (as with opal), the amount after desiccation at 16° and 100° being 9·1 per cent. (corresponding to $3SiO_2.H_2O$) and 4·7 per cent. (corresponding to $6SiO_2.H_2O$) respectively.

Tripoli, a more compact and laminated variety from Tripoli and Bohemia, is used as polishing material, and kieselguhr is used as absorbing material for nitro-glycerine in the manufacture of dynamite.

Elongated forms of diatoms like naviculæ make good insulating material, having the greatest porosity.

Kieselguhr is mostly obtained from Naterleuss, between Hamburg and Hanover, where the deposit extends about 150 ft. downwards from the surface, and three portions are distinguishable. The top stratum consists of white kieselguhr, and contains some sand, but very little organic matter; the washed product is very pure and porous. The next stratum produces grey kieselguhr, and contains very little sand, but sufficient organic matter for calcining the material; when calcined it yields the best quality of kieselguhr. The lowest stratum—and much the largest, being 50 to 100 ft. thick—produces green kieselguhr, containing up to 30 per cent. of organic matter; the dry material when heated glows like peat. It is calcined in small furnaces, which, when filled, are lighted at the bottom, and no additional fuel is needed; the furnaces are continually fed with the raw material at the top, and the calcined product, which has a reddish colour (due to ferric oxide) is taken out from the grates below.

In Scotland, deposits of diatomite occur with peat in several localities, and in the Isle of Skye beds up to 40 ft. thick have been worked. In Ireland, kieselguhr has been found in County Antrim. In the United States enormous deposits occur at several places, sometimes reaching a thickness of 1000 ft. (2)

Kieselguhr varies greatly in composition, the general range being 70 to 80 per cent. silica (largely in the soluble opaline form), 10 to 20 per cent. water and organic matter, with small amounts of alumina, ferric oxide, lime, etc. Its high non-conducting power—due to its great porosity—fits it for coating steam boilers and pipes. It is also used by safe makers, cooking stove and kitchener manufacturers, for filling up bulkheads in steamships, for making fireproof rooms, etc. It has been made into fireproof bricks of low specific gravity for the setting of steam boilers, the lining of blast furnaces and the associated hot air pipes, and for the backs of fireplaces. It has further been suggested as an absorbent for bromine for disinfecting purposes, and for making "dry sulphuric acid" by saturating calcined kieselguhr with sulphuric acid, the product, which contains 75 per cent. of its weight of sulphuric acid, being said to be transportable by land or sea in iron vessels without damage.

Kieselguhr is used by soap makers, by manufacturers of ultramarine, and for making imitation meerschaum.

Amorphous Silica.—Calcined silica obtained by calcination of any variety of hydrated silica, whether from action of acid on sodium silicate or decomposition of silicon fluoride by water, is usually described as amorphous silica. The impalpable powder of which this silica consists evades all means of optical investigation, so it is not known whether it is crystalline or not. The expression "amorphous silica" is therefore inappropriate in this case. The region of stability of the amorphous state always corresponds to higher temperatures than those of the crystallized state, so it would seem logical to suppose this material were crystallized, because of the low temperature at which it is obtained.

Fused Quartz was the first really amorphous silica obtained—by Gaudin, about 1839. The melted quartz on cooling did not crystallize like alumina, but lost its double refraction and formed a true glass. Attempts were made to use this glass for chemical instruments, but without much success until 1899. It proved to be permeable to gases, and so cannot be used for thermometers.

Silica Threads were obtained by Boys in 1887 from melted silica, and were used for suspension of galvanometer needles. These threads offer two marked advantages over ordinary glass threads. The residual torsion of melted silica threads is very weak, the threads returning to zero immediately even after considerable torsion, whereas with other substances the return is made only very slowly. Again, when conducting threads are required, the greater infusibility of silica permits the use of hot platinizing or gilding, which is much stronger than the cold silvering alone possible on glass. These superficially conducting silica filaments have been used by Einthoven for making extremely sensitive galvanometers. The filament is stretched vertically between the two poles of a powerful electro-magnet; its surface, silvered and illuminated laterally by an arc lamp, the light from which is reflected on the generatrix at 45° from the cylindrical filament, gives an infinitely thin luminous line. A microscope objective magnifying 700 times projects the image of this illuminated generatrix on a transparent screen or on a photographic plate animated by a movement of translation.

Fused Silica is also used for making photographic objectives. Crystallized quartz has remarkable transparency for ultra-violet radiation, and the same property may be expected in fused silica with less inconvenience from double refraction. Fused silica is a non-conductor of electricity even in a moist atmosphere and at high temperatures.

Fused silica in considerable quantity was first made by Moissan in an electric furnace, and it has since become a regular commercial product in England since 1904. It is difficult to obtain silica in a really fluid condition in bulk, but it is much more readily obtainable in a plastic condition in which it can be worked, and much of the silica glass products on the market are produced in this way. The temperature at which carborundum is formed is very close to the temperature needed for working silica, but the relatively easy accurate measurements with an electric furnace make it possible to control the temperature. A hollow cylinder of plastic silica is formed by heating a mass of sand round the central core through which the current is passed. The heating core being then withdrawn, the hollow cylinder is removed from the furnace and drawn into tubing. For moulded articles, such as a pipe, the hollow plastic cylinder is closed at one end by mechanical pressure, and into the other end is pressed a refractory nozzle for delivering compressed air; the softened mass is then placed in the mould, and compressed air applied to give the shape. More than 200 lbs. of the softened material can be worked. In the plastic condition the silica is extremely ductile, and can be drawn out like glass in lengths of 90 to 100 ft. Articles made as described have a rough external surface, but small laboratory ware is ground and finally glazed by melting the surface (electrically or by means of the oxyhydrogen blowpipe). Transparency is impaired by the air-bubbles associated with sand, which are very difficult to remove from the very viscous plastic silica. At 1200° C. devitrification commences in fused silica, so that it cannot be used for continuous work at higher temperatures. It is quite satisfactory for pyrometric measurements, etc.

Transparent Fused Silica.—Herschkowitsch first made fused silica optically homogeneous, and exhibited specimens in Paris in 1900. The great difficulty in accomplishing this arises from an allotropic transformation at 575° C., accompanied by sudden and considerable expansion, which causes repeated shivering, and after re-melting air bubbles are imprisoned. Herschkowitsch heated quartz crystals to about 550° C., then suddenly transferred the material to an electric furnace to melt quickly. Heraeus, in Germany, about the same time obtained transparent silica, though not so good. Bredel in 1905 obtained fused silica without bubbles by a process depending on the permeability of silica to hydrogen.

Transparent fused silica is now made in England.

Optical Properties.—The refractive index for fused silica is for the D line 1·4585, being lower than that for quartz, but its transparency for ultra-violet rays is less than that of quartz, though it is sufficiently transparent for all rays active on the ordinary photographic plate.

Specific Gravity of fused silica is 2·204 (about 2·07 when made from sand) as against 2·651 for quartz and 2·330 for cristobalite produced by transformation of quartz on heating.

Expansion is very irregular for all varieties of crystallized silica. Amorphous (fused) silica has extremely regular expansion, and extraordinarily low coefficient of expansion. Silica bricks which were quickly heated to 1650° C. showed very regular expansion, only one-third that of quartz, but this was not pure silica.

The mean coefficient of expansion of amorphous silica between 0° and 1000° is given by Le Chatelier as 70×10^{-8}, and by Holborn and Henning as 54×10^{-8}. The coefficient of expansion of this amorphous silica is sensibly constant at all temperatures. A crucible heated to bright redness can be plunged into cold water without risk.

LITERATURE.

(1) "La Silice et Les Silicates," H. Le Chatelier. 1914.

(2) "Dictionary of Applied Chemistry," edited by Thorpe, 5 vols. (Chiefly articles by L. J. Spencer and the late F. W. Rudler.)

(3) *Encyclopædia Britannica*, 11th edition. 1911. (Chiefly articles by L. J. Spencer, the late F. W. Rudler, and Dr. J. S. Flett.)

(4) *Encyclopædia Britannica*, 9th edition. (Article on "Mineralogy" by the late Dr. M. F. Heddle.)

(5) "The Data of Geo-Chemistry," F. W. Clarke, 3rd edition. 1916.

The small "Introduction to the Study of Minerals," sold at the British Museum of Natural History is a very useful little work.

SECTION II.—SILICATES

SILICATES, like silica itself, easily preserve the vitreous state, that is, the state of an amorphous solid, and some of them have never been obtained in the crystallized state, others only with difficulty. Many natural crystallized silicates cannot be reproduced in crystalline condition by melting mixtures containing their components in proper proportions, and then cooling, the products of such action being only glass.

The destruction, by heat, of the crystalline condition of a silicate does not always result in the immediate production of a homogeneous and transparent substance—that is, a glass. Felspar, for example, between 1100° and 1200° C. gives a white material resembling porcelain or devitrified glass in appearance. The felspar has really become decomposed, with formation of microscopic crystals of silica. At a higher temperature the material becomes completely vitreous and transparent, and remains so unless cooled too slowly. Felspar is employed in this way in the manufacture of *transparent pearls*.

The tendency of silicates to keep the vitreous state is increased by mixing several silicates together. Thus, glasses are mixtures of silica and silicates, and the tendency of such mixtures to crystallize is much less than that of silica or individual silicates. Silicates of sodium and magnesium can be easily crystallized separately, but a mixture of one with 20 per cent. of the other will not crystallize at all.

Complexity is a very common characteristic of silicates. Crystals which under the microscope seem absolutely homogeneous show very great variations of chemical composition. Felspars, for example, contain potassium, sodium, and calcium in very variable proportions, and there is also wide variation in the relation of the quantity of silica to the total of the basic oxides. So also the pyroxenes, whose chief components are silica and magnesia, include varying amounts of iron oxides, lime, and sometimes alumina and other metallic oxides. Micas are more complex still, though retaining the same crystalline form and optical properties, etc.

Mitscherlich's Law.—It was supposed that only chemical elements or definite compounds formed crystalline bodies. Amorphous substances in many cases were homogeneous mixtures of different kinds of matter, and in the case of solids like glass are considered to be *solid solutions.* But substances in the crystallized state were found to show distinct variations in the composition of precisely similar crystals. Mitscherlich concluded that identity of chemical constitution and identity of crystalline form were equally indispensable for the formation of crystals of variable composition, and enunciated the relationship in a law which bears his name. He called these mixtures of crystallized bodies *isomorphous mixtures.*

Without going further into this question of isomorphous mixtures, it may be stated that though the conditions of identity of crystalline form and of chemical constitution facilitate the formation of mixed crystals, they are not indispensable. It is better, therefore, in general to use the expression "mixed crystals" or solid solution rather than isomorphous mixture; solid solution includes both crystalline and amorphous mixtures, and has the advantage of including mixtures which obey certain common laws of chemical mechanics, irrespective of the presence or absence of crystallization.

Solid Solutions in Minerals.—These were first studied accurately by Tschermak, in the case of the felspars. Tschermak concluded that the felspars form a continuous series, ranging between the two extreme members, the felspar orthoclase or albite, $6SiO_2.Al_2O_3.K_2O$ or $6SiO_2.Al_2O_3.Na_2O$, and the felspar anorthite, $2SiO_2.Al_2O_3.CaO$, the chemical constitution of the latter being obviously quite different from that of the alkali felspar. This conception agrees with the fact that in chemical analyses of felspars an increase in lime is accompanied by a proportionate decrease in silica. Though at first strongly opposed in some quarters, Tschermak's views are now generally accepted.

Constitution of Mixed Silicates.—The existence of mixed crystals of different silicates greatly facilitates an understanding of the constitution of natural silicates of variable composition. They are really mixtures of a limited number of relatively simple compounds, and the problem of the constitution of silicates is the determination of the comparatively few compounds which when mixed together give rise to the extensive series of natural silicates.

As regards the felspars, the problem is simple, because all the intermediate stages are known between the two definite compounds albite and anorthite. To verify the accuracy of the constitution attributed to mixed crystals, it is enough to establish that the numerical relation between the quantities of silica, lime, and alkaline bases is in agreement with what the formulæ of the two extreme compounds (albite and anorthite) require. That is, for one molecular proportion of alumina (Al_2O_3) the molecular proportion of silica (SiO_2) will be equal to twice the number of molecular proportions of lime (CaO) plus six times the number of molecular proportions of alkaline bases (Na_2O, K_2O). This is illustrated by the following composition of a felspar given by Rammelsberg :

	Percentage Composition.	Molecular Composition.	Molecules for $1Al_2O_3$.
Silica	58·32	1·94	3·72
Alumina	26·52	0·52	1·00
Lime	8·18	0·29	0·56
Soda	6·16	0·17	0·33
Potash	2·36	0·05	0·10

The total of the lime, soda, and potash is 0·99 (practically 1·0) to 1 of alumina, as would be required for the formula of felspar ; the corresponding proportion of silica according to Tschermak's law is $0{\cdot}56 \times 2 + 0{\cdot}43 \times 6 = 3{\cdot}70$, practically identical with the 3·72.

With the pyroxenes the problem is more complex, mainly owing to the presence in some of them of alumina, and apparently the silicate of magnesia crystallizes with alumina in various proportions; this, however, is highly improbable, and has not been seriously suggested. It is admitted that the simple silicate of magnesia can crystallize with an alumino-silicate of magnesia (of rare occurrence in the separate condition as the mineral kornerupine) of the formula $SiO_2.Al_2O_3.MgO$, or with garnet, $3SiO_2.Al_2O_3.3MgO$. This hypothesis would readily explain the composition of aluminous pyroxene, but other hypotheses would be equally satisfactory for that purpose, and there is not a continuous series (as in the felspars) from pyroxene to kornerupine, a considerable gap occurring between the latter and the pyroxene minerals with most alumina.

In micas the problem is more complicated owing to the presence of water, but certain micas (as white mica or muscovite) have a relatively simple composition and correspond to definite compounds.

Other silicates—such as tourmaline, which occurs in very large homogeneous crystals—have very complicated and variable compositions.

Many silicates contain combined water, some of which by analogy with other salts (phosphates, bicarbonates, bisulphates, etc.) is regarded as water of constitution, and another portion, usually more weakly combined, is considered to be water of hydration. It is, however, not always easy to distinguish water of hydration from water of constitution. Many hydrated salts which lose their water of hydration on heating can take it up again. With hydrated silicates this happens only with a few alkaline and alkaline earthy silicates.

In some silicates which only lose their water at a very high temperature, as kaolinite and apophyllite, the water is considered as water of constitution.

Silicates as a rule do not easily enter into chemical reaction like ordinary soluble salts. Hydrofluoric acid destroys silicates and silica by forming silicon fluoride, which escapes in the form of a gas. Fusion with alkalies or alkaline carbonates also completely destroys silicates by converting them into silicates of the alkali metals.

Silicic Acids.—From analogies with organic compounds a normal silicic acid or *orthosilicic acid* is presumed to exist of the composition represented by the formula $Si(OH)_4$ or H_4SiO_4 or $SiO_2.2H_2O$. It has never been produced, but normal esters are known, like ethyl orthosilicate, $(C_2H_5)_4SiO_4$, and many metallic silicates corresponding to it occur, as olivine, Mg_2SiO_4 or $SiO_2.2MgO$, fayalite, Fe_2SiO_4 or $SiO_2.2FeO$.

Removal of a molecule of water from orthosilicic acid would leave metasilicic acid, $SiO(OH)_2$ or H_2SiO_3 or $SiO_2.H_2O$. In this case also the acid itself is unknown, but many silicates corresponding to it are known, as wollastonite, $CaSiO_3$ or $SiO_2.CaO$, enstatite, $MgSiO_3$ or $SiO_2.MgO$; no esters are known.

From these two acids, other acids are derived by polymerization and removal of water:

Diorthosilicic acid, $Si_2O(OH)_6$ or $H_6Si_2O_7$ or $2SiO_2.3H_2O$.
Dimetasilicic acid, $Si_2O_3(OH)_2$ or $H_2Si_2O_5$ or $2SiO_2.H_2O$.

In this way an indefinite series of acids could be derived theoretically.

Classification of Silicates.—For different purposes, silicates have been classified in various ways. Mineralogists and geologists classify minerals in accordance with their crystalline forms and their power of crystallizing together mixed in various proportions—that is, of forming solid solutions of mixed crystals. This property of silicates, of mixing thus, notwithstanding very great differences of composition, forming very fine and apparently more or less homogeneous crystals, is shared only with metallic alloys. Geologists lay special stress on the occurrence of the minerals in the same rocks. Thus in granites and similar rocks felspar is often associated with mica and kaolinite, so these three minerals are classed together by geologists.

Chemists have classified silicates in several distinct ways, but in most of them difficulties have arisen in connection with the silicates which contain alumina. Vernadsky proposed to overcome those difficulties by assuming the existence of complex alumino-silicic acids, comparable to the thoroughly investigated silico-tungstic and silico-molybdic acids. Many authorities have adopted this view, and it seems to afford the readiest means of showing the relationships existing among the silicates, based on the relation between the silica and alumina. This must, however, be combined with the mineralogist's classification based on crystalline forms, which brings together silicates having the property of forming mixed crystals, as this classification is certainly the best for the rock-forming minerals of the earth's crust.

Others who have sought to elucidate the constitution of silicates include F. W. Clarke, who made a keen study of the subject, and W. and D. Asch, who assumed the existence of closed rings consisting of six or five groups of SiO_2, or of half (Al_2O_3), connected with one another and with different elements and radicles in various ways. Unfortunately, though highly ingenious, these can only be regarded as speculative attempts to explain the facts, and considerations of space preclude further attention to them here.

Non-aluminous Silicates include dibasic silicates, monobasic silicates, and sundry silicates.

Dibasic non-aluminous Silicates or **Orthosilicates.**—The most important member of this group is *olivine*, consisting of magnesium orthosilicate, $SiO_2.2MgO$ or Mg_2SiO_4, with ferrous silicate and other isomorphous silicates of the same family, partly replacing the magnesium silicate; it constitutes an essential component of the most basic rocks. The name "olivine" was given in allusion to the olive-green colour often possessed by the mineral. The hardness is between 6 and 7, and the specific gravity about 3·3. The refractive power and double refraction are higher than in many other minerals. Olivine occurs usually as compact or granular masses, or as grains and blebs in certain basic igneous rocks, including basalt and dolerite, diabase, gabbro, peridotite, etc. It also occurs in meteorites.

Hot hydrochloric acid decomposes olivine, gelatinous silica being separated. Olivine rather readily changes under the influences of atmospheric and other natural agencies into serpentine, which is a hydrated magnesium silicate.

Transparent varieties of olivine are used in jewellery under the names of *chrysolite* and *peridot* (or peridote), but various green stones are incorrectly called olivine by jewellers. The name chrysolite is sometimes restricted to pale yellowish-green transparent olivine, and the name peridot to darker and decidedly green kinds. Being of inferior hardness the polished stone is readily abraded by wear. The final polishing of olivine is effected on a copper wheel moistened with sulphuric acid. Most of the peridot of commerce is from an island in the Red Sea. Transparent pebbles of olivine, suitable for cutting, are found in Arizona, Montana, and New Mexico, and from their shape and pitted surface they are called " Job's tears."

Olivine in its different varieties contains from about 5 to 30 per cent. of ferrous oxide, the proportion in the varieties used as gems being about 9 per cent. When ferrous oxide is less than 5 per cent. the colourless or yellowish mineral is *forsterite*, $SiO_2.2MgO$ or Mg_2SiO_4, which is found in many crystalline limestones. *Hyalosiderite* contains over 25 per cent. ferrous oxide. On the other hand, with ferrous oxide practically the only base present, the mineral is *fayalite*, $SiO_2.2FeO$ or Fe_2SiO_4, which is dark brown or black; it occurs in the Mourne Mountains and elsewhere in the North of Ireland, at Fayal in the Azores (whence the name), and also in crystalline iron slags.

When the basic constituents consist essentially of magnesia and lime in molecular proportions the rare mineral *monticellite*, $SiO_2.MgO.CaO$ or $CaMgSiO_4$, is formed; it occurs as yellowish-grey crystals and grains in limestone at Monte Somma (Vesuvius).

All the minerals mentioned are isomorphous with olivine.

Calcium Orthosilicate or **Dicalcium Silicate**, $SiO_2.2CaO$

or Ca_2SiO_4, is not known to occur in nature, but is of importance in connection with some industries, including hydraulic limes and cements, metallurgy (blast furnace slags), etc. It was obtained by Le Chatelier by heating a mixture of its components to nearly 1600° C. It has the property of falling into a white impalpable powder on cooling. The white powder as seen under the microscope consists of prismatic fragments. This spontaneous pulverization has been observed with all blast furnace slags sufficiently calcareous, and has been attributed to atmospheric moisture causing slaking of the slags by hydration, as happens with lime. Similarly pieces of burned cement, drawn hot from the kiln, are pulverized after a time. This transformation is accompanied by disengagement of heat. This dust has very little value as cement, and represents serious loss in manufacture. Le Chatelier has established that this property belongs to $SiO_2.2CaO$ only.

The mixture $SiO_2+1{\cdot}5CaO$ gives fragments not pulverized. Pulverization is diminished by replacing part of the lime of $SiO_2.2CaO$ by magnesia. Addition of alumina and iron oxide equally diminishes pulverization; it is thus that blast furnace slags often take several days to become disintegrated and sometimes give only a coarse sand very different from the impalpable powder produced by the pure silicate. The explanation is similar to that for dimorphous potassium sulphate.

Unlike the metasilicate, calcium orthosilicate is readily decomposed by ammonium salts, hot or cold, in concentrated or dilute solution. Acids act still more rapidly, but water neither directly hydrates nor decomposes it.

The true melting point of calcium orthosilicate is 2080° C.

In constructing cement kilns, cement already burned can be used as a refractory, which is softened and agglomerated during the first firing; in a second firing it no longer melts at the same temperature.

The melted silicate crystallizes at 2080°, giving a variety α, of specific gravity 3·27, hardness between 5 and 6, crystallized in the monoclinic system. It is stable down to 1410° C., being then transformed (with slow cooling) into a second variety β. By sudden cooling from a temperature above 1410° it can be preserved unchanged to ordinary temperature. Unlike the pulverulent variety of calcium orthosilicate obtained by slow cooling, it exhibits hydraulic properties. Certain very calcareous blast furnace slags are transformed into true cements by sudden cooling. Cements thus tempered do not fall into powder.

The superiority of Portland cements made in rotary kilns is due to the same cause. In the ordinary fixed kilns the cooling of the cement is always very slow, about a third of the cement falls into powder and it loses at the same time a similar proportion of its hydraulic properties. Cement from rotary kilns, going out from the hottest region of the kiln, gives no dust and preserves its full hydraulic properties.

The β variety of calcium orthosilicate, produced by cooling slowly below 1410° C., crystallizes in the orthorhombic system, but it cannot be preserved to ordinary temperature. At 675° C. the variety β is transformed into a third variety γ with great increase of volume, which causes pulverization of the whole mass. The specific gravity changes from 3·280 to 2·974, and the existence of three easy cleavages in the crystals facilitates complete fragmentation. Even slow cooling will not prevent this transformation, and pulverization can only be avoided—at least with pure silicate—by tempering from a temperature above 1410° C.

In the presence of certain foreign matters, calcium orthosilicate can apparently be preserved, even by slow cooling, under its hydraulic form α. Specimens of hydraulic lime and of cement are sometimes found closely approaching the composition of this silicate, and not pulverized. The cause was not at first recognized. Candlot showed that artificial cements could be prepared poor in lime, which normally would be completely pulverized on cooling, and would have no hydraulic properties, by adding to the mixture a certain quantity of calcium sulphate. All the natural cements which harden quickly, generally little charged in lime, include sulphate.

Disintegration on cooling melted mixtures of calcium silicates and lime begins with a lime content of 51 to 54 per cent., according to rapidity of cooling. The mixtures with less than 34 per cent. of lime remain vitreous; with between 34 and 47 per cent. of lime, fibres of pseudo-wollastonite are formed.

Tri-calcium Silicate.—Le Chatelier has recognized crystals closely approaching $SiO_2.3CaO$ in composition, without any iron, but only silica and lime, and they are more abundant as the iron and alumina in the cement is less. There is no free lime in them, for in presence of water these cements harden, and do not swell like lime, whereas with addition of only 0·5 per cent. of free lime a distinct swelling is produced.

It is possible it may be only a solid solution of lime and calcium orthosilicate with the lime reaching the proportion $3CaO$ to $1SiO_2$. It is, however, established that the essential constituent of all hydraulic products, is a mixture or compound of lime and silica, containing more than two molecules lime for one of silica, obviously three molecules.

Hydrated Silicate of Lime.—No definite hydrated silicate of lime (calcium silicate) has been obtained by the direct action of water on the anhydrous silicates. Calcium metasilicate does not hydrate, and the other calcium silicates when hydrated are at the same time decomposed, lime being liberated. The best process for obtaining hydrated silicate is the action of colloidal silica on lime-water, when a very bulky precipitate is obtained; 1 g. of this substance in suspension in water occupies about two litres. In presence of almost saturated lime-water, this silicate approaches two molecules of lime to one of silica; in presence of lime-water diluted with 100 volumes of water, the composition is practically one molecule of lime to one molecule of silica.

The hydration of tricalcium silicate in presence of water, which is the fundamental reaction in the hardening of hydraulic cements, is not a simple phenomenon of hydration, since in presence of water the silicates of lime cannot retain more than 1·8 molecule of lime for 1 of silica. In fact, it is easy to recognize in the hydration of cements the formation of hydrate of lime (calcium hydroxide) crystallized in hexagonal lamellæ large enough to be visible to the naked eye, if precautions have been taken to prevent access of atmospheric carbonic acid. The reaction is:

$$SiO_2.3CaO+4{\cdot}5H_2O=SiO_2.CaO.2{\cdot}5H_2O+2CaO.H_2O$$

Part of the hydrate is crystallized, and part fixed by capillary affinity on the hydrated silicate. This hydrated silicate is in crystals so thin that the strongest magnification of a microscope does not suffice to distinguish them. This expresses Le Chatelier's view of the course of the operation.

Willemite, $SiO_2.2ZnO$ or Zn_2SiO_4, is zinc orthosilicate, and has been worked as an ore of zinc in a few places. Willemite has a hardness of 5½, and specific gravity about 4. It is colourless, white, greenish-yellow, apple-green, light red, etc.

Electric Calamine or **Smithsonite** is a hydrated silicate of this class, which forms an ore of zinc.

Phenacite or **Phenakite,** $SiO_2.2BeO$ or Be_2SiO_4, is beryllium (or glucinum) orthosilicate. It is sometimes used as an ornamental stone, and is colourless or bright yellow, transparent or opaque. The hardness is 7½, and specific gravity about 2·98. At first sight it might be mistaken for quartz—hence the name, from Greek *phenax*, "a deceiver"—but the specific gravity is considerably higher. When well cut and polished, phenacite is so brilliant that it may sometimes be mistaken for diamond.

Apophyllite, which may be noticed briefly here, is a peculiar hydrated silicate of lime and potash (generally containing a little fluorine), with a lamellar structure. It is transparent or opaque, white or greyish, sometimes with a tinge of green, yellow, or red. The hardness is 4½ to 5, and specific gravity 2·33. Heated before the blow-pipe, it separates into thin lamellæ (whence the name). It occurs at several places in Scotland and Ireland, as well as in many foreign localities. It is occasionally used as a gemstone, and is then termed *fish-eye stone.*

MONOBASIC SILICATES OR METASILICATES.

Sodium Metasilicate, $SiO_2.Na_2O$, or Na_2SiO_3 in combination with excess of silica, forms the substance well known in commerce as *water-glass* or *soluble-glass,* which (when solid) is glassy in appearance, and dissolves fairly easily in hot water.

Sodium metasilicate is obtained by melting together molecular proportions of silica and sodium carbonate (60 to 106 parts by weight of approximately pure anhydrous materials). The compound melts at 1000° C., and crystallizes on cooling; it is very soluble in water, but often leaves some undissolved silica resulting from partial decomposition. These silicates are quite stable only in presence of excess of free alkali; by evaporation of this solution, various crystallized hydrated silicates are obtained, differing only by slight quantities of water. The metasilicate is the only known crystalline sodium silicate, the others being glassy bodies. Acids, even carbonic acid, decompose an aqueous solution, gelatinous silica being separated, a result which is also effected by alkaline carbonates and chlorides, especially ammonium chloride. Salts of alkaline earths give insoluble double silicates.

Commercial Sodium Silicate or **Soluble Glass** is obtained by melting one molecular proportion of sodium carbonate with from three to four molecular proportions of silica; it is vitreous on cooling. $Na_2O.4SiO_2$ contains about 79 per cent. of silica.

These alkaline glasses when powdered and treated with water dissolve completely when less than three molecules of silica are present to each molecule of soda; otherwise part of the silica generally remains undissolved.

On treating melted soluble glass—corresponding to $3SiO_2.Na_2O$ or thereabouts—with sufficient water to give a solution of specific gravity 1·16, the compound $2SiO_2.Na_2O$ (or Na_2SiO_5) is found in the solution, leaving a residue of insoluble silica. Concentration of the solution to a density of 1·53 results in precipitation of more silica, the definite silicate SiO_2Na_2O (or Na_2SiO_3) being left in solution.

The addition of ammonia to silicate of soda solution produces a precipitate which is redissolved on boiling.

Industrially, silicate of soda is prepared by wet and dry methods: (1) by melting silicious sand with sodium carbonate, (2) by substituting a mixture of sodium sulphate and carbon for the sodium carbonate in the preceding method, (3) by the action of water vapour on a strongly heated mixture of sand and sodium chloride, and (4) in solution directly by heating in an autoclave lye-washings of soda with ground flint or infusorial earth. The dry method (1 or 2 above) is carried out in a Siemens or similar gas-fired furnace heated at about 1100° C. for 5 to 8 hours. Continuous coal fires are also used for the same process, producing 1250 kilogs. of water-glass in 24 hours with 1500 kilogs. of coal. The fused product is run into an iron receptacle to cool. Typical mixtures for the charge are: 28 lb. calcined Na_2CO_3, or 60 lb. calcined sodium sulphate and 15–20 lb. coal, to 100 lb. powdered quartz; or 110 lb. sodium sulphate and 10 lb. coal, or 100 lb. of 50 per cent. sodium carbonate and 3 lb. coal to 180 lb. white sand; the coal assists reduction.

The fused product is broken up by a stone breaker or ground by suitable machinery, and dissolved in water by long boiling, best under pressure. The resulting solution, clarified by standing, is evaporated to 40° Bé. in iron pans, 100 lb. of the solid yielding about 300 lb. of this solution. Sulphide, when present, may be removed by adding some copper scale or litharge when preparing the solution.

The wet method is much used because of the greater uniformity of the product, and because it is obtained in solution at once. Silica (preferably infusorial earth) is digested with a solution of caustic soda of specific gravity 1·22–1·24 (not higher) under 3 or 4 atmospheres pressure. (The caustic soda is prepared by causticizing a solution of sodium carbonate with lime.) The liquid is heated by blowing in steam, and is kept agitated by machinery. Complete solution is effected in about 3 hours; it is indicated when, in a sample withdrawn, the suspended matter settles quickly and has a brick-red colour (Fe_2O_3), and the liquid has no more than a faint alkaline reaction. Stronger caustic soda solution holds the fine sand and ferric oxide in suspension so long that the liquid would not be properly clarified in several days.

The clarified liquid is drawn off and concentrated (usually to a specific gravity of about 1·7) in iron pans; 2·8 parts of infusorial earth are used to 1 part of caustic soda, the resulting solution having a specific gravity of about 1·18 (due to condensed steam). Powdered flints, quartz, etc., could be used, but would need longer digestion and under 7 to 8 atmospheres pressure.

A pure silicate may be made from the crude product by passing a current of carbon dioxide through the solution, filtering off the precipitated hydrated silica, and redissolving it in caustic soda.

The aqueous solution of specific gravity 1·7 usually contains 32 to 33 per cent. silica, 16 to 16½ per cent. soda, 2½ to 3 per cent. other sodium salts, and 48 to 49 per cent. water.

Commercial water-glass is usually brownish or greenish, but sometimes colourless. It is nearly insoluble in cold water, but dissolves completely (though slowly) in boiling water, the solubility decreasing with increase of silica. Silicates richer in alkali than $Na_2O.2{\cdot}25SiO_2$ are deliquescent and too poor in silica for ordinary uses of water-glass.

A water-glass known as "double soluble-glass" is prepared by using, instead of sodium carbonate, sodium and potassium carbonates in quantities to give about equal proportions of sodium and potassium silicates. It is said to give a thinner solution than either silicate of corresponding strength.

Potassium Silicates are prepared like sodium silicates by simply substituting potassium carbonate (or sulphate) for the sodium compound. They furnish, on cooling, an uncrystallizable glass, even more soluble and deliquescent than the corresponding sodium silicate. The preparation of hydrated silicates is more difficult than in the case of sodium silicates.

Potassium silicates are soluble in water up to four molecular proportions of silica to one of potash. Solution of soluble potash glass of specific gravity 1·25 includes 28 per cent. of the soluble-glass; when made into a paste with chalk or zinc oxide it gives cements which soon become very hard, adhering to glass and porcelain, and so are used for repairing broken domestic articles. A mixture of 2 parts of fluorspar and 1 part powdered glass made into a thick paste with water-glass is used as a cement for glass and china.

Solutions of soluble-glass give by desiccation a transparent vitreous mass which is firm and elastic without being deliquescent. Hence their employment for hardening the linen bandages on fractured limbs, for making very resistant junctions between pieces of chemical apparatus, after mixing with kaolin or asbestos, for coating paper labels on glass so as to resist washing with water; it is also sometimes used for rendering theatre decorations incombustible.

Sodium silicate is largely used, owing to its detergent properties, as an addition to soap (chiefly toilet soap), to which it imparts hardness and durability. Two typical analyses of such soaps show:

	Soda.	Silica.	Water.	Fatty Acids.
I ..	12	10	30·0	48·0
II ..	12·5	8·5	33·0	46·0

Water-glass is used as a fixing agent for pigments in the calico-printing and dyeing industries, and in printing indigo; also as a resist for certain colours, and in the finishing of cotton goods. It is a component of certain leadless enamels for glazing pans, etc., for domestic use, and is sometimes used in the basic linings of Bessemer converters. Other uses are for fixing fresco-painting, for rendering wood, linen, and paper, etc., non-inflammable, for bleaching jute, for preventing wood from rotting, and for preserving eggs. "Artificial vegetation" (so-called) results from dropping small pieces of certain salts (cobalt chloride, ferrous sulphate, and many others) into a solution of sodium silicate, when frond-like appearances are produced, due to the formation of insoluble metallic silicates.

Sodium silicate is much used for impregnating sandstone and other porous stones as a protection against weathering. The stone is first treated with a solution of water-glass, then with a solution of calcium chloride or aluminium sulphate, which causes the deposition of an insoluble silicate in the pores of the stone, greatly increasing its hardness and durability. The soluble sodium salt formed is removed by a subsequent washing.

Water-glass plays an important part in the manufacture of *artificial stone*. The following process is used at an English works for making chimney pots, mouldings, etc. The sand or sandstone used is ground wet and passed through a 40-mesh sieve; it is then thoroughly dried and mixed with enough water-glass solution in a revolving pan provided with scrapers and edge mixers to form a moist coherent mass. It is next pressed into moulds and before removal is saturated with a solution of calcium chloride (prepared by running hydrochloric acid over calcspar) drawn through by a vacuum equal to about 20 inches of mercury, calcium silicate being thus formed. The stones are transferred to a boiling tank heated by steam, and after the setting is completed are conveyed to washing tanks, in which they are subjected to the action of running water for a fortnight, to remove all the sodium chloride.

Sand of any origin and size of grain, gravel, clay calcined or uncalcined, granite fragments, etc., mixed with little more than 10 per cent. of highly silicious alkali silicate melt and pressed together, combine in superheated steam to considerable hardness, which does not differ materially from that of natural sandstone, clay, slate, etc. Of the artificial stone samples thus obtained, only those cemented with potassium silicate are durable in water, and when fixed for a time some potassium disilicate ($K_2Si_2O_5$) is given up, the alkali being thus gradually lost, but nothing is lost in hardness. Those obtained with sodium silicate melts, on the contrary, in spite of originally greater hardness, decompose completely in water within a short time.

Stereochromy, or the art of mural and monumental painting, is a special application of water-glass. A suitable ground of stone or cement is first coated with lime-mortar to form the under-ground and after it has hardened and become thoroughly dried, water-glass solution is allowed to soak well into the mortar. On this is laid the over-ground, consisting of similar constituents, except that the sand used should be of a good sharp type, and that a thin lye of calcium carbonate is added to the mixture. This over-ground of fine cement is levelled, and when dry it is well soaked with water-glass solution. After this has dried, the painting is done on the surface in water colours. The colours are finally fixed by treating with water-glass, preferably a mixed potash and soda water-glass. Colours used include zinc white, chrome and some other greens, chrome-red, several yellows and blues, iron oxide, etc. Such paintings are unaffected by rain, smoke, or temperature changes.

Calcium Metasilicate or monocalcium silicate, $CaSiO_3$ or $SiO_2.CaO$, is dimorphous. It occurs naturally (chiefly in crystalline limestones) as the mineral *wollastonite* or *tabular spar,* the latter name being in allusion to its frequent occurrence in flattened crystals. Its hardness is 5, and its specific gravity 2·85. It is formed during crystallization (devitrification) of certain acid blast furnace slags and ordinary glasses, chiefly bottle-glass; in these cases it is the second form, known as *pseudowollastonite,* which is produced. Vitreous calcium metasilicate is easily obtained by running the melted material into water. This glass devitrifies rapidly between 800° and 1000° C., forming a fibrous mass of crystals of wollastonite.

THE PYROXENES.

Wollastonite may be regarded as a member of the *pyroxene* family of minerals, which, excepting only felspars, are the commonest ingredients of nearly all igneous rocks, especially the basic rocks. The name pyroxene (from Greek *pur*, "fire," and *xenos*, "a stranger") was originally given by Haüy to black crystals of what is now called augite, occurring in lavas of Vesuvius and Etna, because of the mistaken assumption that they had got into the lavas accidentally. The name pyroxene is now used merely as a group name.

The pyroxenes crystallize in three different systems, but they all show distinct cleavages parallel to prism faces, with angles between them of about 87° (and 93°)—the corresponding cleavage angle of the amphiboles (another family of minerals showing great similarity in chemical composition and general character to the pyroxenes) being about 56° (and 124°). The composition and physical characters vary considerably in the different species.

Apart from wollastonite—and *rhodonite*, the corresponding manganese silicate, which, as the name implies, has a rose colour, and which is sometimes used for ornaments—the simplest member of the pyroxene group is *enstatite*, which is essentially magnesium metasilicate, $MgSiO_3$ or $SiO_2.MgO$, but it often contains a little iron partly replacing magnesium. With a larger proportion of iron it becomes *bronzite*, and with still more iron it passes into *hypersthene* or *paulite*. Enstatite (from Greek *enstates*, "an opponent," because it is nearly infusible before the blow-pipe) and olivine form the bulk of most meteoric stones. It is white, greenish, or brown, its hardness is about 5½, and its specific gravity about 3·2. Bronzite is a green or brown variety of enstatite containing about 5 to 14 per cent. of ferrous oxide, with a bronze-like lustre (hence the name) produced by separation of very fine films of iron oxide and hydroxide on the cleavage surfaces. Le Chatelier ascribes this metallic lustre to the presence of inclusions of titanium compounds. Hypersthene contains 15 to 30 per cent. of ferrous oxide, and has an even more pronounced metallic sheen than bronzite. Bronzite may be represented as $(Mg,Fe)SiO_3$, and hypersthene as $(Fe,Mg)SiO_3$. Bronzite is sometimes cut and polished for small ornaments, and hypersthene is more extensively used in the same way. An altered form of enstatite or bronzite called *bastite* or *schiller-spar* is hydrated and has nearly the composition of serpentine; it is brown or green, and has the same metallic sheen as bronzite, and can also be used as an ornamental stone.

The magnesium of enstatite may be more or less replaced by other metals, such as calcium, manganese, zinc, iron (ferrous or ferric), aluminium, sodium, lithium. Thus equal molecules of magnesia and lime give *diopside*, $2SiO_2.MgO.CaO$ or $CaMg(SiO_3)_2$, which is chemically a combination of enstatite and wollastonite, or intermediate between them. Clear crystals of diopside have been cut as gem-stones. Diopside is the magnesian silicate most easily reproduced artificially. It has been found in masses resulting from fusion of schists through fires in coal-mines, and also in devitrified masses of bottle glass.

Ægirite or **Acmite**, $4SiO_2.Fe_2O_3.Na_2O$ or $NaFe'''(SiO_3)_2$, is essentially a sodium and ferric meta-silicate, of a dark-brown or very dark-green colour; its hardness is 6 to 6½, and its specific gravity 3·55. **Jadeite** (sometimes called *jade*) has a similar composition to ægirite—$4SiO_2.Al_2O_3.Na_2O$ or $NaAl(SiO_3)_2$—but with aluminium replacing the iron, and is generally whitish or greenish unless it contains much iron. The specific gravity is 3·30–3·35, and it is more easily fusible and rather harder than nephrite (true jade), and colours flame yellow. It was used by the ancients like flint for making various carved objects, including hatchets and other implements. It is highly valued as an ornamental stone, especially by the Chinese.

Spodumene contains lithium instead of the sodium of jadeite, and is usually light grey to greenish; hardness nearly 7, and specific gravity about 3·3; a rare emerald-green variety called *hiddenite* from North Carolina has been brought into use as a precious stone. Ordinary spodumene is occasionally used as an ornamental stone.

Augite (Greek *auge*, "brightness") is the most important of all the pyroxenes. It appears to be an intimate mixture of two minerals, one corresponding to diopside in which part of the magnesium has been substituted by iron, and the other corresponding to the rare mineral kornerupine, $SiO_2.Al_2O_3.MgO$, but with more or less of the alumina and magnesia replaced by ferric and ferrous oxides respectively. The alumina and ferric oxide together amount to 10 to 15 per cent., with also 2 to 6 per cent. of alkalies. Augite is an important constituent of volcanic rocks and basalts, etc. It is opaque and black or greenish-black. The hardness is 5 to 6, and the specific gravity 3·33 to 3·36.

The Amphiboles.

The **amphiboles** (from Greek *amphibolos*, "ambiguous," because some of the minerals had been confounded with tourmaline), as previously mentioned, closely resemble the pyroxenes in their chemical composition and general characters, but differ in the inclination of their cleavage planes, the angles being 124° and 56°, whilst for pyroxenes they are 93° and 87°. These cleavage planes are indicated by cracks or striæ when minerals or rocks are examined with a lens, or in thin sections under the microscope. The amphiboles have lower specific gravities than the corresponding pyroxenes. As in the case of the pyroxenes, the magnesian silicates form isomorphous mixtures and mixed crystals of very variable composition, but *anthophyllite* is essentially magnesium and iron silicate, $SiO_2.(Mg,Fe)O$, or $(Mg,Fe)SiO_3$, and occurs as brownish fibrous or lamellar masses in mica schists.

Tremolite is a magnesium silicate in which one-fourth of the magnesium is replaced by calcium, the formula being $4SiO_2.3MgO.CaO$ or $Mg_3Ca(SiO_3)_4$. It is a variety of amphibole occurring in long, flat crystalline fibres, or in coarse columnar forms, and as it contains little or no iron the colour is white, grey, pale greenish or yellowish. The hardness is about 5½, and the specific gravity 2·9 (the lowest for an amphibole). **Actinolite** has the same composition as tremolite, except that part of the magnesium of the latter is replaced by iron. It forms radiating groups of acicular crystals, hence the name (Greek, *actis*, "a ray," and *lithos*, "a stone"); the colour is bright green or greyish green. The most important amphibole industrially is **asbestos** (a Greek word, meaning "unconsumable"), which is a pale—white, green, or brownish—fibrous variety of tremolite or actinolite. The fibres are sometimes so fine and flexible that they can be woven into cloth. **Amianthus**, a corruption of amiantus (Greek, *amiantos*, "undefiled"), is a term applied to the finer kinds of asbestos. Cloth made of this material was used in the process of cremation so that the ashes of the body might be kept separate from the fuel ashes. Incombustible wicks were also made of it. Napkins of asbestos were made by the ancients, and cleansed (when soiled) by being thrown into the fire. Other uses are in gas stoves, for lining iron safes, as a packing for steam pipes and boilers, and in Corsica asbestos has been mixed with clay to make a kind of pottery. Short-fibred asbestos is utilized for making paper and cardboard, etc., for heat-insulating purposes, etc. Chrysotile (fibrous serpentine) is often used as a substitute for asbestos. The South African blue asbestos or Cape asbestos is crocidolite.

Jade or **Nephrite**, $4SiO_2.CaO.3MgO$ or $CaMg_3(SiO_3)_4$, is essentially a silicate of magnesium and calcium, often regarded as a compact variety of tremolite or actinolite, according as it is whitish or greenish. It is very tough, has a hardness of about 6½, and specific gravity about 3. It is used like jadeite for ornaments, etc. The colour is mostly green, grey, or white. Like jadeite, it has always been highly prized by the Chinese, and also by the Maoris in New Zealand. Jade implements have been found widely distributed in Alaska and British Columbia. In some cases nephrite has been formed by alteration of jadeite.

Crocidolite is a combination of sodium ferric metasilicate and ferrous metasilicate, $NaFe'''(SiO_3)_2.Fe\ SiO_3$, and is a blue fibrous amphibole mineral resembling asbestos; it is sometimes called *blue asbestos* and *Cape asbestos* (in contradistinction to the Canadian chrysotile or "white asbestos").

It also occurs compact. It is worked industrially in South Africa, where it is used like asbestos. It undergoes alteration by removal of alkali and conversion of ferrous iron into ferric condition, accompanied by deposition of silica between the fibres or by their replacement by silica. The hard silicious mineral thus formed is a blue or golden-brown ornamental stone called "hawk's-eye" or "tiger-eye" respectively. The latter represents the final alteration product, and is often called crocidolite though it is practically only a mixture of quartz with brown oxide of iron. When polished, hawk's-eye or tiger-eye has a silky lustre. Each contains about 93 per cent. silica, most of the remainder being iron oxide (partly ferrous in the case of hawk's-eye).

Hornblende occupies the same position among the amphiboles as augite among the pyroxenes, and forms a common mineral component of many igneous and metamorphic rocks, especially those whose constituents have assumed entirely or mainly a crystalline structure. In most of its physical characters it closely resembles augite, but in common with the other amphiboles it differs as regards cleavage angles and certain optical properties. Hornblende is also generally similar to augite in chemical composition, sometimes containing over 20 per cent. of alumina and ferric oxide.

HYDRATED MAGNESIUM SILICATES.

These are very abundant in nature, but only in cryptocrystalline masses—never well-formed crystals. Hydrated silicates are not known corresponding to the two simple anhydrous magnesian silicates. The most important of the natural hydrated silicates of magnesia are talc, steatite, meerschaum, and serpentine.

Talc, $4SiO_2.3MgO.H_2O$ or $H_2Mg_3Si_4O_{12}$, is a soft, friable material, unctuous to the touch, and yields to the finger nail. It occurs sometimes in thin hexagonal plates, splitting into lamellæ. The colour is white, grey, green, brown, or red, the hardness 1 to 1½, and specific gravity about 2·7. Common talc coloured by a vegetable extract forms the rouge used by ladies as a cosmetic. Talc powder is used to make new boots and gloves slip on more easily, and in like manner it is used for reducing friction in machinery. Talc is also used by tailors as a kind of chalk for making lines on cloth. It was formerly used in porcelain manufacture to increase the translucency. Other uses for talc are, for the removal of grease from cloth and silk, as a soft polishing powder, as a coating for pills, in the manufacture of paper, and for adulterating soap.

Steatite or **Soapstone** is a massive variety of talc without foliated structure. It is easily cut, and when heated becomes very hard. It is worked into ornaments by the Chinese, and is made into gas burners, linings for stoves, electric insulators, and is also employed for other purposes, including most of those for which ordinary talc is used (see above).

Agalite is a trade name for a fibrous variety of talc. It is greenish-white, and is readily reduced to short fine fibres. It is nearly all used in the American paper trade, giving weight and body, and producing a fine gloss on the surface of the paper.

Meerschaum (meaning sea foam), $3SiO_2.2MgO.2H_2O$, is a soft white mineral sometimes found floating on the Black Sea. It has also been called sepiolite from a rather fanciful resemblance to the "bone" of the cuttle-fish (sepia). It is sometimes grey or creamy in tint, has a hardness of about 2 (being easily scratched by the finger-nail), and a specific gravity of about 1 to 1·28. Most of the commercial meerschaum comes from Asia Minor, where it is associated with magnesium carbonate (magnesite); both these minerals have resulted from the decomposition of serpentine. Meerschaum also occurs to a smaller extent in a number of other localities. It has sometimes been used instead of soap and fuller's earth, but its main use is for making tobacco-pipes and cigar-holders; these are first roughly shaped by scraping, and then polished with wax; the rudely-shaped articles are next sent to Vienna, etc., and are turned and carved, smoothed with glass-paper and Dutch rushes, heated in wax or stearine, and finally polished by means of bone-ash, etc.

In preparing substitutes for meerschaum, shavings, dust, chips, etc., of real meerschaum are worked up with freshly precipitated silicates of aluminium, calcium, magnesium, etc., as binders, three grades of ware being sorted out. Other materials used include celluloid, infusorial earth, casein, water-glass, zinc oxide, phosphates, glue, calcium sulphate, caustic potash, etc.

Serpentine is the most abundant of the hydrated silicates of magnesia, being mainly made up of a silicate having the composition $2SiO_2.3MgO.2H_2O$. **Chrysotile** is a fibrous variety resembling asbestos, and is often used in the same way as asbestos. Serpentine is mostly green, but generally shows several tints, arranged in dots and streaks, etc. The name serpentine is derived from a supposed resemblance to the markings on a serpent's skin. The hardness is 3 to 4, and specific gravity about 2·5 The purer translucent and massive serpentines are called *precious* or *noble serpentine.* Though a soft mineral (and easy to work) serpentine takes a good polish, and accordingly is in demand as an ornamental stone for making chimney-pieces, columns, table tops, vases, etc.; many such ornaments have been made in Cornwall, the Lizard district being famous for its serpentine deposits. Formerly much serpentine was sent to Bristol to be made into magnesium carbonate.

The hard compact variety of serpentine called *bowenite* (specific gravity 2·6) and other similar minerals are readily distinguished by their specific gravity from jadeite and nephrite (jade), the specific gravity of these latter being about 3·0 to 3·3.

The hydrated magnesium silicates are all derived from pyroxenes and olivine rocks, the alteration being produced by the combined action of water and carbonic acid (carbon dioxide), as is indicated by the magnesium carbonate and calcareous materials with which they are often associated.

ANHYDROUS SILICATES OF ALUMINA.

Only one anhydrous silicate of alumina of very definite composition is known to exist, and it corresponds to the formula $SiO_2.Al_2O_3$ or Al_2SiO_5. This occurs in nature as three (if not four) different minerals with different crystalline forms, andalusite, cyanite, or disthene, and sillimanite or fibrolite. **Andalusite** crystallizes in the orthorhombic system. Its specific gravity is 3·15, and hardness 7½. The colour is grey to brownish in opaque crystals, green or reddish-brown in transparent pebbles, and it is harder and more infusible than felspar. The pebbles make good gem-stones. Andalusite occurs chiefly in gneiss, mica-slate, and clay-slate.

Chiastolite is a variety of andalusite occurring in white or grey rhombic prisms, which enclose some of the slate or argillaceous schist in which the crystals are embedded, and the dark-coloured carbonaceous matter therein is arranged so that a cross section of a crystal shows a dark cross (at the middle) or a rectangle (at the ends) or some intermediate figure. Cut and polished crystals of chiastolite are worn as charms.

Cyanite, Kyanite, or **Disthene** crystallizes in the triclinic system. Its specific gravity is about 3·6. The colour is generally pale blue (whence the name cyanite or kyanite), but sometimes white, grey, greenish, yellowish, and black. The hardness varies, being 5 on the lateral planes and 7 on the extremities (whence the name disthene). It occurs chiefly in gneiss and mica-slate. Transparent blue specimens are sometimes used as gem-stones.

Sillimanite or **Fibrolite** crystallizes in the orthorhombic system, but in forms different from those of andalusite, which also differs in some of its optical properties. The specific gravity of sillimanite is almost 3·2, its hardness about 7, and its melting point 1850° C. The colour is greyish, greenish, or brown. The name fibrolite is sometimes restricted to a fibrous massive variety, consisting of a confused mass of very fine crystalline needles; this was used for making many tools in the Stone age. Sillimanite occurs in gneiss and schists. Sillimanite is produced by the action of heat (at about 1350° C.) on andalusite or cyanite, or even on kaolinite or kaolin, or other hydrated compounds of alumina and silica, and its formation is attended by a remarkable disengagement of heat. Vernadsky used this heat in producing sillimanite by fusion of its components (alumina and silica) on heating to about 1600° C. Le Chatelier gives the following approximate fusing points:—

Al_2O+SiO_2	1850° C.	$Al_2O_3+15SiO_2$	1600° C.
$Al_2O_3+2SiO_2$	1770°	$Al_2O_3+20SiO_2$	1670°
$Al_2O_3+10SiO_2$	1630°	SiO_2	1770°
Al_2O_3	2000°		

Ceramic products burned to high temperatures, especially refractory clay firebricks and hard porcelain contain long needles of sillimanite. Its hardness readily distinguishes sillimanite from anthophyllite (one of the amphiboles) for which it was formerly mistaken.

Topaz, $SiO_2.Al_2O_2F_2$ or $Al_2SiO_4F_2$, differs in composition from the three last minerals in having fluorine substituted for a portion of their oxygen. When topaz is heated very strongly, a mixture of sillimanite and alumina is produced. Topaz crystallizes in the rhombic system. The specific gravity is about 3·5, and the hardness is 8. Topaz is typically yellow, but also occurs colourless, blue, green, and pink. Most varieties of topaz are cut for gems. Topaz becomes electrified by moderate heating or friction, which distinguishes the colourless variety from the diamond, and topaz in general from many other minerals; the same treatment causes yellow varieties to become pink. Aquamarine (beryl) and chrysolite (olivine) are sometimes substituted for topaz, but are easily distinguished by differences in hardness, etc. Yellow quartz is sometimes called Spanish topaz, Scotch topaz, or occidental topaz; oriental topaz is yellow corundum (consisting almost exclusively of alumina). The colourless topaz exhibits far more lustre than rock crystal (quartz), and the purest specimens, when cut in facets like the diamond, rival the latter in lustre and brilliance.

Staurolite or **Staurotide** is another mineral conveniently placed here, though its composition is very variable; it contains, besides silica and alumina, sometimes a considerable amount of iron oxide, and nearly always 1·5 per cent. of water which can only be driven off at a red heat. Staurolite crystallizes in the rhombic system. Twin crystals in the form of a cross are common, whence the name (meaning cross stone, from Greek *stauros*, "a cross"). The specific gravity is about 3·6 and the hardness about 7. The colour is generally reddish-brown to brownish-black.

HYDRATED COMPOUNDS OF SILICA AND ALUMINA.

These are often grouped as salts of certain silicic acids—H_4SiO_4, $H_6Si_2O_7$, H_2SiO_3, $H_2Si_2O_5$, and $H_4Si_3O_8$. The present tendency is to consider them as alumino-silicic acids, as proposed by Vernadsky, whose hypothesis takes account of the important fact that the same proportions of silica and alumina are present in a number of silicates containing also oxides of other metals. Five alumino-silicic acids were enumerated, but Dr. J. W. Mellor recognizes six, as follows:—

Alumino-monosilicic acid (Allophanic type) ..	$Al_2O_3.SiO_2.nH_2O$
Alumino-disilicic acid (Kaolinic type)	$Al_2O_3.2SiO_2.nH_2O$
Alumino-trisilicic acid (Natrolitic type)	$Al_2O_3.3SiO_2.nH_2O$
Alumino-tetrasilicic acid (Pyrophyllitic type) ..	$Al_2O_3.4SiO_2.nH_2O$
Alumino-pentasilicic acid (Chabazitic type) ..	$Al_2O_3.5SiO_2.nH_2O$
Alumino-hexasilicic acid (Felspathic type) ..	$Al_2O_3.6SiO_2.nH_2O$

The value of n in the above formulæ in the case of several of the types may be one, two, or three; in other cases it does not assume all these values. In a few instances n equals four or five.

Hydrated compounds resembling kaolinite behave like acids, as by displacing carbon dioxide from carbonates, sulphur trioxide from sulphates, chlorine from chlorides, etc. Kaolinite and clays are therefore considered to be more or less impure alumino-silicic acids rather than hydrated aluminium silicates. Zeolites and related compounds are regarded as salts of alumino-silicic acids.

As there is no known means of determining the exact molecular weight of such compounds, the ordinary molecular proportion of alumina may be taken as the unit, but to avoid fractions of atomic weights of certain bodies, the formulæ so obtained may be multiplied so as to give whole numbers. Possibly it might be better to base the formulæ on six molecules of silica instead of one molecule of alumina, but in any case it remains hypothetical, and so it is of little importance which of these alternatives may be adopted.

Allophane, $SiO_2.Al_2O_3.5H_2O$ (or perhaps $4H_2O$), has a specific gravity of about 1·9, and hardness about 3. There is no distinct crystalline structure. It is the only compound containing both silica and alumina which is very easily attacked by dilute acids with separation of gelatinous silica. When impregnated with water, allophane becomes translucent, sometimes almost transparent. It occurs of various colours. A snow-white allophane finds industrial use in France by treatment with sulphuric acid in order to obtain aluminium sulphate free from iron. Allophane and certain other hydrated alumina silicates are sometimes considered to be mixtures of colloidal alumina and silica. Sillimanite may be the anhydride corresponding to allophane.

Pyrophyllite, $4SiO_2.Al_2O_3.H_2O$, or $H_2Al_2Si_4O_{12}$, is an alumino-tetrasilicic acid. Its specific gravity is about 2·9, and its hardness is 1–2. It occurs in lamellæ, and also massive, like talc, etc., which it greatly resembles. The colour is generally white or pale green. Several minerals contain the same proportions of silica and alumina, but different proportions of water. They are to be regarded as varieties of alumino-tetrasilicic acid. Pyrophyllite can be considered as the acid corresponding to leucite, jadeite, analcite, etc. Pyrophyllite is applied to many of the purposes for which talc is used. The compact variety of pyrophyllite is made to serve for slate pencils and tailors' chalk, and also for Chinese carvings. The name is derived from Greek *pur,* "fire," and *phullon,* "a leaf," in allusion to the effect of heat in causing separation of the laminæ in foliated varieties.

The Japanese mineral *roseki*, resembling pyrophyllite, is crushed, washed, and prepared much in the same way as China clay, and the product used for making firebricks, and to a smaller extent in making porcelain and paper.

Agalmatolite or **Pagodite** is a soft hydrated compound of silica with certain oxides, which the Chinese carve into images and ornaments. It really includes three different minerals: pyrophyllite, steatite, and pinite, the last named being an alteration product consisting largely of a finely scaly muscovite.

Fuller's Earth is essentially a hydrated compound of silica and alumina but the latter is often largely replaced by ferric oxide. It is soft and opaque, and has a greasy feel. The colour is generally greenish-brown, or greenish-grey, but sometimes blue. When placed in water, it becomes translucent, and falls into a pulpy powder without forming a paste as clay does. Fuller's earth was formerly largely used by cloth manufacturers for "fulling" woollen cloth, that is, cleansing it by absorbing oil and grease. Latterly it has been to a great extent replaced by other substances for that purpose. Fuller's earth occurs at Nutfield, near Reigate, Surrey, and other places in the south of England and in Scotland.

Fuller's earth is sometimes simply dried, but in other cases it is afterwards ground. In some cases it is made into a slurry with water, which carries off the finer material to settle in tanks, to be afterwards dried. It is now very much used in the filtration of mineral oils, and for removing the colour from certain vegetable oils, greases, and fats. It is also used for making certain soaps and cleaning preparations, for pigments, and for printing wallpapers.

Kaolinite, $2SiO_2.Al_2O_3.2H_2O$, and *halloysite,* with $3H_2O$ or $4H_2O$ instead of $2H_2O$, may be regarded as aluminodisilicic acids, and others are *rectorite* with $1H_2O$ and *newtonite* with $5H_2O$, the two latter being of rare occurrence. Halloysite is soft, and adheres to the tongue; it has a specific gravity of 2·0 to 2·2, and hardness 1 to 2. The colour of halloysite is generally white, with a slight bluish tinge, but may be grey, etc. When strongly heated it becomes much harder, and of a milk-white colour. According to J. W. Mellor the molecule of halloysite seems to break down below 200° C. It has not the plasticity of clay. Kaolin and clay consist mainly of kaolinite (which occurs very rarely in a pure state), and have the property of forming with water plastic pastes. Kaolin has been observed in some cases to be the decomposition product of granite and other rocks containing felspar.

Kaolin, or China clay, is generally very pure, and includes little or no iron in its composition, and very small amounts of potash and soda; it is used in the manufacture of porcelain and pottery, and for making aluminium sulphate. Its usual impurities comprise only quartz sand, felspar, and mica, all derived from the parent rock. The so-called rational analysis of kaolin (or of clay) is designed to ascertain the proportions of these substances mixed with the clay basis of the material. The method depends on the assumption that only the clay substance is attacked by sulphuric acid, and that the silica liberated from the clay can then be dissolved by a solution of soda. It has, however, been shown by J. W. Mellor that the assumption is erroneous, and better results can usually be obtained by calculation from the ultimate chemical analysis. Thus the alkalies (potash and soda) present are first calculated to felspar ($6SiO_2.Al_2O_3.K_2O$, and the corresponding sodium compound), the alumina not required for this is calculated as kaolinite ($Al_2O_3.2SiO_2.2H_2O$), and the remaining silica—not needed for either felspar or kaolin—is reckoned as quartz. Certain refinements may be introduced if desired, as calculating mica instead of felspar, etc.

Kaolin usually has a fine white colour, which it keeps after heating. Inferior qualities burn to a yellowish colour, and some have a similar tint in the raw state. Unlike most clays, kaolin is always practically free from titanium, and it has generally less than 1 per cent. of iron. Most of the impurities can be removed by washing with water. In ordinary washing by water, the particles of kaolin become coagulated through the presence of calcium salts, and form small clots which are soon deposited.

Clay is often coloured grey or black by the presence of more or less bituminous organic matters, which of course burn off when the clay is heated. The general presence in clays of 1 to 2 per cent. of titanium dioxide (often called titanic acid) produces on heating a yellowish grey coloration. The titanium greatly exaggerates the red coloration due to the presence of iron. Kaolins containing 1 per cent. of iron oxide burn nearly white, whereas clays with the same content in iron burn to rose-colour and nearly red. With a few hundredths of iron the coloration becomes blood-red.

Iron colours some clays green, and is then present in the state of ferric oxide, forming nontronite, $2SiO_2.Fe_2O_3.2H_2O$, which occurs in isomorphous admixture with kaolinite.

Many common clays are coloured reddish-brown by the ordinary hydrate of ferric oxide.

Yellow *ochres* include iron in the state of free hydrate, of which the formula is not known with certainty.

Certain clays present a blood-red coloration, as also does bauxite; they contain free anhydrous ferric oxide.

Some clays of a whitish grey colour contain a notable proportion of iron, but not uniformly distributed; the colour due to iron appears on burning.

Clays always include amounts (sometimes considerable) of quartz and mica, the quartz being much the more abundant. As they are constituents of all clays, they can hardly be regarded as impurities.

Ball Clay contains rather more iron than kaolin, and appreciably more alkali (potash and soda), and has a cream or ivory colour when burned; it also contains more free silica (quartz) than kaolin. It is accordingly less refractory than kaolin.

Fireclay is a refractory clay containing only a small percentage of alkali, but enough oxide of iron (usually accompanied by titanium) to give it a more pronounced colour after burning. Some fireclays are about as refractory as kaolin; others are less refractory than ball clay.

Impure clays are used for making common building materials—bricks and tiles. They contain as impurities notable quantities of iron oxide and carbonate of lime, the latter in particular rendering the material very fusible. Small crystals of gypsum (sulphate of lime or calcium sulphate) also often occur, which give rise to white spots at low temperatures, and to yellow spots at the temperature of fusion, the colour in the latter case being due to combined oxide of iron.

Calcareous clays are known as *marls*, but the same term is often applied locally to fireclays.

Common clays include impurities occurring in isolated fragments, giving rise to various inconveniences after burning. Flint gives white spots without disturbing the solidity; oxide of iron and pyrite produce holes bordered by a black ring of magnetic oxide, giving a very disagreeable appearance to the brick without reducing the strength; limestone, in grains larger than 1 mm., leaves fragments of free lime, the slaking of which makes the bricks or tiles split later.

Most of the brick earths collected superficially are not true clays; they are complex mixed residues proceeding from disintegration of surface rocks, in which true clay is present in small quantities or sometimes perhaps wholly absent.

MONOBASIC ALUMINO-DISILICATES.

The chief members of this group are lime-felspar and nephelite.

Anorthite or **Lime-felspar,** $2SiO_2.Al_2O_3.CaO$, is the most basic of the felspars. It has a hardness of 6 to 7, and a specific gravity of about 2·7. It occurs in white or colourless crystals, and is a constituent of many igneous rocks, but in itself has no industrial importance. It is classed with the felspar family because it can form mixed crystals with felspars in all proportions.

Nephelite or **Nepheline,** $2SiO_2.Al_2O_3.(Na,K)_2O$ or $(Na,K)Al(SiO_4)_2$. The proportion of sodium to potassium is about 3Na : K. In volcanic rocks, nephelite and leucite take the place of the felspars present in older rocks. Nephelite has a hardness of 5½ to 6, and specific gravity about 2·5. Two varieties of nephelite are met with. The glassy nephelite occurs in small colourless and transparent crystals and grains.

The other variety, *elæolite,* occurs either as large rough crystals or (more frequently) as irregular masses, which are opaque or at best translucent, and of a reddish, greenish, brownish, or grey colour. When of a good green or red tint and showing a kind of "cat's-eye" effect, elæolite is occasionally cut with a convex surface as a gem-stone. The closely related mineral *cancrinite* is also sometimes cut as a gem-stone when bright yellow; this is a hydrated mineral of the nephelite type as regards composition, but with calcium instead of potassium, and including some sodium carbonate; its hardness is 5½ to 6, its specific gravity about 2·5, and its colour white, grey, yellow, green, blue, or light reddish. Two other related minerals are *sodalite,* which includes some chloride, and *hauyne* (or *hauynite*), which includes some sulphate in its composition, both being frequently of a blue colour. Hauyne has sometimes been used as a gem-stone, and sodalite has been quarried in Canada as an ornamental stone under the trade names "Princess Blue" and "Alomite"; it takes a good polish, and looks somewhat like marble, but is harder (its hardness being 5½); its specific gravity is 2·3.

Lapis Lazuli, Azure Stone, or **Azure Spar,** sometimes called *lazulite,* is a valuable ornamental stone because of its fine blue colour. It was also prepared by grinding and levigation to give the pigment ultramarine, but for that purpose is now practically superseded by artificial ultramarine.

Lapis lazuli generally occurs in masses with a finely granular structure, and only rarely as distinct crystals. Its hardness is about 5½, and specific gravity about 4·4.

Some varieties are green, violet, red, or colourless. Generally lapis lazuli is opaque, with only slight translucency where the edges are thin. Its composition is variable, and microscopic investigation has shown that it is a rock rather than a mineral.

Most lapis lazuli consists of a blue mineral allied to sodalite and hauyne, called *lazurite*, which is a sodium and aluminium silicate containing sulphur, of the formula $Na_4(NaS_3Al)Al_2(SiO_4)_3$. Mixed with the lazurite is a varying proportion of hauyne, and along with the blue hauyne and lazurite are the pyroxene diopside (without iron), an amphibole (koksharovite), orthoclase and other felspars, a mica resembling muscovite, apatite (calcium phosphate with some fluoride and chloride), zircon, sphene (titanite), calcite, and pyrite, the latter being often altered to limonite. Lapis lazuli generally occurs in crystalline limestone.

Ultramarine was first made artificially on a large scale by Guimet in 1828, but was independently prepared on a small scale by Gmelin about the same time. It is also said to have been made by Kottig, at Meissen.

Artificial **Ultramarine Blue** is sold as a bright azure blue impalpable powder, which is insoluble in water, and contains the elements sodium, aluminium, silicon, sulphur, and oxygen. When heated with water in a sealed tube to 200°–300°, a colourless residue free from sulphur is left, and sodium sulphide is found in the solution.

Ultramarine is not changed by alkalies, but dilute acids readily decompose it, precipitating sulphur, and liberating sulphuretted hydrogen. The presence of a polysulphide seems to be indicated by these reactions, but ultramarine is not affected by concentrated and fuming sulphuric acid or certain other reagents which promptly decompose polysulphides and thiosulphates. Heating to redness causes ultramarine to lose its brilliancy and to become greenish, but there is no other noteworthy change; the blue colour therefore can hardly be attributed to free sulphur. When heated strongly in hydrogen, ultramarine blue becomes brownish yellow, and when heated to dull redness in chlorine it becomes violet. It possesses hydraulic properties, and so increases the binding power of cement.

By substitution of silver for sodium, a **Silver Ultramarine** of dark yellow colour is obtained, but no silver sulphide. By fusing this substance with metallic chlorides or iodides, the silver is replaced by another metal, potassium or lithium giving a blue ultramarine, barium yellowish-brown, zinc violet, etc.

Ultramarine blue crystallizes in the regular or cubic system, isomorphous with sodalite and hauyne.

Green Ultramarine is formed as an intermediate product in the manufacture of ultramarine blue, being converted into the latter by roasting with sulphur.

White Ultramarine is obtained when air is excluded during the roasting of the materials for making ultramarine; it is converted into blue ultramarine by heating in either oxygen, sulphur dioxide, or chlorine.

Red Ultramarine was obtained by Scheffer by heating the ordinary raw materials strongly in a muffle with free exposure to air; it contains more aluminium and less sodium than the blue variety. Red ultramarine has also been prepared by passing chlorine and steam over heated ultramarine blue.

Yellow Ultramarine is formed by heating the red variety in air at 360° for a short time.

Violet Ultramarine is obtained by first passing chlorine over ultramarine at 410°, before it has acquired its blue colour, when a green, and then a reddish yellow product is obtained, and then heating the latter with sodium hydroxide. It has also been prepared in several other ways. It has been manufactured from ultramarine blue by heating thin layers (on earthenware trays) at 280°, passing steam over it to remove sulphur, then lowering the temperature to 160°, and leading a mixture of steam and chlorine over it for three hours.

Commercial blue ultramarines are made in three different grades, containing different proportions of sulphur and silica.

The same proportions of raw materials and the same conditions do not give products of identical composition. Thus in ultramarine blue the silica was found to range from 38·9 to 42·7, the alumina from 24·0 to 29·5, the soda from 18·7 to 21·0, and the sulphur from 10·8 to 15·4. In the range of different coloured products, the component showing the greatest fluctuations is the sulphur, and next to that the soda. No very clear deductions can be drawn from the variations in composition, for in two similar blues the proportion of sulphur in one was exactly double that in the other, and the only other very marked difference was in the alumina, that with the lower sulphur containing about 20 per cent. more alumina; further the red, violet, and light blue (in that order) contained least soda.

The constitution of ultramarine is very uncertain.

Uses of Ultramarine.—As a body colour it is used in calico-printing, and wallpaper printing, for colouring writing paper and printing ink, preparing blue pigments, and blueing mottled soap. As a whitening agent, the great strength and purity of its blue tint correct the yellowness of writing and printing papers, cotton and linen goods, paper pulp, whitewash, soap, starch, and even sugar. It is largely used for making square and ball blue for laundry use.

Manufacture of Ultramarine.—Only blue and green sodium—sulphur—ultramarines are made on a large scale. The three chief commercial varieties of ultramarine blue are:—

Glauber Salt or **Sulphate Ultramarine,** which is the palest variety, and has a slight greenish tinge. It has small covering power, and is more readily attacked by alum than the others.

Soda Ultramarine low in Sulphur, which is a pure blue variety, darker and with more covering power than the preceding.

Soda Ultramarine rich in Sulphur and Silica, which is the darkest variety and has a reddish tinge. It has high covering power, and being the least affected by alum it is much used in paper blueing.

Ultramarine is formed by calcining a mixture of aluminium silicate and sodium sulphide. In practice China clay (sometimes with addition of silica) is used for the former, and the sodium sulphide is produced during the process of manufacture from either sodium carbonate or sodium sulphate, with sulphur and carbon. With the best materials, the following mixtures are said to give the best results for the three varieties of ultramarine blue mentioned :—

	China clay.	Soda.	Glauber salt.	Carbon.	Silica (kieselguhr).	Sulphur.
Pale ..	100	9	120	25	0	16
Medium	100	100	0	12	0	60
Dark ..	100	103	0	4	16	117

If the clay used varies in composition the proportions of clay and silica should be adjusted.

All ultramarine blues rich in silica are prepared by the *direct method* ; most of those poor in silica are prepared by the *indirect method*, in which ultramarine green forms an intermediate product. These are both dry processes, and though wet methods have been proposed, they have apparently not been adopted on a large scale.

Raw Materials.—*China clay* and certain foreign *pottery clays* are used, and always need levigation so that the clay may be in a very finely divided state ; it should also contain very little iron and manganese oxides. *Soda* is used in the form of the best soda ash. *Glauber salt* should be free from acid and iron, well calcined, and ground before use. *Sulphur* is generally used in the form of rod or stick (but powdered), as poorer forms of sulphur give dirty tints. *Carbon* should not have above 4 per cent. of moisture, the charcoal from pine trunks being preferred, of course finely powdered ; pitch, tar, resin, etc., sometimes replace charcoal ; when coal is used, it should be free from sand, stones, and pyrites. *Silica* is generally used as kieselguhr, but sometimes as quartz, the latter being calcined, quenched in water, dried, and ground. Silicious carbon (as charred rice husks, etc.) may be substituted for corresponding amounts of carbon and silica.

Direct Process.—The well-mixed raw materials are roasted with access of air. The series of operations include (in order) mixing, roasting, lixiviating, wet-grinding, levigating, pressing, drying, and sifting. The roasting should always take place as soon as the mixtures are prepared, and the great aim is to secure uniform heating of the intimately mixed materials. Different types of furnace are used according to the magnitude of the charge. The heat is raised slowly to a bright red, and held for 12 to 18 hours, or until the change is completed as indicated by a sample drawn. The yellowish grey mixture becomes in turn brown, green, and blue, the brown and green being both unstable. The roasting operation is followed by slow cooling (for a week or ten days). About one-third of the original weight is lost. Shaft furnaces are used for a large output, and a number of special furnaces have been patented.

A patented rapid direct process consists in heating quickly to 600°–700° a mixture of 35 parts China clay, 10 carbon, 40 sodium alum, 8 resin, and 7 sulphur, keeping at that temperature about three hours, then raising to 900°, stirring well for an hour to facilitate oxidation; powdered sodium chlorate is next added, the mixture is stirred for 15 minutes, and finally there is a further 30 minutes' heating; very fine ultramarine is said to be produced in this way.

In Curtius' patented continuous process, cast-iron retorts (similar to gas retorts) lined internally with fireproof cement, are used.

Indirect Process.—Here the successive stages are mixing, calcining for ultramarine green, crushing, roasting to ultramarine blue, and then lixiviating, etc., as in the direct process.

The ultramarine green is prepared in a *crucible* furnace or a *shaft* furnace, for smaller and larger quantities respectively.

The crushed ultramarine green is roasted with sulphur to convert it into blue. The operation is carried out largely in *cylindrical* or *retort furnaces*, and *muffle furnaces*. The sulphur may be added before the ultramarine green is heated, or added gradually during the heating. With green made from soda, 7 per cent. of the weight of the crude green is required, and with Glauber salt green 9 to 10 per cent.

In making the cheaper brands of ultramarine blue, the pure material is mixed with 10 to 50 per cent. of gypsum, which greatly reduces the brightness of certain kinds of ultramarine; this effect is minimized by incorporating a little glycerine or vaseline into the mixture.

When first manufactured, artificial ultramarine was about 16*s*. per lb., but this was soon reduced through competition.

In 1913 about 100 factories were at work, mostly in Germany and France, with a few in England, Austria, and the United States. The average price was less than 30*s*. per cwt. for an annual production which had reached to between 10,000 and 15,000 tons.

MICA.

Mica comprises a group of rock-forming minerals which occur frequently in nature. Some of them have commercial applications of considerable importance. The chief micas are muscovite, biotite, phlogopite, and lepidolite.

The general characters of the micas include a very easy cleavage in a single direction (so that they split up into very thin sheets), and the great flexibility, elasticity, and toughness of the cleavage flakes. They all crystallize in the monoclinic system. The colour varies from perfectly colourless and transparent (as in muscovite) through shades of yellow, green, red, and brown to black and opaque. The colourless and transparent varieties have a pearly lustre on the flat surfaces, whereas something approaching a metallic lustre is found on the others.

The hardness of mica is 2 to 3 (the smooth surfaces can be just scratched with the finger nail), and the specific gravity ranges from 2·7 to 3·1 in the different species.

They are poor conductors of heat and electricity, and therefore are useful for insulating purposes.

The chemical composition of micas exhibits great complexity. They are usually orthosilicates of aluminium with alkali metals, basic hydrogen, and in some species magnesium and iron (ferrous and ferric), and rarely other metals. Fluorine is often an essential constituent.

Micas may be subdivided into two groups: alkali micas, including muscovite, paragonite, and lepidolite; and ferro-magnesian micas, comprising biotite, phlogopite, and other less important varieties. In a rough way, these two groups answer to the light and dark-coloured micas respectively. Biotite is usually a deep black, but in thin films is dark brown, or yellow, or a hazy green.

The water present in micas—4 to 6 per cent. in muscovite, and scarcely as much in the others—can only be driven off at a high temperature, and is therefore water of constitution, not merely water of hydration.

Artificial crystals of micas have been observed in furnace slags, and in silicate fusions.

The composition of muscovite is perhaps most simply represented by the formula $H_2KAl_3(SiO_4)_3$. It may also be represented as $2SiO_2.Al_2O_3.\frac{1}{3}K_2O.\frac{2}{3}H_2O$, which shows it as differing from anorthite by the presence of potash and water instead of an equivalent amount of lime. A third way of representing the composition of muscovite is by the formula $6SiO_2.3Al_2O_3.K_2O.2H_2O$, which avoids fractions of molecules. In the rare mica paragonite, the potassium of muscovite is simply replaced by sodium. Lepidolite, which seems to be a metasilicate of alumina and lithia, has a more complex formula, including some fluorine.

Biotite is essentially an orthosilicate of alumina, magnesia, and potash, with some of the last-named replaced by water, and some of the magnesium and aluminium replaced by ferrous and ferric iron respectively. The composition of phlogopite is somewhat similar, but with little iron and relatively more magnesia, and some fluorine.

Muscovite is commonly known as white mica or potash mica. The large sheets of commercially valuable muscovite are only met with in very coarsely crystalline veins of pegmatite running through granite, gneiss, or mica schist. Such veins are worked for mica in India, the United States, and Brazil. In Canada and Ceylon the micas of commercial value are chiefly phlogopite. In India, "books" of mica have been obtained as much as 10 to 15 ft. across, and sheets 30 × 24 ins., without cracks or flaws.

Uses of Mica.—Its transparency, and its resistance to fire and to sudden temperature changes, has led to the extensive use of mica for the windows of stoves and lanterns, peep-holes of furnaces, and lamp chimneys and gas burners. It was formerly used for the windows of houses, and in the port holes of Russian war vessels. Spangles of mica are largely employed for decorative purposes. Powdered mica is very much used in the manufacture of wallpaper and other papers, for "frosting" toys and stage scenery, etc., for the manufacture of paints, as a lubricant, and for absorbing nitroglycerine and disinfectants. Sheets of mica are used for painting on, for making lantern slides, for supporting photographic films, for covering pictures and valuable documents. Other uses are for supports for preserved natural history specimens (in spirit), for mirrors of delicate scientific instruments, for vanes of anemometers, and for a variety of optical and other purposes. Its insulating properties as regards heat make it valuable for the packing and jackets of boilers and steam pipes. The resistance offered by mica to acids also finds useful application.

The most extensive application of mica is for electrical insulation. The smooth and flexible mica sheets are in great demand for electrical machinery, including armatures of dynamos. Small sheets of mica cemented by means of an insulating cement (as shellac) on paper or cloth finds various uses under the name of "micanite" or "micanite cloth."

Phlogopite seldom occurs in colourless, transparent sheets, so its use is nearly confined to electrical insulation.

The mica mined in Canada and Ceylon is mostly phlogopite, and is used chiefly for insulation. The colour of phlogopite is dark grey, smoky, or yellowish to brown-red—more usually yellowish-brown—the latter being known as amber mica in commerce, or "silver amber mica" in allusion to the frequent silvery lustre on the cleavage surfaces.

Muscovite is of more frequent occurrence, and of more general application. Other kinds of mica (than muscovite and phlogopite) are scarcely used commercially.

Mica has some value as a fertilizer because of the potash it contains.

A bright green variety of muscovite called *fuchsite*, or chrome-mica, has been used as an ornamental stone, and also *lepidolite* or lithia mica.

In dressing mica the "books" are split into sheets of suitable thickness, and the sheets trimmed with a sharp knife, shears, or guillotine. The dressed sheets are sorted according to size, transparency, colour, and freedom from spots and stains. Scrap mica is ground, or used for making micanite.

Chlorite is a hydrated silicate of magnesium and aluminium, with the two metals partly replaced by ferrous and ferric iron respectively. The ferrous oxide often amounts to 8 or 9 per cent., or even more. The colour is green, yellowish, or white, the hardness 1 to 1½, and specific gravity about 2·8. It is usually foliated and scaly; massive chlorite is amorphous and darker in colour. Earthy chlorite consists of small scaly particles with a somewhat greasy feel. The laminæ are flexible, but not elastic like those of mica. At Portsoy, in Banffshire, chlorite is mixed with serpentine, and is often cut and polished, notwithstanding its softness.

Tourmaline is a well-crystallized mineral of rather complex composition, roughly represented by $2SiO_2.Al_2O_3.MgO.0{\cdot}33B_2O_3$. It is a boro-silicate of aluminium, with variable amounts of ferrous oxide, magnesia, and alkalies. Tourmalines are closely associated with micas. The colour ranges from colourless to jet black, and may be any shade of red, yellow, green, or blue. Some crystals show different colours in different parts. The opposite ends of crystals are usually different. Crystals are often triangular, from suppression of alternate faces. The crystal faces are generally long and striated. The hardness is 7 to 7½, and specific gravity 2·94 to 3·3. Coloured transparent tourmalines are used for gems, especially *rubellite* or red tourmaline. Another use is in the tourmaline pincette, consisting of two mounted transparent plates of tourmaline cut parallel to the principal axis; it is used for the examination of crystal sections in convergent polarized light. Black tourmaline is called *schorl*, the red is *rubellite*, and the indigo blue is *indicolite*. Tourmaline is pyroelectric. It is usually found in granite, gneiss, mica slate, certain limestones and sandstones.

Axinite is a complex aluminium and calcium borosilicate, the aluminium being partly replaced by ferric iron, and the calcium by ferrous iron and manganese, etc. The name alludes to the wedge-shaped crystals. The colour is mostly clove-brown or violet, but different colours may be seen in different directions (as cinnamon-brown, violet blue, olive-green). The hardness is 6½ to 7, and the specific gravity 3·28. The hardness, colour, and transparency enable axinite to be used as a gem-stone, and it is sometimes so used, but it is easily fractured. It occurs in Cornwall and Devonshire, but the best crystals are found in Dauphiné (France).

Epidote is a basic calcium, aluminium, and iron orthosilicate, $6SiO_2.3(Al,Fe)_2O_3.4CaO.H_2O$, containing 5 to 17 per cent. of ferric oxide. It has the same ratio of silica to alumina (with ferric oxide) as in anorthite, etc. Some of its characters vary with the proportion of iron. The hardness is 6½, specific gravity 3·3 to 3·5, colour usually a yellowish-green, but sometimes green, grey, brown, or nearly black.

Epidote is an abundant rock-forming mineral, but is of secondary origin, having been formed during metamorphic changes in the rock. It occurs in many schists and crystalline limestones, and also results from the weathering of felspars, micas, garnets, pyroxenes, amphiboles, and other mineral constituents of igneous rocks.

Transparent dark-green crystals of epidote have sometimes been cut as gem-stones.

Zoisite closely resembles epidote, from which it differs chiefly in containing little or no iron. The same formula serves, if the Fe be omitted. Hardness 6½, and specific gravity about 3·3. The colour is mostly white or grey. A Norwegian rose-red variety, called *thulite*, has been used to some extent as an ornamental stone.

ALUMINO-TRISILICATES.

To this class belong *natrolite* and several other zeolites, and *garnets*. *Natrolite* is one of the commonest of the group of zeolites, and has a composition represented by $Na_2Al_2Si_3O_{10}.2H_2O$, or $3SiO_2.Al_2O_3.Na_2O.2H_2O$. It is usually found as radiating fibrous masses in the steam cavities of volcanic rocks. Hardness 5 to 5½, and specific gravity about 2·25; usually colourless or white, but sometimes greyish, yellowish, or reddish-brown. A German compact mass of radiating fibres with concentric yellow bands has sometimes been cut and polished for ornaments.

GARNETS.

The garnets are alumino-trisilicates of lime, magnesia, ferrous oxide, etc., which crystallize in the cubic system, and form isomorphous mixtures in which lime, magnesia, ferrous oxide or manganese oxide are mutually replaceable, and in which the alumina may be partly or wholly replaced by ferric or chromic oxide.

In ancient times garnets were used as beads, and for making engraved gems.

The general formulæ of garnets is $R_3''R_2'''(SiO_4)_3$, all being orthosilicates in which R''=Ca, Mg, Fe'', or Mn, or more than one of them, and R'''=Al, Fe''', or Cr.

Garnets may be grouped under six types as follows :—

1. Lime-alumina garnet, $Ca_3Al_2(SiO_4)_3$, or $3SiO_2,Al_2O_3.3CaO$, including *grossularite*, *essonite*, or *cinnamon stone*, etc.

2. Lime-iron garnet, $Ca_3Fe_2(SiO_4)_3$, or $3SiO_2.Fe_2O_3.CaO$, including *andradite*, etc.

3. Lime-chromium garnet, $Ca_3Cr_2(SiO_4)_3$. or $3SiO_2.Cr_2O_3.3CaO$, including *uwarowite*.

4. Magnesia-alumina garnet, $Mg_3Al_2(SiO_4)_3$, or $3SiO_2.Al_2O_3.3MgO$, or *pyrope*.

5. Iron-alumina garnet, $Fe_3Al_2(SiO_4)_3$, or $3SiO_2.Al_2O_3.3FeO$, including *almandine* (precious or noble garnet) or *carbuncle*.

6. Manganese-alumina garnet, $Mn_3Al_2(SiO_4)_3$, or $3SiO_2.Al_2O_3.3MnO$, including *spessartite*.

The types are usually modified by isomorphous replacements.

The hardness of garnets ranges from $6\frac{1}{2}$ to $7\frac{1}{2}$, and the specific gravity also varies from 3·4 (in lime-alumina garnets) to 4·3 (in iron-alumina garnets). The colour is often red, but may be brown, yellow, green, or even black or colourless.

Garnets are very widely distributed, occurring in crystalline schists, gneiss, granite, serpentine, and certain altered limestones, etc. Garnets used for industrial purposes are mostly found loose, weathered from the rock in which they occurred, but sometimes the rock is quarried for garnets.

Jewellers class garnets as Syriam or oriental (so-called from Syriam, the capital of Pegu), Bohemian, or Cingalese, according to relative fineness rather than place of origin. The most valued garnets are the Syriam, of violet-purple colour (unmixed with black), distinguished from oriental amethyst in being orange-tinted by candle-light. Bohemian garnet is generally of a dull poppy-red colour, with distinct hyacinth-orange when placed between the eye and the light. When of a full crimson colour, the stone is called pyrope or fire-garnet, which is valuable when large and perfect. Cut garnets hollowed out on the under side, and set with silver foil, have often been sold as rubies. *Melanite*, a black variety of andradite, was formerly used for mourning jewellery. *Spessartite* is a fine aurora-red garnet, cut for jewellery when clear enough, and somewhat resembles *cinnamon-stone.* A variety of *essonite* or cinnamon-stone known as romanzowite, from Finland, is often polished and sold as hyacinth, the true hyacinth being a reddish variety of zircon. A rose-red American garnet called *rhodolite* forms a fine gem-stone.

Besides being cut as gems, garnets are used for the bearings of pivots in watches. The coarser garnets have been used in powdered condition as abrasives, for which purpose it is superior to sand, though inferior to emery in hardness. The powder is also used for cutting gems. Garnet paper is largely used instead of sand-paper for smoothing woodwork, and for scouring leather in the boot trade.

ALUMINO-HEXASILICATES.

Felspars form a very important group of mineral silicates. *Orthoclase* or potash felspar, $6SiO_2.Al_2O_3.K_2O$, and *albite* or soda felspar, $6SiO_2.Al_2O_3.Na_2O$, are the most abundant silicates occurring in such old crystalline rocks as granite and gneiss. They give mixed crystals with the alumino-disilicate, *anorthite,* $2SiO_2.Al_2O_3.CaO$, which on this account is classed with the felspars. Albite is usually white, as the name implies. Orthoclase has a hardness of 6, and specific gravity about 2·56; the crystals show two well-marked cleavages at right angles, whereas the two corresponding cleavages in other felspars are not rectangular. Occasionally orthoclase is colourless, but it is generally white, red, yellow, grey, or green. Varieties of orthoclase include: (1) *Common felspar,* which is generally white or red; also the yellowish-grey or flesh-red *murchisonite;* (2) *adularia* and *ice-spar,* transparent or translucent, and nearly colourless, including *moonstone* with bluish opalescence; (3) *sanidine* or glassy felspar.

Microcline resembles orthoclase in composition, but is like the other felspars in crystallographic characters. The bright verdigris-green *Amazon stone* of Sutherland, etc., is a variety of microcline.

Albite or soda felspar forms mixed crystals with anorthite or lime-felspar in various proportions to form a number of intermediate felspars, the series in order including albite, *oligoclase, andesine, labradorite, bytownite,* and anorthite.

Several varieties of felspar have been cut as ornamental stones, including the moonstone (adularia), the green Amazon stone, and labradorite; *sunstone* or aventurine felspar (oligoclase) and occasionally colourless, transparent, glassy felspar have been used as gem-stones.

Orthoclase felspar is largely used for the manufacture of porcelain and stoneware, and for ceramic glazes. For these purposes it is crushed and ground before being mixed with the other ingredients. Other felspars have been similarly used to a small extent, especially albite. Orthoclase has also been used as a source of potassium compounds.

FELSPAR AND OTHER SILICATE MINERALS AS SOURCES OF POTASH.

The comparative abundance of certain natural silicates was bound sooner or later to excite speculation as to the possibility of extracting potash from them. As far back as 1857, F. O. Ward took out a patent (No. 3185, Dec. 30) for the preparation of potassium and sodium compounds from such materials as orthoclase, albite, pumice, lava, etc., by mixing them with calcium fluoride and lime (or calcium carbonate) and heating to bright redness; the alkali was extracted from the frit by lixiviation with boiling water. Since then many other methods have been devised for the purpose. It is known that simple wet grinding extracts some of the potash, but less than 0·5 per cent., and even enormous pressure does not enable water to decompose felspar readily. By digesting felspar and lime (in the proportion of 1 : 1·7) with water under a steam pressure of 10 to 15 atmospheres, W. H. Ross claims that about 90 per cent. of the potash is dissolved, the insoluble residue being suitable for making Portland cement. Generally speaking, it may be said that a process can only be successful commercially when the residue can be usefully employed.

Attempts have been made to solve the problem by the use of acids as well as alkaline substances; among others hydrofluosilicic acid followed by sulphuric acid, or dilute hydrofluoric acid. Above 100° hydrofluoric acid acts as a catalyst in presence of sulphuric acid, sulphates of aluminium and potassium being formed. Spiller proposed to produce the same sulphates by heating felspar with calcium fluoride and sulphuric acid, and a somewhat similar method has been patented by Hone, who collects the escaping silicon fluoride to form a fluosilicate, which in turn can be used in place of simple fluoride with more of the mineral.

Hart obtains sulphates (potash alum) by fusing orthoclase with the proper quantity of barium sulphate and coal, and acting on the powdered products with sulphuric acid.

Thompson claims that 80 to 90 per cent. of the potassium in felspar can be obtained as sulphate from such mixtures as 5 parts each of felspar and acid sodium sulphate, and 1·8 parts of sodium chloride, by heating to redness for 2 or 3 hours, grinding the cooled product, lixiviating, and crystallizing out.

Ashcroft treats crushed felspar, etc., with fused sodium chloride (or calcium chloride) excluding air and moisture, and thus obtains potassium chloride. In another patented process he heats felspars, etc., with excess of potassium chloride (or sulphate, or nitrate) to replace soda by potash, and washes out the soluble salts; the product is treated with lime (or magnesia, or both) and water or steam to get caustic potash and a residue suitable for making cement. In a more recent patent, Ashcroft treats felspar, etc., in a converter at about 800° to 1100° C. with chlorine gas while in a bath of fused sodium chloride (or potassium chloride, or both). Potassium chloride is separated by lixiviation.

Scholes fuses a mixture of felspar, etc., and alkali compounds. The product is ground, boiled with water, and treated with carbonic acid, when alkaline carbonate is left in solution, while hydrated silica and alumina, etc., are precipitated.

Potassium carbonate may thus be obtained by roasting mixtures of felspar, etc., with calcium compounds (carbonate, hydroxide, etc.), and blowing steam through the product, and in this case the residues might be made suitable for making Portland cement.

In other processes, felspar is fritted with salt, with or without lime, to give potassium chloride, and in some cases (where calcium compounds are used) the residue is suitable for making Portland cement. In some processes, the potash or potassium chloride is volatilized and collected by condensation; this is especially the case with cement kiln dusts and blast-furnace dusts. During the war, K. M. Chance and others averted a serious deficiency by combining extraction of potassium chloride with purification of blast-furnace gases; sodium chloride was added to the furnace charges to convert the potassium present into chloride.

In some instances the product is adapted for use for fertilizing purposes.

In Frazer, Holland, and Miller's process, felspar is mixed with potassium hydroxide or sodium hydroxide, and the dried mixture heated for an hour at 300° C., then treated with water and filtered. The alkali used may be recovered from the filtrate. The insoluble part, consisting of an artificial leucite, $KAl(SiO_3)_2$, is treated with hydrochloric acid to form potassium chloride, and the insoluble aluminium silicate is easily decomposed by sulphuric acid, producing aluminium sulphate.

ZEOLITES.

The **Zeolites** form a group of minerals which are hydrated compounds consisting of silica, alumina, and alkaline or alkaline earthy bases or both. They readily give up their water—though in some cases part of it is only lost at a red heat—and when they are heated by the blow-pipe flame its expulsion is accompanied by swelling (hence the name zeolite, from Greek *zein*, "to boil," and *lithos*, "a stone"). Their water can be replaced by ammonia, alcohol, etc. They are all readily soluble in hydrochloric acid, and generally with separation of gelatinous silica. In some cases the composition of the same mineral varies to a certain extent, which may be regarded as indicating the presence of isomorphous mixtures of different molecules. The zeolites are mostly glassy looking or white, but sometimes red, grey, or yellow. They generally occur as crystals (often with agate, calcite, etc.) lining cavities or fissures in basalts and other crystalline igneous rocks, as though they were deposited from percolating water, and they probably result from decomposition of nepheline, or sodalite, or felspars. They often form fine crystals, but rarely constitute rock-forming minerals.

Analcite, $NaAlSi_2O_6+H_2O$, or $4SiO_2.Al_2O_3.Na_2O+2H_2O$, has been found in the form of irregular grains as a primary constituent of certain basalts and other igneous rocks.

The hardness of zeolites ranges between $3\frac{1}{2}$ and $5\frac{1}{2}$, and the specific gravity between 2·0 and 2·4, but rather low.

When a partially dehydrated and opaque crystal is exposed to moist air, water is reabsorbed, and the crystal regains its transparency and optical characters.

Prehnite, $H_2Ca_2Al_2(SiO_4)_3$, or $3SiO_2.Al_2O_3.2CaO.H_2O$, unlike analcite and ordinary zeolites, loses its water (amounting to between 4 and 5 per cent.) only at a red heat. Its hardness is a little over 6, specific gravity about 2·9, and colour usually pale green. Prehnite is sometimes cut and polished for small ornaments, and then appears rather like chrysoprase.

Among the more important zeolites are *natrolite*, a sodium zeolite (already noticed among alumino-trisilicates, immediately before the garnets), and thomsonite, chabazite, heulandite, and stilbite, all calcium zeolites.

The natural zeolites themselves have no direct industrial importance, but an indefinite zeolitic component of soils, known as *geolyte*, seems to give valuable service to agriculture by retaining, in a form easily soluble, the potash and soda released when felspar is decomposed on weathering.

Artificial zeolites have been prepared, including a sodium aluminium silicate called *permutite*, which is now largely used for softening water, and in sugar refining.

WATER SOFTENING BY THE PERMUTITE PROCESS.

Though only introduced about ten years ago, by Dr. Gans of Berlin, this process is coming more and more into use for industrial purposes, because of its simplicity and effectiveness. It has the great advantages of not requiring the addition of chemicals, and of avoiding the accumulation of sludge or slime. The hard water (sometimes after partial softening) is simply passed through a bed of granulated permutite. It resembles a filtration process, but differs materially from ordinary filtration in the fact that no solid matter is deposited; indeed it is necessary for the water to be quite clear when subjected to this treatment.

Permutite (or sodium permutite) has a composition represented by the formula $2SiO_2.Al_2O_3.Na_2O.6H_2O$, or $Na_2Al_2Si_2O_8.6H_2O$, and is practically insoluble in water. It is now manufactured (at Brentford) from sodium silicate and sodium aluminate, and is supplied in the form of hard granules resembling coarse quartz. Permutite has also been made by melting together a mixture of sodium carbonate, China clay, or alumina, and silica (as quartz, etc.). During the passage through this material of water containing bicarbonate or sulphate of calcium or magnesium, or salts of iron or manganese, the sodium of the permutite is exchanged (whence the name) for the metal of the dissolved salt:—

$$Na_2Al_2Si_2O_8.6H_2O + CaH_2(CO_3)_2 = CaAl_2Si_2O_8.6H_2O + 2NaHCO_3$$
$$Na_2Al_2Si_2O_8.6H_2O + MgSO_4 = CaAl_2Si_2O_8.6H_2O + Na_2SO_4$$

All traces of calcium and magnesium are removed.

When the permutite ceases to be effective because of substitution of alkaline earthy metal for sodium, or rather before that stage is reached, its activity can be renewed—without removing the material—by washing it for about 10 hours with a 10 per cent. solution of sodium chloride (which must be free from magnesium chloride), the converse change taking place. According to the hardness of the water and the quantity of permutite in use, a certain quantity of the hard water is passed through before the permutite is regenerated. This avoids the risk of failure through going on too long. It has been found that water with much magnesium requires more permutite than water containing calcium salts. The calcium and magnesium chlorides formed during the regeneration are washed away.

Before the introduction of the salt solution, the permutite is agitated for a few minutes, and so loosened, by water being made to enter the bottom of the filtering bed, any air channels formed during the softening process being destroyed at the same time. The salt solution percolates slowly downwards through the permutite, and after about 10 hours the remaining salt solution is washed out; the softening process can then begin again.

When very hard water requires thorough softening, the ideal plan would be to remove the bulk of the hardening substances by means of one of the ordinary lime and soda softening contrivances, and the remaining hardness by the permutite method. In some works this plan has failed after some years, owing no doubt to the alkalinity (from free lime, sodium carbonate, or caustic soda) of the water from the lime and soda plant. Free lime passing through the permutite produces caustic soda, which will gradually dissolve it. Sodium carbonate passing through partly altered permutite will give rise to sodium permutite and calcium carbonate, the latter being sometimes carried onward to make the water look opalescent. Free alkali causes a further deposition of chalk from the residual hardness. As is well known, water even after filtering through wood-wool will on filtering through sand give a further deposit of chalk (with further softening of the water), the sand accelerating the softening action. Permutite acts like the sand, but perhaps more energetically because of its porosity.

In cases where permutite works successfully after previous softening, the water rests for some time before passing on to the permutite, thus permitting calcium carbonate to settle; such water even after two or three days' rest was still alkaline.

Attempts have been made to overcome this difficulty (of alkaline water) by taking advantage of the fact that calcium permutite can absorb free lime to the extent of the amount it originally contains, and on subsequently passing hard water in the opposite direction the additional lime becomes removed as chalk, which is washed away. This method works well for a while, but later free lime again passes through without being absorbed by the calcium permutite. As P. E. King points out (*Society of Dyers and Colourists*, xxxiv. No. 12; *Chemical News*, *118*, 16, 1919), even if this difficulty should be overcome, a plant consisting of three systems—lime and soda, then say calcium permutite, followed by sodium permutite—would probably cost more to work than a sodium permutite system operating directly on the crude hard water.

In like manner, for removing iron and manganese from water, Gans employs a *manganese-permutite*, consisting of silica, alumina, and a higher oxide of manganese, the material being regenerated as required by treatment with a solution of potassium or calcium permanganate. Manganese-permutite can also be applied for sterilizing water, the water being first treated with potassium permanganate to destroy the bacteria, and then filtered through manganese-permutite so that the filter may remove the manganese.

Calcium Permutite has been used for removing potash from molasses, the lime being afterwards substituted by soda on passing the solution through sodium-permutite.

The use of the permutite process for softening water has been found specially advantageous in the case of dye-works, bleacheries, etc.

According to E. Ramann and A. Spengel (*Zeits. anorg. Chem.*, *95*, 115, 1916), in the presence of small quantities of calcium purification is effected more rapidly by treating with 10 per cent. ammonium nitrate solution, followed by reconversion of the ammonium permutite into sodium permutite. The granular permutite is freed from small particles, and the reacting solution is run through it at the rate of 50 c.c. per hour. In this way complete equilibrium is obtained.

Sodium permutite yields the corresponding potassium permutite with potassium chloride and potassium sulphate, and the ammonium permutite is also completely converted into potassium permutite. The total concentration of the solution does not affect the composition of the final product, nor does the nature of the alkali in the original permutite.

OTHER ALUMINOSILICATES.

Beryl consists of silica, alumina, and oxide of beryllium (or glucinum, as it is sometimes called), and has the formula $Be_3Al_2Si_6O_{18}$. It usually occurs in long hexagonal prisms showing vertical striations. The colour of beryl may be blue, green, yellow, brown, or rarely pink, but it is sometimes colourless. The specific gravity is about 2·7, and the hardness 7½ to 8. The gem varieties are transparent, but coarse varieties of beryl may be opaque. It is found in several parts of Ireland, in the Grampians, and in Cornwall, as well as in numerous foreign localities. A large crystal found in the United States weighed more than 2½ tons. By weathering, beryl undergoes alteration, and may give rise to kaolin and mica.

Aquamarine is a variety of beryl of a pale-green or sky-blue colour, and is made into various articles of jewellery (brooches, necklaces, bracelets) and also into seals and intaglios (the latter having the engraved parts below the general level of the surface, as compared with cameos, in which the engraved parts stand out in relief). Weak colour and deficient lustre are the most noticeable defects of beryl, which is a stone easily worked without risk during cutting and polishing. The only stone for which the aquamarine is likely to be mistaken is the blue topaz, but the latter is harder, heavier, and more lustrous.

Emerald is a bright green transparent variety of beryl, the other characters being mostly the same. The colour is probably due to a little chromium present. The stone losos its colour when strongly heated.

"Oriental emerald" is a green corundum (consisting essentially of alumina, like the ruby and sapphire); "lithia emerald" is the rare mineral hiddenite (a variety of spodumene, already referred to among the pyroxenes); "Brazilian" emerald is green tourmaline; "evening emerald" is the peridot; "pyro-emerald" is fluor spar which phosphoresces with a green glow when heated; and "mother of emerald" is usually a green quartz, but possibly sometimes a green felspar.

Euclase is a rare mineral composed of silica, alumina, beryllium oxide, and water, represented by the formula $HBeAlSiO_5$ or $Be(AlOH)SiO_4$, or $2SiO_2.Al_2O_3.2BeO.H_2O$. The colour is generally pale blue or green, but sometimes colourless. Its hardness is 7½, and its specific gravity 3·1. It cleaves readily (whence the name), which makes it difficult to work, but it is sometimes cut as a gem-stone. The cut stone resembles aquamarine and topaz, but its specific gravity serves to distinguish it.

Idocrase or **Vesuvianite** consists of silica, alumina, and lime, with ferric oxide and magnesia partially replacing alumina and lime respectively. The hardness is 6½, and the specific gravity about 3·4. The colour is mostly brown or green, but sometimes yellow or blue, and rarely black. It is generally translucent, and sometimes nearly transparent. Italian specimens are cut as gems for rings and other ornaments at Naples and Turin, and often sold as hyacinth, chrysolite, etc. A compact massive variety from California called *californite* is extensively used as a gem-stone, and also for larger ornaments. This variety is somewhat translucent, takes a high polish, and is bright-green to yellowish-green and white, closely resembling jade in appearance.

Iolite, Cordierite, or **Dichroite** contains silica, alumina, magnesia, and ferrous oxide. Hardness 7 to 7½; specific gravity about 2·6. It is transparent or translucent, usually of a pale or dark-blue colour, but sometimes colourless, or grey, or brown, etc. It occurs at Dalkey (county Dublin) and Rathlin Island, Inverness-shire, and various places abroad. It is sometimes used as an ornamental stone. Small transparent rolled masses of a blue colour (but partly colourless) give the *Sapphire d'eau* of jewellers. Iolite is remarkable for the different colours it displays when looked through in different directions.

Pinite is an alkaline variety of altered iolite, in which magnesia and ferrous oxide are partly replaced by potash. It is slightly translucent or opaque, with hardness about 2½, and specific gravity about 2·8. It occurs in Cornwall and Aberdeenshire, and in many foreign localities.

Leucite, the composition of which is represented by $KAlSi_2O_6$, or $4SiO_2.Al_2O_3.K_2O$, is a whitish or greyish volcanic mineral. Hardness 5½ to 6, specific gravity about 2·49. It has been proposed as a source of potash, being easily decomposed by hydrochloric acid, like nephelite. Leucite has sometimes been termed *white garnet.*

OTHER SILICATES, ETC.

Glauconite is a green mineral, a hydrated silicate of iron and potassium. It occurs in green sands and muds now accumulating at many places on the sea bottom. The mud and sand are derived from the wear of the Continents, distributed by sea currents. The material consists mainly of quartz, felspar, mica, chlorite, and calcite, the latter probably derived from organisms. The colouring matter is believed to be glauconite, which is crystalline, but never occurs well crystallized, but only as clusters of extremely small particles which slightly affect polarized light. They often form rounded lumps, which in many cases are certainly internal casts of empty shells of Foraminifera. The mineral originated among the sand and mud on the sea bottom, and is so soft and friable that it cannot have been transported far by currents. Small rounded lumps of glauconite, common on the sands, but showing no indication of having filled the shells of Foraminifera, may have arisen by redeposition of broken-down casts. The green sands, when weathered, are brown or rusty coloured, the glauconite being oxidized to limonite.

Glauconite has been suggested as a source of potash, but British glauconites only contain 1 to 4 per cent. It may, however, act as a fertilizer by supplying potash to the soil.

Zircon, $SiO_2.ZrO_2$ or $ZrSiO_4$, zirconium orthosilicate, is transparent to opaque, and is mostly red, brown, yellow, green, or grey, but rarely white. The hardness is 7½, and specific gravity 4 to 4·8; it is transparent to opaque. When strongly heated it loses its colour without melting. Transparent varieties which are colourless or nearly so are called *jargon* or *jargoon*, and red transparent varieties constitute the *hyacinth* or *jacinth*, both of these being valuable gems. The colourless varieties are sometimes sold for diamonds, and the commercial hyacinth is often essonite, a variety of garnet. Zircon is often used in jewelling watches. Zircons are found in several localities in Scotland, and in Ireland, as well as in many places abroad.

Sphene or **Titanite,** $SiO_2.TiO_2.CaO$, or $CaSiTiO_5$, is a silicate and titanate of lime. It is transparent to opaque; and brown, grey, yellow, green, or black. The hardness is 5 to 5½, and specific gravity about 3·5. It occurs in various localities in Scotland, Ireland, England, and Wales, as well as abroad. It is occasionally used as an ornamental stone.

GRANITE AND OTHER IGNEOUS ROCKS.

By the term *igneous* is implied that the rock is or was at some time in a melted condition, and according to the circumstances attending the cooling they acquire certain distinctive characters which enable them to be classified.

Granite is a name commonly applied to almost any kind of rock which is crystalline, and is like true granite in appearance and properties. Strictly the name should be applied only to rocks which are completely crystalline in structure, contain a relatively large proportion of silica (approaching 70 per cent., or over), and consist essentially of quartz and felspar, generally along with relatively small amounts of mica, hornblende, augite (rarely), and other minerals.

True granites vary much in colour and appearance according to the condition of the felspars which constitute their most abundant minerals, and to the relative proportions of biotite, hornblende, and other dark-coloured silicates. The colour ranges from white or grey to pink, greenish, or yellow. Some granites contain large prominent crystals of felspar, as Shap granite and some Cornish granites. Other granites are more or less fine grained, and when larger crystals appear distributed through a fine-grained mass, the rock becomes a porphyry.

From the main body of the granite rock, veins or other branches often run out among the surrounding rocks, showing that the granite has forced its way upwards by splitting the strata among which it is placed. This conclusion is confirmed by the effects caused by the forcible passage of highly-heated material through the surrounding rocks. Thus limestones become recrystallized as marbles. As the result of long continued weathering, some granites form large blocks which may give rise to structures suggestive of cyclopean masonry, as in the tors of the west of England. Such differences depend on the arrangement of the joint cracks in the rock, since it is along these that weathering action proceeds.

Most granites are coarse grained enough to enable the chief mineral constituents to be distinguished by the unaided eye. The felspar appears pearly, usually white or pink, with smooth flat cleavage surfaces; quartz is generally transparent and glassy, with rough and irregular fracture surfaces; micas form light or dark flakes. Sometimes small dark green or black prisms (crystals) of hornblende can be detected, and sometimes reddish grains of garnet or of sphene. In tourmaline granites prisms of black schorl occur.

Very coarse granite is called *pegmatite,* a variety which commonly contains little besides felspar and quartz. It is much used on the Continent as an ingredient for hard porcelain.

Many varieties of granite have received distinctive names, and some rocks popularly regarded as granites should properly be referred to other types. This applies especially to rocks in which the amount of quartz is materially reduced, and consequently the total percentage of silica is less.

Thus *syenite* consists essentially of hornblende and orthoclase, and *diorite* mainly of hornblende and plagioclase felspar, often with some dark mica (biotite) ; the presence of these dark-coloured minerals makes the rock itself darker in colour. A variety of syenite containing elæolite (a form of nephelite) is called *elæolite syenite.*

Uses of Granite.—As building stone, for monumental stones, and for interior decorations. Also for curbing, paving, etc., and often as road metal. Also as ballast, rubble, etc.

Disintegration of Igneous Rocks.—As a result of weathering and other influences, the minerals of rocks gradually undergo decomposition, and among the first to suffer such changes are the felspars. The decomposition of rocks containing felspar sometimes results in the production of China clay. Partially decomposed granite is extensively used in the ceramic industry under the name of *Cornish stone* or *China stone.*

Lava is the name given to liquid products of volcanic activity. Geologically the term includes all matter derived from volcanoes, which flows or did flow in a molten condition. A lava is said to be acid when high in silica, and basic when comparatively low in silica. Basic lavas are generally darker and specifically heavier than acid lavas, as well as less viscous.

On exposure to the air, lava quickly solidifies on the surface to form a crust, which is often broken up by the continued flow of the liquid lava below, resulting in the formation of a rugged surface.

Each type of crystalline igneous rock has its corresponding lava, *rhyolite, trachyte,* and *andesite,* being the lavas corresponding to granite, syenite, and diorite respectively, whilst basic lavas are known as *basalts.*

Basalt, as previously indicated, is an igneous rock of a basic type, with low percentage of silica. It is of a dark colour, and weathers brown. Many basalts are very fine grained and compact, but most of them show larger crystals of olivine or augite, and often felspar in a finely crystalline ground mass. The olivine is green or yellowish, augite black, and felspar dark grey with smooth cleavage faces. Basaltic lavas are often spongy or pumiceous, especially near the surface ; the steam cavities in course of time become filled with secondary minerals (calcite, chlorite, zeolites, etc.). Many basaltic rocks show columnar jointing, famous examples of which occur at the Giant's Causeway. The olivine in basalt is often partly altered to serpentine.

In many basalts small crystals of felspar and augite form a matrix including more or less of a brown isotropic glass. Olivine is rarely an ingredient of the ground mass.

In the vitreous basalts, most of the rock is a dark brown glassy substance, generally containing black grains of magnetite with skeleton crystals of augite or felspar, spherulites, perlitic cracks, or steam vesicles. In other basaltic rocks called *dolerites* there is no glassy material, the whole mass being thoroughly crystallized.

Among other minerals sometimes present in basaltic rocks are black hornblende, hypersthene (usually replacing olivine), and black mica (biotite), nephelite, leucite, etc.

Basalt is largely used in the construction of permanent roads.

Volcanic Tuff or **Tufa** is a consolidated mass of volcanic ashes, composed of loose fragments ejected from volcanoes. It is occasionally used for building stone.

Certain volcanic ashes have been largely employed for making hydraulic mortars, and will be referred to more fully in the section on "Lime, Cement, and Mortar."

Obsidian or **Volcanic Glass** is a glassy volcanic rock of acid composition, containing over 70 per cent. of silica. Rhyolitic lavas often tend to be vitreous, and when the glassy material predominates to such an extent that the crystalline portions are insignificant, the lava becomes an obsidian on cooling. The chemical composition is essentially that of granite, and the difference in appearance, etc., is due to the conditions which prevailed during cooling. In the case of the obsidian solidification took place rapidly at the earth's surface, and under low pressure, whereas granite cooled very slowly at a considerable depth below the surface and under great pressure. Most obsidians have small crystals of felspar, quartz, biotite, or iron oxides.

The specific gravity of obsidian is low, about 2·4. In thin splinters or on sharp edges they are transparent, and the prevailing colours are black, grey, yellow, and brown. Obsidian often shows a banded structure, indicating want of homogeneity of the molten material.

Even when crystals seem to be absent, minute imperfect crystallizations called microlites are nearly always very numerous, as well as formations suggestive of skeleton crystals known as crystallites, and also spherulites, or small rounded (generally globular) bodies having a radiating fibrous structure. Sometimes contraction is associated with the formation of minute cracks, occasionally concentrically surrounding little globules of glass; in some cases the minute globules have a somewhat pearly lustre, and this kind of structure is termed perlitic.

Uses of Obsidian.—Arrow-heads, spear-heads, knives, mirrors, etc., of obsidian were much used by the ancient Mexicans and other primitive races. The ancient Greeks and Romans worked obsidian as a gem-stone. It is still sometimes cut and polished as an ornamental stone.

Similar glassy material of basic composition occurs, closely resembling obsidian, but it is rather rare.

When a glassy volcanic rock has a rather dull resinous (instead of bright vitreous) lustre it is termed *pitchstone.* Pitchstone contains 5 to 10 per cent. of combined water, and nearly always contains numerous minute crystallites and microlites.

Pumice is a very porous, froth-like volcanic glass. It cooled too quickly to be able to crystallize, and the sudden release of the dissolved vapours when it solidified caused it to swell up into a froth which at once became solid. If it had cooled under greater pressure an obsidian or volcanic glass would have been formed. Indeed, fragments of obsidian heated until they melt will suddenly change to pumice owing to escape of dissolved gases. Similar material can be formed artificially by blowing steam through molten slag or glass. When slag is cooled very suddenly by being tipped into the sea—as happens at the Whitehaven blast furnaces—it swells up into a pumice-like material so full of bubbles and so light that it will actually float on water. Pumice is often found as a layer above obsidian.

Uses of Pumice.—An inferior pumice is used for smoothing oil-cloth. Much pumice is used in fine powder (produced by crushing the rock) to form an ingredient of metal polishes and certain soaps. Pumice has also been used for polishing stones, glass, and ivory, and in a powdered state (called pounce) for preparing parchment. Powdered pumice has also been used for making bricks of very low specific gravity and good insulating quality.

Gneiss is a metamorphic rock, having undergone important changes from a previous condition. It may originate (like some other metamorphic rocks) from pre-existing sedimentary or igneous rocks. It consists mainly of quartz and felspar, with some mica, hornblende, or augite, and other minerals of less importance. All gneisses have a foliated (or parallel) structure—particularly as regards the mica or hornblende, etc.—and this is generally the chief distinction between gneiss and granite, as they have much the same mineralogical composition.

The felspars of gneiss are chiefly orthoclase and oligoclase. Muscovite and biotite may occur separately or together.

Many gneisses have been called by special names based on a prominent mineral component, as mica-gneiss, hornblende-gneiss, etc.

A *schist* consists of minerals arranged in alternating layers, the foliation being more distinct usually than in gneiss. The most common schist is *mica schist*, consisting essentially of quartz and mica. Among other schists occurring are chlorite schist, hornblende schist, etc.

The foliated structure renders schists and gneiss less suited than granitic rocks for constructional purposes or paving, etc.

Shale is mud or clay consolidated by pressure (therefore fine grained) and with a laminated structure. Consolidated silicious material may be similarly formed from finely divided sand-grains, and a similar shaly rock from minute grains of calcite. In either case, if clayey matter be also present, the resulting rock is best classed as an argillaceous sandstone or argillaceous limestone respectively.

The cohesion of shales results mainly from the pressure exerted during consolidation. Unlike sandstones they have little porosity. Their cleavage is very imperfect.

Some shales are used for making cement, and some for making bricks. Bituminous shales yield many mineral oils.

Slate is a metamorphosed clay or shale, and possesses a good cleavage, resulting from considerable pressure. This cleavage, known as slaty cleavage, does not often coincide with the original lamination (which corresponded with the stratification, when the slate was not of igneous origin). Most slates are of sedimentary origin, and their cleavage was the result of heavy pressure, or of lighter pressure long continued. In a few cases, slates have been formed by the consolidation of volcanic ashes, like the green slates of the Lake district.

In quarrying slates, ordinary blasting powder is generally used, but experience is necessary in order to separate large blocks without shattering the slate.

Channelling machines are often used. In France the method of tunnelling was introduced not long ago, and subject to frequent inspection of roof and walls, this marks a distinct advance.

Manufacture of Roofing Slates.—From the quarry large blocks of slate are taken to the blockmaker, who with the aid of a chisel, hammer, and gouge, divides the large blocks into slabs about 2 ft. by 1½ ft. by 2 ins. thick. These slabs are passed to the splitter, who by means of a long, broad-edged chisel, and a maul, reduces the slabs to a thickness of ⅛ to ¼ in. Finally, the dresser, or trimmer, trims all the slates with a long knife set vertically and hinged at one end, the other end being raised and lowered in turn, either by hand or by a treadle. For splitting, hand labour is still used, but at least one edge of the blocks is often sawn before passing them to the splitter.

The slates are made of various sizes.

Uses of Slate.—Some slates are adapted for blackboards, slates, slate pencils, billiard tables, mantels, and urinals. Others make good roofing slates.

Slates are also used for underpinnings of buildings, for floor tiles, risers and treads of stairs, and for flags. Slates may sometimes be used for inexpensive tablets and grave stones. The high transverse strength of thick slabs of slate fits them as substitutes for concrete beams in many places.

SLAGS.

Silica plays a very important part in many metallurgical operations in connection with the formation of **Slags,** which with rare exceptions are silicates, and are always anhydrous. These slags are generally the means for removing impurities from the ores.

Silica readily combines with most metallic oxides, when an intimate mixture of silica and the oxide is heated to the proper temperature, if the oxide itself is not reducible up to the temperature necessary for combination. Fusion may not be necessary for combination. When certain mixtures of silica and lime are strongly heated, there is no indication of fusion, but the action of hydrochloric acid on the product causes gelatinous silica to separate, which is evidence of the silica having been in combination.

The bases most frequently present in slags are lime, magnesia, ferrous oxide, manganese oxide, alumina, and potash in small amount. The bases and silica are derived from the ore, fuel ash, added flux, and to some extent from the furnace materials. It is only in blast furnaces that the ashes of the fuel pass into the slag.

Slags may consist of a single silicate, of a combination of silicates, or of a mixture of silicates, with or without foreign matter. Slags may be distinctly crystallized, and yet not have a perfectly definite constitution, just like many natural minerals. A South Staffordshire blast furnace slag occurring in translucent square prisms gave the following results on analysis :—

38·05	silica	0·40	manganese oxide
14·11	alumina	1·27	ferrous oxide
35·70	lime	1·85	potash
7·60	magnesia	0·82	calcium sulphide.

This nearly corresponds to $9SiO_2.2Al_2O_3.12RO$ (where RO includes all the oxides other than alumina and silica).

Slags occur crystallized, glassy, or non-crystalline and stone-like, and all these characters may appear in a single piece, in which case the glassy portion (produced by rapid cooling) will be on the outside. Slags bear a close resemblance to volcanic lavas. The more vitreous slags also resemble glass.

Slags may be more or less porous or vesicular. Occasionally slag from blast furnaces has been obtained in the form of spun glass, caught by the blast and blown into fine threads, exactly like the Pelé's hair or capillary volcanic glass from Hawaii.

A slag is generally tougher the more slowly it cools, just as devitrified glass (likewise resulting from slow cooling) is very tough in comparison with the original glass. Some slags are very brittle both in the glassy and crystallized state. When slags are required powdered it is evidently an advantage to cool them very quickly by letting them run into water.

Slags are ordinarily grey, blue, green, red, brown, or black, sometimes veined or marbled with different shades. The colour of a slag sometimes changes on crystallization, as in a blast-furnace slag which is blue when vitreous and yellowish-brown when crystallized, both colorations often appearing in the same specimen. So in bottle-glass works specimens may be found of brown crystallized nodular masses embedded in a blue glassy matrix. The blue colour of many slags was attributed by Kersten to an oxide of titanium. Fournet concluded that the blue coloration of slags and bottle-glass was due simply to a change in molecular arrangement. The blue colour of slags has also been doubtfully referred to vanadium and artificial ultramarine. A small amount of sulphide gives slag a very dark colour.

Some slags when melted are as liquid as water, but others are more or less viscous.

Scoriæ include the lighter, more porous, and imperfectly vitrified materials formed mainly during the puddling and refining of iron, and resembling volcanic scoriæ.

Powdered slags and scoriæ, when mixed with hydraulic limes, make good mortars. Powdered slag alone simply acts like sand, but certain varieties of slag when granulated acquire hydraulic properties, and are used for making slag cements.

Basic slags, when ground, make good fertilizers for soil, owing to the calcium phosphate they contain. They have been extensively used for this purpose.

Many years ago, a paper by Bashley Britten was prepared for a meeting of the Iron and Steel Institute at Leeds (see the *Institute Journal* for 1876, p. 453), in which he strongly advocated the application of blast furnace slags in the fresh molten condition, simply mixed with common ferruginous sand and sodium sulphate, for the manufacture of bottle-glass. Numerous specimens of such glass exhibited were described as being little if any darker than much of the glass used in the form of rough plates for skylights, and of practically the same tint as the glass in the great conservatories at Kew Gardens. The process was patented in 1876. The suggested process would be very economical not only as regards materials, but also by making use of the heat in the molten slag now commonly wasted. This is a problem well worth serious consideration at the present time.

FERROSILICON.

Ferrosilicon or iron silicide (sometimes also termed ferrosilicide) is next to ferro-manganese as regards the amount used in the metallurgy of iron and steel. Ferrosilicons are used as deoxidizers or for making silicon steels, and contain from 8 per cent. to nearly 95 per cent. silicon, the latter being produced in electric furnaces, and the former in English blast furnaces.

The structure of ferrosilicon is finely or coarsely crystalline according to the proportion of silicon; in high grade alloys with more than 50 per cent. of silicon there is no distinct crystallization, the fracture being fine and bluish. At least three iron-silicon compounds exist, Fe_2Si, $FeSi$, and $FeSi_2$; indications of the existence of Fe_2Si_3, Fe_3Si_2, and $FeSi_4$, have also been observed.

Ferrosilicon is made in the blast furnace or the electric furnace: (1) by reducing silica and iron ore with carbon, and (2) by reduction of silica with carbon, iron turnings being added. In the blast furnace, fuel consumption is high even in making 15 per cent. ferrosilicon, and the silicon in the ordinary grades ranges from 8 to 14 per cent. Iron oxide, silicious iron ore, and coke are used in blast-furnace charges, and the most suitable slags are high in alumina and low in lime. According to J. E. Johnson's U.S. pat. 1,231,260 (June 26, 1917) ferrosilicon containing about 50 per cent. silicon is produced by charging the blast furnace with ore and fuel, and supplying a blast containing substantially equal parts by weight of oxygen and nitrogen.

In the electric furnace, quartz or sand, and charcoal, coke, or coal are used, with either wrought iron, steel, or cast-iron turnings, or silicious iron ore. When turnings are used instead of iron ore, the power consumption is less, the operation of the furnace is steadier, and less slag is formed. Most of the phosphorus and sulphur appears in the metal, so the materials should be pure.

The liquid ferrosilicon is highly corrosive towards iron, and is therefore tapped out into sand or carbon-lined cars or sand moulds. The electric furnace product is in four grades, containing respectively 25 to 30 per cent., 45 to 55, 75 to 80, and 90 to 95 per cent. silicon. Alloys with 30 to 65 per cent. silicon are specially liable to disintegrate, hydrogen phosphide and arsenide being evolved, which makes them dangerous to handle. Alloys with less than 30 and more than 65 per cent. silicon are less liable to spontaneous disintegration.

Ferrosilicon is notable for the fact that carbon is excluded from the iron by increase of the silicon from about 4 per cent. From this point the carbon decreases to the stage in which the flakes of graphite, previously uninterrupted in the fracture of the iron, are separated by white spaces, and this action continues with increase of the silicon until eventually the graphite forms isolated black stars in a white field.

The lowering of the carbon, with increase of silicon, imparts to the iron a somewhat greasy look, and irons with 4 to 8 per cent. silicon are called "silvery irons," because of their abnormally light colour. These irons are made to some extent for use in foundries, to increase the silicon in mixtures in which it is low.

Silicon promotes soundness in ingot iron, but should not exceed 0·15 per cent. in metal which has to be rolled. About 0·30 per cent. silicon promotes soundness in steel castings. Carbon is probably detrimental to silicon steel. Usually the 25 to 30 per cent. ferrosilicon is used for making definite additions of silicon to the metal, and the 45 to 50 per cent. grade for deoxidation.

In foundry practice, if special strength is required, the silicon should not exceed about 2 per cent., and the phosphorus should be rather less than 1 per cent. But if softness and fluidity are specially desired, nearly twice these amounts may often be present without serious injury. Silicon steel sheets are used in electric dynamos and motors, for which their magnetic properties make them fit.

In L. Treuheit's Ger. pat. 292,682 (July 27, 1915) complete deoxidation of iron and steel alloys is effected by placing a mixture of equal weights of cryolite and ferrosilicon in the ladle and pouring the steel on it. The formation of blowholes and slag enclosures is said to be almost entirely eliminated.

According to N. G. Petinot's U.S. pat. 1,274,360 (July 30, 1918) molten ferrosilicon, containing 10 to 16 per cent. silicon, is poured into a shaped mould—first into a mixer if necessary—to make shaped castings.

For particular purposes certain special alloys are sometimes used.

Ferrosilicon-aluminium has about 45 per cent. silicon, 12 to 15 per cent. aluminium, the rest being iron. It is used as a deoxidizer for steel made in the electric furnace. It is more effective than aluminium, and is usually put in the ladle before teeming.

Ferrosilico-manganese is of two grades: 60 to 70 per cent. manganese, 20 to 25 silicon, and 3 to 4 iron; and 50 to 60 per cent. manganese, 22 to 25 silicon, and about 19 iron. In both the carbon is about 0·35 per cent., and sulphur and phosphorus low. These alloys are sometimes used for adding silicon and manganese to steel.

Ferrosilico-manganese-aluminium is made in two grades, containing respectively 18 to 20 or 9 to 11 silicon, 18 to 22 or 9 to 11 manganese, and 9 to 12 or 4·5 to 6 per cent. aluminium.

Ferrosilico-manganese-calcium-aluminium has an average composition of 50 to 55 per cent. manganese, 18 to

22 calcium, 12 to 15 iron, 4 to 5 aluminium, and about 1 per cent. carbon. This alloy is a deoxidizer and desulphurizer, used only with high-grade steels.

SILICON CARBIDE (CARBORUNDUM, ETC.).

Silicon Carbide (SiC) occurs in commerce in different forms.

Carborundum, a crystalline silicon carbide, was discovered accidentally by E. G. Acheson in 1891.

Amorphous Silicon Carbide is obtained as a greenish powder by heating a mixture of carbon and silica at about 1200°, but carborundum is only formed at a much higher temperature.

At Niagara, carborundum is made in electric furnaces built of firebricks (E. G. Acheson's Eng. pat. 17911, Oct. 7, 1892). The end walls (carrying the terminals, each consisting of 30 carbon rods 3 ins. in diameter) and the bed are permanent; the sides are built up with the charge, and taken down to get the product. The charge consists of 34·2 parts coke, 54·2 sand, 9·9 saw-dust, and 1·7 salt, the last named serving as a flux. The saw-dust increases the porosity, and so facilitates escape of the carbon monoxide formed—

$$SiO_2 + 3C = SiC + 2CO.$$

About six tons of the gas escapes during the run, and burns at the top of the furnace. The furnace is half filled with the mixed materials, so as not to touch the electrodes. A cylindrical core 21 ins. diameter, composed of coke fragments $\frac{1}{2}$ to $\frac{3}{4}$ in. diameter, is then built up between the electrodes. Over the core the mixed materials are carried to a height of 8 ft. The current passing through the coke forms many arcs which strongly heat the charge.

The alternating current at 2200 volts is transformed down to 165 volts, and the heavy current is regulated or interrupted by means of a large water rheostat. Within $1\frac{1}{2}$ hour of the start the initial E.M.F. of 165 volts is reduced (owing to diminished resistance) to 125 volts, and the current increases from 1700 to 6000 amperes, after which the conditions remain steady during the entire run of 36 hours.

In Tone's modified process (U.S. pat. 908,357, 1908), the charge is preheated by ordinary combustion (of gas or solid fuel). The process can be made continuous (U.S. pat. 937,119, 1909) by changing the position of the arc relatively to the charge.

The charge per furnace is about 30,000 lb., the core being about 3 per cent. of it. The electrical energy used is about 26,400 kilowatt-hours, and the product contains about 6700 lb. of carborundum, and 5000 lb. of amorphous silicon carbide.

The carborundum is dug out and transferred to a mechanical crusher with water, then digested for three days at 100° C. with a mixture of sulphuric acid and 2 parts of water, and afterwards washed with water. The finer material which is washed away is collected by settling for definite periods, and forms carborundum flours. The remaining material is dried in a kiln, then graded by means of screens.

In Weber's method (U.S. pat. 728,528, 1903) a mixture of kaolin and coke is heated in an electric furnace. The product is treated with water, which decomposes the aluminium carbide, leaving the carborundum.

By the action of vapours of carbon and silicon upon silicon carbide, a dense compact variety is produced, which is very hard, resistant to acids, and a good insulator (U.S. pat. 913,324).

In Potter and Westinghouse's method (U.S. pat. 875,673, 1907) a mixture of silicon monoxide and carbon is used.

Articles shaped in carbon may be converted into carborundum by very strongly heating in a bed of very finely powdered carborundum or of sand and carbon (Bölling, Eng. pat. 6693, 1905).

Commercial carborundum contains 62·70 per cent. silicon, 32·26 carbon, 0·93 alumina and ferric oxide, and 0·11 magnesia; after purification by heating in oxygen for one hour and treating with hot sulphuric and hydrofluoric acids, the composition was 69·10 silicon, 30·20 carbon, 0·46 alumina and ferric oxide, and 0·15 lime. Analysis of amorphous silicon carbide gave 65·42 silicon, 27·93 carbon, 5·09 alumina and ferric oxide, 0·38 lime, and 0·21 magnesia. For pure silicon carbide the theoretical figures are 70·00 silicon and 30·00 carbon.

Crystalline products resembling carborundum, bearing the trade names *crystolon*, *carbolon*, etc., are manufactured by other American firms. In addition to the United States, silicon carbide is also manufactured to a limited extent in Canada and in France.

Silfrax is another similar material suitable for electrical resistance material, as a refractory, and for chemical utensils. It has about 91 to 93 per cent. of silicon carbide, the rest being silica, carbon, iron, and aluminium.

Properties.—Carborundum takes the form of flattened hexagonal rhombohedra, with hardness 9½ (inferior only to the diamond), and specific gravity 3·23. Commercial carborundum is greenish-grey to yellow or blue, but when prepared in a pure state from pure materials it is colourless.

Carborundum is infusible, and not affected by heat below 2220°, at which temperature it is decomposed into silicon and graphitic carbon. Acids do not affect it, but fused alkalies attack it, forming a silicate and carbon.

Uses.—The chief use of carborundum is as an abrasive to replace emery; it is more expensive, but acts more effectively in one-third to one-fourth the time. Silicon carbide is the most satisfactory abrasive for brass, bronze, granite, marble, leather, wood, and other materials of lower tensile strength than malleable iron, but for steels in general, and high-speed steels in particular, an aluminous abrasive is better, in spite of its inferior hardness, because of its greater toughness. The powder of carborundum, etc., is used in glass cutting and grinding, and for polishing.

For making wheels, hones, and other useful objects, carborundum is mixed with moistened kaolin and felspar, moulded by hydraulic pressure, and fired in a kiln for 7 days. For special purposes other binding materials are used (as shellac). It is also used for making papers and cloths in the same way as emery and garnet powders. Binding material may be omitted if the carborundum be moulded with water, and the articles heated to 2500° F. in an oxidizing flame.

For drill heads, carborundum can be substituted for diamond, if fixed in a suitable metallic or ceramic matrix.

Silicon carbide is sometimes used instead of ferrosilicon as a source of silicon in the manufacture of steel. About 0·1 to 0·4 per cent. is placed in the ladle, and dissolves readily in the molten steel, ensuring the production of solid castings.

Amorphous silicon carbide, formerly a waste material, is used for making highly refractory bricks, and the retorts for distillation of zinc. It is good for lining electric-resistance furnaces or fuel-fired furnaces, in the latter even as a wash for firebrick walls. It is also useful as a cement for firebricks.

Powdered crystalline silicon carbide, moulded with glue or dextrin, etc., and heated in an electric furnace, gives strong bricks good for the roofs of electric steel furnaces; they must, however, be backed with firebricks or other heat-insulating material.

A refractory cement is made from 90 to 60 parts carborundum, 10 to 40 fireclay, 0 to 4 lime, and 20 to 50 water-glass solution (47 Bé.), the whole being mixed, dried, and powdered again.

By the action of silicon carbide on metallic oxides, many metallic silicides may be obtained. This reaction may be used for the preparation of special ternary or quaternary steels at a single operation.

As far back as 1898 (Eng. pat. 24,378) Engels applied mixtures of silica and carbon to surfaces of bricks, and to walls of furnaces, etc., and fused them by the electric arc to form fireproof and acid-proof coatings of silicon carbide.

Several related substances contain oxygen as well as silicon and carbon.

Siloxicon is produced by strongly heating a mixture of graphite and silica in an electric furnace. The typical formula is Si_2C_2O. When pressed in a mould, and heated to 2500° F. it is found to be self-bonding. It is infusible, but at very high temperatures is converted into carborundum.

Silundum, Si_4C_4O, is another electric furnace product, obtained by the action of silicon vapour or a mixture of silicon vapour and carbon monoxide on carbon at temperatures above 1300° to about 1800° C. Above 1800° it appears to be converted into carborundum, and above 2200° C. graphite is formed. Silundum has hardness 9, and specific gravity 2·9 to 3.

Fibrox (U.S. pat. 1094352, 1914; Eng. pat. 16299, July 15, 1913) is a silicon oxycarbide (approximating to SiCO), prepared by melting silicon with a catalytic agent, as calcium fluoride, in a muffle or crucible, carbon monoxide and carbon dioxide diffusing slowly through the containing vessel, and combining with the silicon to form a soft resilient fibrous material. The specific gravity of the fibres is 1·8 to 2·2, and the apparent specific gravity is 0·0025 to 0·0030 (more than 99 per cent. of the space being occupied by air). It is a very good heat insulator.

GEM CUTTING AND LAPIDARY'S WORK.

Gem carving by the ancients previous to the third or fourth century A.D. seems to have been done by hand with a sapphire point (fixed in a handle), or with a bow drill, but from that time the lapidary's wheel came into extensive use. In the fifth and sixth centuries B.C., and for two or three hundred years later, the Greek cutters preferred the sapphire point for their finest work, though they knew how to use discs and drills. The bow drill was a similar point fixed at the end of a stick, which could be rotated (alternately in opposite directions) by the up-and-down movement of a horizontal cross-bar attached at each end to a string wound around the stick. The two appliances were afterwards worked in combination. Later a hollow tube or drill was substituted for the point.

Until the fourteenth century, nearly all the gems were smoothly rounded, as opals and carbuncles are now, or in the form of beads drilled from opposite sides. The cutting into plane facets is quite modern, and is now almost always done with transparent stones.

Gem cutting and engraving in modern times have been done with the help of a rapidly rotating lathe, carrying a soft iron point or small disc of soft iron, with diamond dust and oil, the discs ranging from the size of a pin's head to $\frac{1}{4}$ in. in diameter. The S. S. White dental engine, first recommended for the purpose by G. F. Kunz, is even better than the lathe, because of the flexibility and sensitiveness of the machine. Applied in this way, diamond dust and oil will carve any stone other than diamond fairly easily.

Garnets have been cut from very early times. In more recent periods, the cutting of garnets has been mainly done in Bohemia, where the red pyrope or Bohemian garnet is abundant enough to maintain an industry in which were engaged about 500 miners, as many cutters, and something like 3000 dealers.

At Jeypore (where many natives taught by Europeans are employed) and other places in India, garnet cutting is also carried on extensively, but in this case mostly almandine (another variety of red garnet), which occurs in larger pieces than pyrope. The same variety occurs in large masses in what was German East Africa.

Ornamental flat plates and dishes, etc., have been carved out of single garnets. Ornamental dishes and other articles have also been carved out of rock crystal, agate, jasper, etc. As previously noted, the agate industry has been chiefly centred along the Nahe river in Germany.

For the grinding, large horizontal wheels are used, about 6 ft. in diameter and $1\frac{1}{2}$ ft. thick, which are worked by water-wheels. Some of these grindstones have faces with grooves of different sizes, so that round objects or convex surfaces can be ground easily and quickly. Thus an agate ball is made from a piece of about the right size (broken from a larger piece if necessary) and held in a semicircular groove until half of it is ground into shape; it is then turned over for the other half to be similarly ground. The polishing is done on wheels of wood with tripoli found locally; a wheel edge or drill is then used to produce any carving or ornamentation which may be desired. The same method is adopted for making spheres of quartz.

Similar work has been done on a large scale in the United States (at Sioux Falls, S. Dakota), including the production of polished table tops and columns of agatized wood. Fine lapidary work has also been done in Russia, chiefly at Ekaterinburg, Peterhof, and Kolyvan (Siberia), as well as in France, China, Japan, etc.

Cutting Precious Stones.—In the case of the more valuable stones it is often necessary to remove flaws from the natural stones in such a way as to reduce the size of the gem as little as possible. This is effected in diamonds by carefully cleaving or dividing them along certain natural planes of weakness, which run parallel to the octahedral faces of the crystals; an alternative modern process is sawing, which has been largely adopted. In sawing, the stone is set in a small metal vessel full of melted aluminium, with only the part to be cut exposed; it is then pressed firmly against the edge of a rapidly rotating metallic disc or thin wheel (4 or 5 ins. across) charged with diamond dust and oil. Then either by hand or by machinery two diamonds cemented at the ends of supports serving as handles are rubbed together until the required general shape is obtained. This preparation is not necessary for the softer stones before proceeding to cut the facets. The prepared diamonds are embedded in a fusible alloy at the end of a handle, leaving exposed only the part to be ground off, and two mounted diamonds are rubbed together until a facet is produced. The alloy is then softened, and the stone set again for grinding another facet, and so on until all are made. The final polishing is effected on horizontal iron wheels rotating very rapidly. Diamond dust (saved from previous operations) and oil are applied, and the facets are polished carefully one by one, either by hand or with the aid of mechanism.

The cutting of other precious stones is accomplished by similar wheels, etc., to those used for cutting diamonds, but the wheels are made of softer materials, and it is rarely necessary to use diamond dust to cover them. The discs or wheels used by ordinary lapidaries are generally of lead, tin, zinc, copper or hard wood, and the powders used include emery (mainly composed of alumina), tripoli or rottenstone (silica), tin putty (tin dioxide), and rouge (anhydrous ferric oxide), with carborundum, alundum, or other modern artificial abrasive in cases where something harder than emery is desirable. Most of the colourless precious stones are cut with a lead wheel and well moistened rottenstone, and this also gives the first polish to the silicious precious stones, like jasper, agate, etc.

Jewelled Bearings for Watches were used first about the beginning of the eighteenth century. Diamonds and sapphires are preferred, and are pierced either by diamond drills or by drills covered with diamond dust. Sapphires and rubies can be made artificially for the purpose at moderate rates.

LITERATURE.

Journal of the Society of Chemical Industry.
Transactions of the Ceramic Society.
"Glossary of Mineralogy," by H. W. Bristow.
For details of Carborundum and Carbide Manufacture see Rideal's "Electrometallurgy," this series, pp. 164–181.
Also the works mentioned at the end of Section I. (p. 45).

SECTION III.—LIME, MORTAR, AND CEMENT

Materials used in preparation of mortars, etc., fall into two chief classes :—

A. Those which set only in the air.

B. Those which set either in the air or under water; from their ability to set under water these are termed hydraulic cements, etc.

Under A are included :—

1. **Gypsum,** which has to be powdered by mechanical means, and sets by taking up into combination again water which previously has been removed.

2. **Lime,** which on addition of water crumbles to a powder consisting of calcium hydroxide (slaked lime), and when mixed with sand hardens to form ordinary mortar.

Under B are included :—

3. **Hydraulic Limes,** produced by the action of heat on limestones containing clay and silica; they fall to powder when slaked with water.

4. **Roman Cement,** produced by heating very calcareous marls below the sintering temperature, and grinding; this does not slake with water.

5. **Portland Cement,** produced by heating to the sintering point either suitable calcareous marls or artificial mixtures of lime and clay. It contains about 2 (1·8 to 2·2) parts of lime to 1 part of silica, alumina, and ferric oxide taken together, and its specific gravity exceeds 3.

6. **Hydraulic Mixtures,** natural or artificial materials which harden in conjunction with quicklime, but not by themselves. They include pozzuolana, trass, blast-furnace slags, etc.

7. **Pozzuolana Cements,** produced by very intimately mixing finely divided slaked lime with trass, etc.

8. **Mixed Cements,** prepared cements to which other substances have been added.

Lime or calcium oxide occurs abundantly in nature, chiefly in combination with carbon dioxide (carbonic acid) forming calcium carbonate, as limestone, marble, chalk, coral, calcite and Iceland spar, aragonite, and in the shells of many animals living in the sea, fresh-water, and land. As calcium phosphate it occurs in bones and also in apatite and other minerals, and as calcium sulphate in gypsum, etc.

The technical applications of calcium carbonate are numerous. Marble is used in building, Iceland spar is used for certain optical instruments, chalk is used for certain colours and drawing materials and for making marks on blackboards and slates. Other uses of calcium carbonate are in the manufacture of artificial mineral waters, etc., and for certain chemical manufactures. It is also largely used as a flux in metallurgical operations, especially in iron smelting.

Calcium carbonate is insoluble in pure water, but when carbon dioxide (carbonic acid) is dissolved in the water, the soluble calcium bicarbonate is formed. When the soluble bicarbonate loses half its carbonic acid by evaporation, the insoluble carbonate is deposited. This action in nature gives rise to the formation of stalactites and stalagmites, and in like manner calcareous sinter is deposited in limestone caverns, and on objects about wells whose water has passed through limestone. At a white heat, calcium carbonate is decomposed, carbon dioxide being given off, whilst quicklime (caustic lime, or calcium oxide) remains.

Lime-Burning.—The object of this process is to decompose the calcium carbonate of the limestone, and to drive off the liberated carbon dioxide and also the water associated with the stone. In ordinary practice a temperature of about 1000° C. is maintained—it should in any case not be outside the range 812° to 1100° C.—until all the escaping gas has been removed, for the action is reversible, the lime being capable of recombining with the carbon dioxide to form carbonate again. The natural draught of the kiln, assisted by the water vapour formed, serves to remove the carbon dioxide, which is generally wasted in British works, but elsewhere (as in the United States and Germany) it is collected for use. Water is sometimes added purposely. The water vapour not only helps to drive out the carbon dioxide but by diluting it promotes the decomposition of more limestone.

The time required for complete removal of carbon dioxide depends on the size, the specific gravity, and the moisture of the pieces of stone. It is better to break the limestone up rather small, but if this would be too expensive, the larger pieces are placed where they will be subjected to most heat. The large size of the stones usually necessitates a much higher temperature in a kiln than is actually required for the decomposition.

In the case of limestones containing clay the latter gives off additional water vapour, and removal of the carbon dioxide is also promoted by the tendency of the lime to combine with silica and alumina, as well as with any ferric oxide present.

There are two classes of lime kilns, *intermittent kilns*, in which the calcined material is withdrawn after cooling, and a fresh charge put in, and *continuous kilns*, in which the raw material is fed in at the top as required, and the lime is removed at the bottom. Continuous kilns include stationary or vertical kilns, and rotary kilns.

Vertical (or stationary) kilns may have a mixed feed (in what are called *running kilns*) or separate feed.

Among intermittent kilns the simplest is a *flare kiln*, built of the limestone itself, forming an arch or arches at the bottom, under which the fuel (mostly wood or peat) is burned. Such kilns are often built of brick or stone-work with an inner lining of firebricks.

Vertical continuous kilns are taller than flare kilns, and when the limestone and fuel are introduced in alternate layers the kilns are called *running kilns*. These, when properly managed, are more economical than the preceding, but the resulting lime is contaminated with the ashes of the fuel. Special forms of running kilns include the Aalborg kiln, Dietzsch kiln, etc., which have distinct pre-heating, burning, and cooling zones.

Vertical continuous kilns with separate feed are much used in America and abroad. The fuel is burned in fireplaces separate from the kiln proper. The Rüdersdorf kiln has a high central shaft. Rumford's kiln is a modified form. Another type is Schmatolla's kiln, in which generators (or producers) are used instead of fireplaces. In the Hoffmann ring kiln, which as a whole is continuous, each of the chambers is practically an intermittent kiln. It is very economical as regards fuel, but is costly in labour. It is chiefly used on the Continent.

Rotary Kilns are sometimes used for the burning of lime, the temperature being much lower than for cement.

Properties of Lime.—When a limestone is nearly pure calcium carbonate, the lime obtained from it is called a "fat" or "rich" lime. When the limestone contains notable proportions of magnesium carbonate, the lime produced from it forms with water a thin "milk of lime," and is said to be "lean" or "poor." Lime is distinctly poor when it has 10 per cent. of magnesia, and 25 to 30 per cent. renders it almost useless. Fat lime when slaked with water expands, gives off much hot vapour, and quickly falls to powder. Lean lime falls to powder within a few minutes, but there is little heat, and scarcely any expansion. Some pieces of limestone are only burned on the surface, and contain unaltered limestone within, whilst other pieces are overburned. Overburning may cause superficial sintering of the little silica and alumina present, a coating of silicate thus preventing the lime within from combining with water to form a cream, or a half-burned lime may be formed by a sudden strong heating, in which only part of the carbonate is decomposed.

Pure quicklime is white and amorphous, but it can be obtained in a crystalline form; the specific gravity of the latter is 3·25, and that of the amorphous lime 3·15. Lime melts only at a very high temperature, but it is strongly basic, and when highly heated it combines with silica or alumina. Water added to quicklime—1 volume to about 3 volumes, or about 32 parts to 100 parts (18 to 56) by weight—causes it to slake very violently, with great evolution of heat. Any excess of water is driven off as vapour. The slaked lime is a soft white powder, which occupies more than three times the volume of the original quicklime, and consists of calcium hydroxide, CaH_2O_2. If less water be added, a sandy powder is obtained, which has little technical value. Hence lime should not be left in damp places. For building purposes, after slaking the lime with about one-third its weight of water, an equal quantity of water is added to form a thin cream. Further addition of water to this cream gives milk of lime or lime-water, a saturated solution of the hydroxide. The solubility varies according to the mode of preparing the lime or calcium hydroxide.

Slaked lime can be heated to 250° or 300° C. without losing any water, but at 530° to 540° C. water is driven off and quicklime left. Lime-water is a strongly alkaline solution, which turns red litmus blue, and readily absorbs carbon dioxide to form calcium carbonate. Lime exposed to the air gradually becomes slaked by absorbing moisture, part of it being converted into carbonate. Air-slaked lime has a composition nearly represented by $CaCO_3.CaH_2O_2$.

Calcium hydroxide mixed with a little water forms a paste which, when left exposed to the air, dries and shrinks, leaving a not very hard porous mass. The paste slowly takes up carbon dioxide from the air, gradually forming a harder crust of calcium carbonate, but this action does not extend to the interior. When protected from the air, the paste or dry powder equally remains unchanged, even after many years. *Setting* of pure slaked lime depends on this property of drying to a cake of moderate hardness, as in the case of other finely divided amorphous materials. *Hardening* of the lime results from later absorption of atmospheric carbon dioxide, though the coating of calcium carbonate first formed generally prevents further action within it.

Limes for building purposes are made from limestones containing as impurities clayey and silicious materials, iron oxides, alkalies, etc., the amounts of which affect the behaviour of the lime. When such impure limes are calcined, the lime enters into combination with the constituents of the impurities present; thus with clayey limestones the lime combines with silica and alumina of the clay to form calcium silicates and calcium aluminates, and it also combines with any iron oxides present to form calcium ferrite.

For making products known as "hydrated lime," "new process lime," etc., the quicklime is ground, the powder thoroughly slaked with water, and the product either sieved or passed through air separators, to give a uniformly fine powder. The slaking is sometimes done by simply sprinkling with water, but to obtain more thorough saturation special appliances—such as the Kritzer hydrator—are often used.

Hydraulic Lime.—The process of slaking lime is much modified by the presence of other substances, and may even take place without noticeable evolution of heat and with insignificant change of volume. The hydrated calcium silicates and aluminates have the power of setting and hardening under water, and a lime containing enough of these compounds to thus set and harden is termed a *hydraulic lime,* or *water lime* (the old name). Limestone with more than 10 per cent. silica usually gives on calcination a hydraulic lime. If only *moderately hydraulic* the lime when slaked with water may show no action until 5 to 15 minutes, after which steam is given off, but less abundantly and with less manifestation of heat than with ordinary lime (either fat or lean); such a hydraulic lime would set under water in 15 to 20 days, but would harden further for some months; it may require 2 days or more to slake, whilst more hydraulic limes might need 7 to 14 days. Ordinary or *normal hydraulic limes* after treatment with water remain inactive for an hour or more, and subsequently do not give off much steam or heat, but fall to powder; these limes set in water after 6 to 8 days, and harden further for a few months. Very hydraulic limes remain inactive for indefinite periods, and evolution of heat is hardly noticeable, while the material does not readily fall to powder; these limes set under water within 3 or 4 days, and are quite hard after a month, but harden further.

Some French limestones contain finely divided silica, which in burning combines with the lime, as in the *Chaux de Theil* (made from a limestone found at Ardèche), which contains 65 to 75 per cent. lime, 20 to 22 silica, about 2 per cent. alumina, with a little magnesia, ferric oxide, etc., and has been much used, especially for marine construction.

In this country hydraulic limes are generally sold in lumps (as obtained from the kiln). French hydraulic limes are slaked and sieved at the lime works. The hard lumps which will not pass through the sieves are partly useless unchanged limestone and partly calcium silicates. The lumps are collected and finely ground to form what is called in England and America *grappier cement.* The well-known *La Farge cement,* much used in the United States, belongs to this class. In France, part of the ground lumps is mixed with the lime to increase its hydraulic properties.

Calcium Sulphate occurs naturally in several forms. In the anhydrous condition it is the mineral *anhydrite,* which is often found in crystals and in semi-crystalline masses in limestones or associated with common salt deposits. The sulphate is much more abundant as the hydrated mineral *gypsum,* $CaSO_4.2H_2O$, which occurs in more or less transparent crystals called *selenite,* which crystals easily split into thin laminæ, have hardness 1·5 to 2, and specific gravity 2·28 to 2·33. Other special forms are the fibrous *satin-spar* and the granular crystalline *alabaster.* These two varieties are worked into ornaments and artistic products. *Massive gypsum* or *plaster stone* is a stratified variety mostly used for making plaster. *Earthy gypsum* consists of small grains of gypsum, with much clay and sand.

Gypsum is sparingly soluble in water, requiring over

400 parts of water for complete solution at ordinary temperatures. When heated to 100° to 120° C., gypsum loses three-fourths of its water fairly rapidly, but the remainder is only driven off at or above 204° C. (400° F.), forming "soluble anhydrite." When the heating is continued further, the dead burned or over-burned gypsum no longer hardens by combining with water, which it takes up very slowly. The anhydrous sulphate melts without being decomposed when heated to redness, and resembles anhydrite on cooling. When gypsum is dried at about 100° C., the hemihydrate, $2CaSO_4.H_2O$, or $CaSO_4.0{\cdot}5H_2O$, is formed, the specific gravity of which is 2·7; this product constitutes plaster of Paris, which when mixed with water combines with it to form the dihydrated sulphate again, solidifying to a hard mass, and gives off heat, at the same time expanding and filling a mould in which it is cast; it is because of this that plaster of Paris is so largely used for casting.

The water of crystallization in gypsum can be removed by adding salts, as dilute solution of potassium sulphate or carbonate; the hardness which results in this case takes place more rapidly than with burned gypsum and water. When gypsum has been hardened in this way, if it be powdered and treated again with the same solution (potassium sulphate or carbonate), it hardens again. This property is employed technically in re-hardening old gypsum, and in hardening incompletely-burned gypsum, by using solution of potassium carbonate instead of water.

The good qualities of plaster depend chiefly on the raw material used and on the method of burning it. The best commercial results are obtained from the denser (and therefore heavier) varieties of gypsum. The lowest temperature at which gypsum can be burned to plaster is 80° C., but from a technical standpoint the best results are attained at 110° to 120° C. As a rule, the smaller the pieces of gypsum, the more uniform the product.

Burning of Gypsum.—Gypsum is burned in ovens or kilns in such a way as to avoid the reduction to sulphide by the fuel.

A common form of kiln on the continent consists of strong walls crossed by a low arch with ventilating openings. The gypsum only is placed in the upper space, above small arched fire-chambers in which brushwood is burned, or sometimes coke or coal. The arrangement is very simple, but wasteful of raw material and fuel. Scanegatty's kiln is essentially similar, but the walls and roof arch are much thicker, and the series of small fire arches is replaced by a single low arch about a foot above the floor; the flames from a furnace connected with the lower chamber strike against the under side of the arch, and the hot air and gases pass through openings into the upper chamber. The water vapour and waste gases pass out through a central opening at the top of the kiln. Dumesnil's kiln, which is economical in working (though expensive to build), and has been much used, differs from Scanegatty's chiefly in the arrangement of the lower fire-chamber, which has twelve openings to the upper chamber, and passages continued along this to the walls by the arrangement of large blocks of gypsum; the lower layers of gypsum are disposed so as to offer every facility for the draught to circulate. The firing is conducted gently for four hours, then more vigorously for eight hours, after which all the openings are closed, and 5 to 6 cubic metres of coarse gypsum powder spread evenly over the top of the gypsum in the kiln, thus burning more material and saving fuel. After twelve hours' cooling the gypsum is all removed. If not in fairly uniform powder, it must be ground, usually in a stamp or roller mill. The powdered gypsum is sifted, and stored in a dry place. Sometimes the operations of grinding and sifting are combined in one apparatus.

Improvements have been introduced by making the process continuous, and securing more equal distribution of heat. Uniform dehydration is also facilitated by grinding the gypsum before calcining it. Petry and Hecking's kiln is a rotary kiln. Perin's barrel kiln is a revolving cylinder on hollow trunnions, through one of which the heated gases from the furnace enter while the other serves for exit. It is charged through a door in the side of the cylinder, and the burned product is discharged at the same place.

Some kilns are heated by means of steam, a jet of steam at about 200° C. being blown alternately into each of two chambers containing raw gypsum. Waste gases from coke ovens are also used to dehydrate gypsum.

The best quality of plaster is sometimes made on a small scale by "boiling," the finely powdered gypsum forming a layer 2 or 3 ins. deep upon a metal plate or shallow dish, which is placed over a fire in such a way as not to be over-heated; the material is stirred at intervals until no more steam escapes, and the plaster is then ready for use. In the United States plaster is often prepared in a similar way by "boiling" ground gypsum in cylindrical iron kettles, with constant stirring by machinery. The method is slow and expensive, though superior to the older European processes, so calcination of roughly crushed gypsum in rotary kilns is gradually superseding it. The Cummer rotary calciner is largely employed in the United States. The Mannheim calciner is a rotating cylinder provided with a forewarmer, and the heat is so well used up that the escaping gases have a temperature of only about 80° C.

Gypsum when heated to higher temperatures, as above 130° C., becomes converted into anhydrous calcium sulphate, which appears to exist in two or more modifications, the behaviour of which with water is different. Eventually all varieties become hydrated, but they do not all set as plaster.

Keene's Cement, and **Flooring Plaster** or **Estrichgips,** consist essentially of anhydrous sulphate, and their setting is affected by the burning temperature and by the presence of minute proportions of other substances in the calcium sulphate, but the nature of the action is not well understood. However they may be prepared, the final product of setting is the dihydrated sulphate, $CaSO_4.2H_2O$.

Keene's Cement is usually made in Britain by burning gypsum to plaster, dipping the burned lumps in a solution of alum or aluminium sulphate, then drying, and burning again at about 500° C., avoiding contact with the fuel, and finally grinding again. Typical Keene's cement is nearly pure $CaSO_4$, with a small percentage of carbonate, the added alum, etc., being present only in traces. It takes several hours to set. Sometimes the first calcination takes place at a high temperature, and sometimes alum is replaced by some other salt.

Flooring Plaster (Estrichgips) is made by burning coarsely crushed gypsum at about 400° to 500° C. for not more than four hours. Longer heating causes the plaster to lose its power of setting. After calcining, the flooring plaster is ground very finely. Such plasters set very slowly, but eventually become very hard, and are much used in Germany for floors, etc. Prolonged heating at high temperature, or more intense heating for a shorter time, causes dehydrated gypsum to gradually lose its power of combining with water.

Plaster of Paris sets in a few minutes when pure. In order to cause slower setting, retarders such as glue, blood, vegetable juices, etc., are often added to plaster, and probably act by interfering with the growth of crystals. From 2 to 15 lb. of retarder per ton of plaster is usually added, and well mixed. Occasionally accelerators are added to plaster, sodium chloride (common salt) being one of the best.

The chief uses of plaster prepared from calcium sulphate are for plastering interiors of buildings, but owing to its solubility in water it cannot be similarly used out of doors.

It is also largely used for making moulds and casts which do not require a high temperature, and also for preparing surgical supports for broken limbs, for adding to Portland cement to make it set more slowly, for cementing small objects, and for spreading over soil for agricultural purposes. Clear gypsum is ground and polished for cheap jewellery. Gypsum is also much used in paper-making.

For making casts, 1 part plaster is made into a thin paste with 2½ parts water, which should harden in a minute or two, or even more quickly with moderate heating. The object is previously well oiled.

Gypsum dissolves easily in excess of sodium thiosulphate, a soluble double thiosulphate of calcium and sodium being formed.

A mixture of equal weights of anhydrous calcium sulphate and potassium sulphate, when stirred up with less than its weight of water, solidifies suddenly; with 4 to 5 parts of water, the solidification is somewhat slower, but it gives casts with polished surfaces.

Hardening of Plaster.—Plaster may be hardened by adding to it lime-water, or solution of gum arabic or glue, or a decoction of mallow root. A very good method, which is much used, is to mix the plaster with alum solution (containing 20 oz. alum in 6 lb. water); the mixture hardens completely in 15 to 30 minutes, and is known as *marble cement.* Alternatively, the cast piece may be left for a few weeks in an alum bath, and then dried slowly, or the plaster itself may be soaked in the solution, dried again, and calcined.

Addition of a little lime (as by mixing the plaster with lime-water) increases the hardness, and gives an appearance resembling marble; such mixtures are much used for architectural purposes, under the name of *stucco.* When dry, the surface is rubbed down with pumice-stone, usually coloured to represent marble, and polished with Tripoli and olive oil.

Stucco may also contain other ingredients. It is largely used for decorative purposes in architecture, chiefly indoors.

Another method of hardening plaster is to add a little slaked lime, and to dip the cast piece in a strong solution of magnesium sulphate (Epsom Salt).

Parian Cement is plaster mixed with borax solution (1 part borax in 9 parts water, or better with addition of 1 part cream of tartar). It may be prepared like Keene's cement, using borax instead of alum.

Solution of water-glass does not act well in hardening plaster. An artificial stone is obtained by Fissot by burning gypsum, immersing it in water for half a minute, then exposing to the air, and again immersing for two to three minutes, after which the block appears as a hardened stone. This method suggests a new crystallization as the cause of the increased hardness.

Hardened plaster, when treated with stearic acid (stearine) or with paraffin (wax), and then polished, bears a close resemblance to meerschaum, and still closer on imparting a faint reddish-yellow tint by a solution of gamboge and dragon's blood. Cheap artificial meerschaum pipes are made in this way.

Scott's Cement or **Selenitic Cement** was produced by the action of sulphur fumes on ignited lime, but it is more simply obtained by grinding quicklime (preferably feebly hydraulic) with 5 per cent. of plaster. Selenitic cement sets rapidly and soon hardens. It is better than ordinary hydraulic lime, but is not suitable for use in work exposed to weather or salt water. The better appreciation of Portland cement has prevented it from coming into general use.

Tripolite is merely impure gypsum (containing sand, with calcium and magnesium carbonates), burned with one-tenth of its weight of coal or coke.

Hard-finish Plasters are plaster cements consisting (like flooring plasters) essentially of anhydrous calcium sulphate, but they are calcined at even higher temperatures —sometimes at red heat. Keene's cement and Parian cement are of this class.

Martin's Cement resembles Keene's cement, but potassium carbonate solution replaces alum.

Mack's Cement is made by adding sodium sulphate or potassium sulphate to dehydrated gypsum.

All these plasters set quickly, and are hard and durable, but they are expensive.

MORTARS.

Mortar is made by mixing sand with milk of lime.

Common Mortar (ordinary mortar) sets and hardens only in the air. Slaked lime when exposed to the air absorbs carbon dioxide, and the material shrinks greatly and cracks. The calcium carbonate formed in this way, when thoroughly dry, becomes as hard as marble, and so is well suited for binding together bricks, stone blocks, etc. To avoid the great irregularities which would result from the shrinking, this is lessened by the addition of sand or some other suitable substance. Common mortar is usually prepared by intimately mixing slaked lime, sand, and water, preference being given to sand consisting of angular grains rather than smooth round grains, because mortar made with round-grained sand is very brittle. Sometimes instead of sands for making mortar are used burned clay (only occasionally raw clay for mud walls, etc.), pozzuolana, or certain artificially calcined products, such as cinders, furnace slags, etc. The quality and hardness of the mortar depend much on the proportion of sand to lime. Fat limes can be mixed with sand of 2 to 2½ times the volume of the quicklime previous to slaking, whereas lean limes and hydraulic lime should be mixed with smaller proportions of sand, sometimes not more than an equal bulk (especially for important work). Mortar made from fat (or pure) lime is disintegrated by water. In bricklaying, the surface of the brick is moistened, mortar is laid between the bricks, and left to dry. Small quantities of mortar are often mixed by hand, but large quantities usually by machinery.

Hardening of Mortar.—The hardening or setting of mortar takes place very rapidly; it becomes quite firm in a day. The setting of the mortar is due simply to the drying of the lime, no chemical action being involved, and the sand being merely mixed with lime. Later hardening of the mortar arises from gradual combination of atmospheric carbon with lime, but the action is only superficial, a skin of calcium carbonate being produced.

Hydraulic Mortar.—As the name implies, this contains hydraulic lime instead of ordinary lime. Hydraulic mortars are made from milk of lime and sand, or from ordinary air-mortar mixed with cement and water. Water is absorbed during the slaking of hydraulic lime, but there is no notable rise of temperature or increase in volume. Good hydraulic mortars may be made by mixing lime with furnace ashes or burned clay. They are used in the same way as ordinary mortars, the brickwork or masonry being moistened. The mortar should be laid on thickly between the layers of bricks.

Hydraulic limes form links between ordinary limes and Roman cement.

All limes, as shown by Vicat, lose much of their strength if mixed with excess of water. Hence it is better to wet the bricks and stones, and to use a stiff mortar, than to use very soft mortar like many bricklayers and masons do. The system of grouting increases the difficulties of setting owing to the extra water.

Mortars made in summer are always less effective than those made in winter, probably because of drying too quickly. Watering of brickwork and masonry constructed in summer is recommended, as a safeguard.

The volume occupied by mortar may generally be considered as equal to about three-quarters of the total volume of sand and lime used.

Cement Mortar is a mixture of sand, Portland cement, and water, but sometimes natural cement or slag cement is used instead of Portland cement. Cement mortar is far stronger than ordinary mortar, but to make it spread more readily some lime is usually added or sometimes loam. These additions reduce the strength, though builders do not seem to realize the fact. The materials for cement mortar should be well mixed in the dry condition, either by hand or in a mixing machine, and the water should then be sprinkled on the mixture through a rose. The sand should not usually exceed 3 to 1 of cement, and in no case should it be more than 4 to 1.

Cement mortar is used for special purposes, as for masonry exposed to running water or to sea water, and also in large land works where great strength is necessary. Another use is to cover the surface of masonry and concrete walls.

ROMAN CEMENT.

Roman cement belongs to the class of natural cements produced by the calcination of certain argillaceous limestones, and the fine grinding of the product. These natural cements represent extreme cases of hydraulic limes containing so little free lime that water does not cause disintegration of the clinker; they consist essentially of silicates and aluminates, possibly with alumino-silicates, as do also all other hydraulic calcareous cements.

Roman cement (originally called *Parker's cement*) was discovered by James Parker of London. He took out a patent (No. 2121) in 1796 for making a cement from the septaria nodules of the London Clay, by calcining the broken nodules to sintering point, and grinding the resulting clinker. Similar nodules from various other localities were afterwards used. The composition of the stones varies much, but they mostly included between 60 and 70 per cent. calcium carbonate, 14 to 20 per cent. silica, 5 to 10 per cent. alumina, with varying amounts of iron oxide and water, and sometimes small quantities of magnesia and other substances. The raw stone is fine grained, yet so porous that it cleaves to the tongue. Calcination changes the colour from (usually) greyish to brownish, and increases the porosity, while about a third of the weight is lost. The powder is generally reddish brown, and has a specific gravity of 2·5 to 3·0.

Calcination is now carried out at somewhat lower temperatures than originally—about a moderate red heat—for it has been ascertained that sintering is not necessary (as Parker supposed). This has the effect of reducing the cost of grinding. The clinker may be kept for a long time without becoming changed, and it takes up water with great difficulty. After crushing and fine grinding, it should be used as soon as possible, as moist air causes rapid deterioration.

Roman cement generally contains between 45 and 60 per cent. of lime, about 3 magnesia, 5 to 10 alumina, 5 to

12 ferric oxide, and 20 to 30 silica, with 1 to 2 per cent. manganese oxide. It sets very rapidly, the exact time of setting depending on the temperature and quantity of water used, and also, when exposed, to the temperature and hygroscopic condition of the air. A neat Roman cement of good quality, gauged with water at 15° C., will set in air in about 5 or 10 minutes, and under water in 15 to 60 minutes. Setting proceeds more slowly in sea water, and is also retarded by addition of plaster of Paris.

Mixtures of Roman cement and sand (hydraulic mortars) set more slowly than the cement alone, but have much less strength. The strength and hardness of Portland cement are far greater, and so it is much more extensively used. Owing to its rapid setting, Roman cement proves useful for protecting marine work constructed of Portland cement or concrete.

Natural cements, more or less resembling Roman cement, have been made on the Continent, and in the United States, some of them being termed *natural Portland cements.* They are inferior in strength.

Roman cement and similar products differ from Portland cement in having more variable composition, in setting more quickly, but having much lower strength and hardness.

PORTLAND CEMENT.

Portland cement, when set, presents an appearance similar to Portland stone, hence the name. It was first made in 1824, by Joseph Aspdin, of Leeds, who mixed well equal weights of clay and finely-ground limestone, and calcined the mixture in a lime kiln. The product, being rather lightly calcined, was very different from modern Portland cement. In 1826, General Pasley prepared a cement by calcining a mixture of river mud (from the Medway) with limestone or chalk. The special suitability of Medway mud is probably owing to the presence of salts derived from sea water, and mud from about the mouths of other rivers are similarly used for making Portland cement.

In general, Portland cement is obtained by grinding finely the clinker produced by strongly heating an intimate mixture of calcareous and argillaceous materials; the heat should cause sintering (incipient fusion). The choice of raw materials may be made from limestone, chalk, cement rock (an argillaceous limestone softer than pure limestone, with 50 to 80 per cent. calcium carbonate, but with not more than 4 per cent. magnesium carbonate for Portland cement), chalk marl, clay shale, slate, blast-furnace slag, alkali waste (material produced in the manufacture of caustic soda, but it should not contain sulphur), etc., but

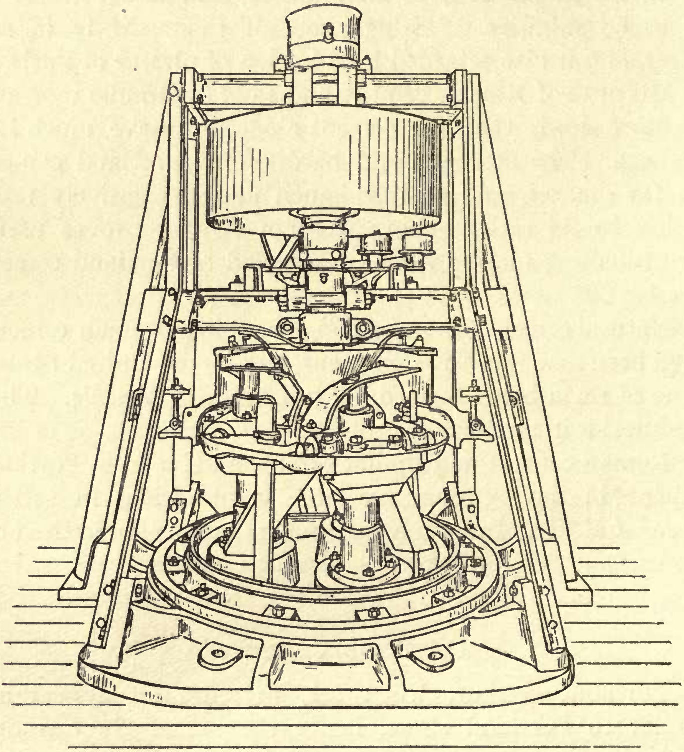

FIG. 2.—The Bradley three-roll mill.

the composition of the product must be kept within narrow limits; the mixture should be finely divided, uniform, and should contain about 75 per cent. of calcium carbonate and 25 per cent. of aluminium silicate and free silica with iron oxide (to include not more than 5 per cent. of magnesia, alkalies, and sulphur trioxide). The limestone for cement should not contain more than 2 per cent. magnesia.

Three processes are in use for mixing the raw materials: the wet, semi-wet or semi-dry, and dry processes.

The *wet process* is General Pasley's original process, and is now used almost exclusively in old works where soft raw materials—as chalk and river mud (or occasionally gault clay)—are readily available, but chiefly about the Thames and Medway. Suitable proportions of the materials (about 3 of chalk to 1 of mud by weight), with enough water to make about 80 per cent. in all, are intimately mixed in a wash-mill to make *slurry* or *slip*. The wash-mill is a vessel about 15 ft. in diameter, the contents of which are agitated and mixed by means of radial horizontal arms fixed on a rotating central vertical shaft. The prepared slurry is run off through sieves (or gratings) into troughs leading to large tanks called *backs*. After settling in the backs, the water at the top is drawn off, the moist pasty mass is dug out, dried, and burned. The drying is mostly effected by waste heat from kilns, but drying floors, heated by means of waste gases from coke ovens, may be used. This wet process is almost obsolete. On the Continent the stiff slurry from the backs is made into bricks, and dried by a current of hot air in tunnel dryers.

The plant for the wet process costs much less than that for the dry, and requires less labour and no rotary dryers, etc. The process also is simple, the mixture kept perfect, and with long kilns scarcely requires more fuel.

In the *semi-wet* or *semi-dry process*, sometimes termed the *Goreham process*, the mixing and grinding usually take place in wash-mills like those used in the wet process, but only about 40 to 50 per cent. of water is present, forming *thick slurry*. When the materials are hard, they are as a rule ground in a wet ball-mill or a wet edge-runner. Thorough grinding and mixing are extremely important. To ensure extremely fine grinding of the slurry, it must be further reduced in other mills, or by passing through a series of wash-mills, or in a special wash-mill—known as Clarke's mill— in which a rotating iron plate carries brushes; the centrifugal action of the brushes casts the slurry (which enters the Clarke's mill through a perforated iron plate) against the outer wall of the tank, where the finer part passes through sieves, and the coarser portions are swept away by the brushes and sent back to the grinding mills through an outlet near the bottom of the tank. The slurry is finally collected in large tanks called *mixers*, where it is subjected to continuous agitation by mechanical stirrers or compressed air. The slurry is tested, and any necessary adjustment made by adding slurry of clay or chalk. The slurry is pumped from the mixers to the kiln, or to the drying floors if briquettes

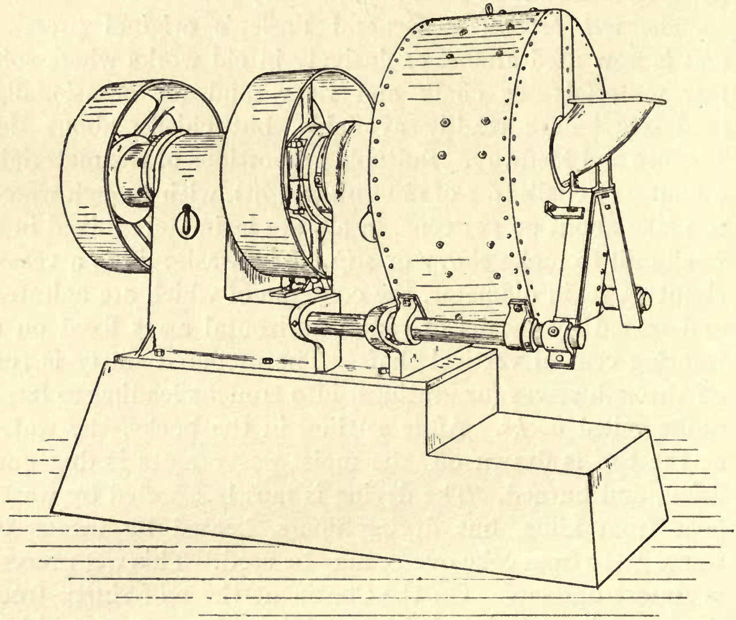

FIG. 3.—" Hecla " disc crusher. (Hadfields, Ltd.)

are to be made. On the Continent, briquettes are generally dried in tunnel dryers. This process is termed in America the wet process, the old wet process not being known there.

The *dry process* is used mostly for hard, raw materials, though soft materials can be treated similarly. Hard materials are first crushed, usually in jaw-crushers (in this country) or in gyratory crushers (in the United States). Wet, soft materials are crushed in rotary crushers. The crushed material is dried, generally in rotary dryers, and then ground, usually in a ball-mill and a tube-mill, but sometimes in one operation, as in a Griffin mill. The limestone may be burned first, the lime mixed with clay, and the mixture burned; the grinding of the hard limestone is thus obviated at the expense of fuel for the extra burning.

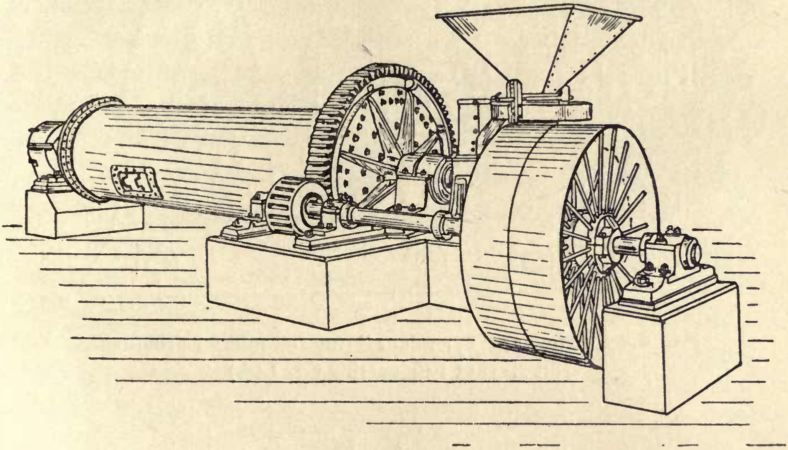

FIG. 4.—Allen's Stag tube-mill. (Edgar Allen & Co., Ltd.)

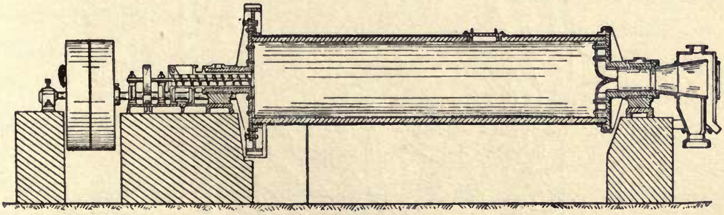

FIG. 5.—Allen's Stag tube-mill (sectional view).

Ball-mills are very good for preliminary grinding, but

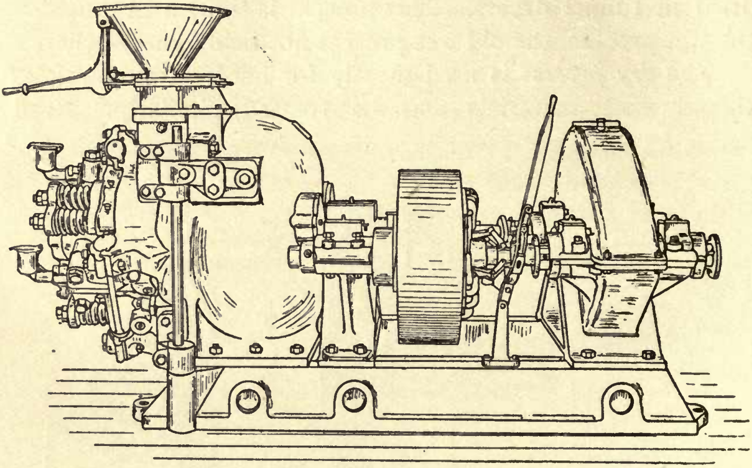

FIG. 6.—Sturtevant "open-door" ring roll-mill for grinding. (Sturtevant Engineering Co., Ltd.)

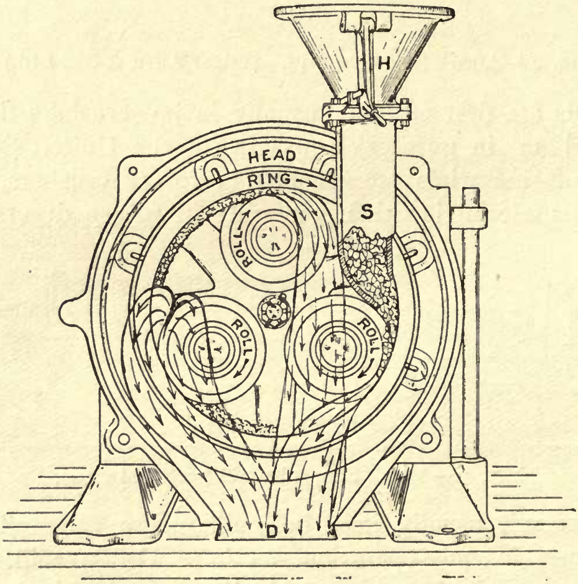

FIG. 7.—Sturtevant "open-door" ring roll-mill.

not so well adapted for producing fine flour. They consist of a circular drum which can be rotated about a horizontal axis, and is charged with forged steel balls. The material to be ground is fed into the drum, and is crushed by the action of the balls. The details vary in the mills of different makers. Edge-runners are in some cases used for dry grinding instead of ball-mills, and must either be followed by a tube-mill for finishing, or used along with sieves or air separators. The preliminary grinding is sometimes done in short tube-mills or pre-grit mills, charged with steel balls, or in other special forms of grinder.

Tube-mills are used as finishing mills for the fine grinding of the grit from the preliminary grinders (ball-mills, etc.). They differ much in details, but consist of a steel tube which can rotate about a horizontal axis, the cylinder being lined with chilled iron plates or quartzite blocks, and about half filled with flint pebbles, arranged so that the larger pebbles are near the inlet and the smaller ones near the outlet, where the ground material passes out through grids.

Compound mills, comprising a ball-mill and a tube-mill, are sometimes used. Centrifugal roller-mills with sieves, such as the Griffin mill, are sometimes used for grinding the raw materials in one operation. In other types of mill, balls driven by propelling lugs take the place of the rollers.

Raw Flour, Raw Meal, or **Compo,** are names applied to the ground product from finishing mills. It is tested for fineness (90 to 95 per cent.—say 92 per cent.—should pass through a sieve with 180 meshes per linear inch), and the proportion of calcium carbonate is ascertained so that any necessary change may be made. When shaft kilns are used for the burning, the compo is stored in *mixing silos* with constant stirring, but for rotary kilns it is taken at once to the small bins from which the kilns are charged. The compo from the silos is mixed with a little water when required, and made into rough bricks which are dried by waste heat, or in tunnel dryers. A little lime is added to the compo sometimes, to increase its binding power, and sometimes bricks are made of mixed compo and fuel.

Some works combine the wet and dry process, by making dry flour from hard materials and wet slurry from soft materials.

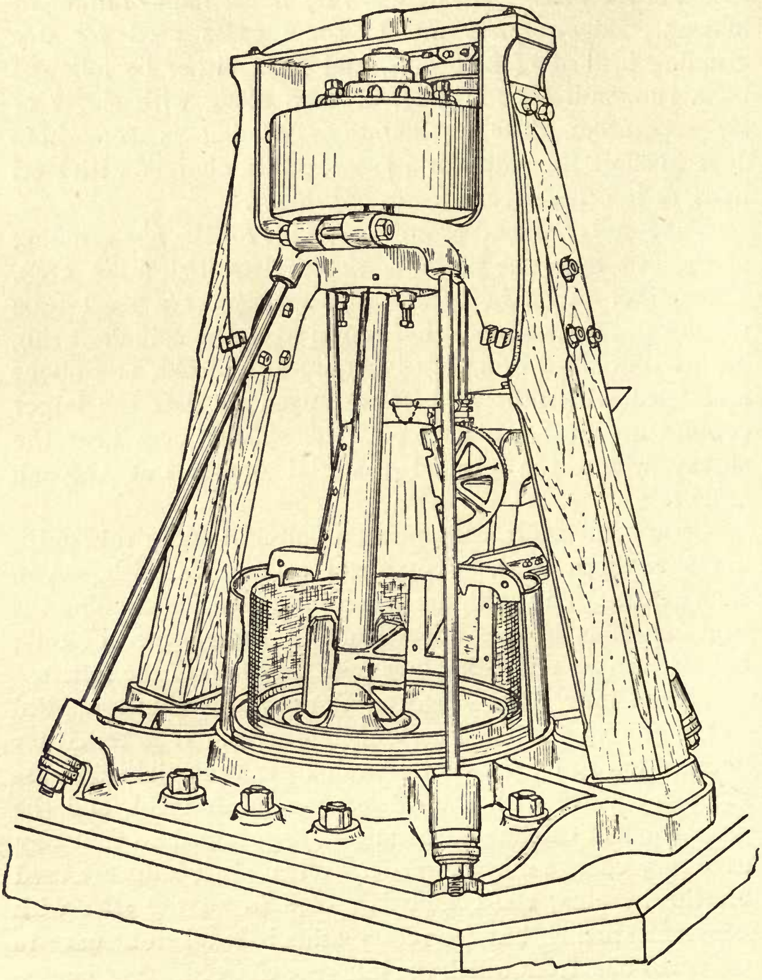

Fig. 8.—The Griffin mill.

The two are then pugged in suitable proportions and made into briquettes.

In the burning the raw materials are heated gradually to about 1400° C. In this operation, water is first expelled, then carbon dioxide from carbonates, and eventually the free lime combines with silica, alumina, and iron oxide.

The kilns for burning cement are either rotary kilns, or stationary or vertical kilns, and the latter are intermittent or continuous according as the burned clinker is discharged before adding fresh material, or fuel and raw material are fed into the kiln as the burned product is gradually removed. The rotary kiln is always continuous in its action. Intermittent kilns are now in use only in some old and small works. Stationary continuous kilns are much used for burning cement, but the rotary kiln is the most generally used, especially in America. The kilns used include bottle kilns open at the top, stage kilns like the Dietzsch kiln, other shaft kilns, chamber kilns, the Hoffmann or ring kiln, etc. The clinker from an ordinary fixed kiln may contain 5 to 15 per cent. of underburned material.

The rotary kiln furnishes a striking example, of an English invention which, after being used for a time, was given up, and later was perfected elsewhere and made completely successful. Crampton patented a rotary kiln as early as 1877, but Ransome in 1885 patented the first practical rotary kiln, which consisted of an iron cylinder 25 ft. long, and 5 ft. in diameter, slightly inclined, supported on rollers and rotated by means of worm gearing. The cylinder was lined with firebricks, longitudinal ribs being formed by setting every fourth row of bricks on edge (instead of flat). The raw materials, dried and ground, entered at the higher end of the cylinder, were gradually raised to the clinkering temperature as they descended slowly, and eventually the clinker passed out at the lower end. The fuel (producer gas) was burned at the lower end of the cylinder, where it entered. Ransome claimed that clinker calcined in this way would not need crushing before grinding, but the highly-heated material always caked and yielded clinker in small but very hard lumps. English cement manufacturers, after a time, abandoned the rotary kiln, including the improvements of Stokes. After some years it was tried in the United States, and soon proved successful in the hands of Hurry and H. J. Seaman (the latter an

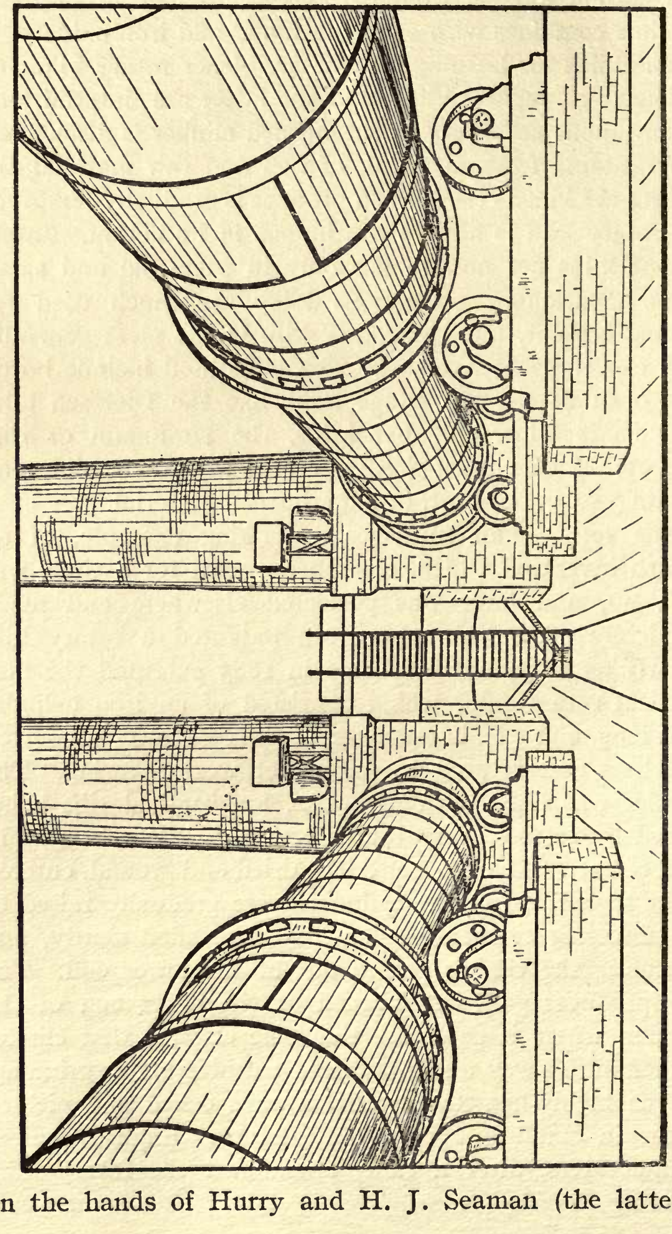

FIG. 9.—Rotary cement kiln.

Englishman), and others. A longer cylinder was found to give much better results, and as fuel, instead of producer gas or oil, finely-ground coal dust was adopted, and is now in general use for the purpose. Modern rotary kilns are much larger, seldom less than 100 ft. long, and sometimes more than twice that length; the increased length gives great economy of fuel.

The cylinders are usually constructed of riveted steel plates, and lined with bricks—ordinary building bricks at the cooler higher end, common firebricks about the middle, and special aluminous bricks at the hot lower end. A concrete lining is used in many cement works, the concrete being produced from a mixture of hard-burned clinker (small enough to pass easily through a half-inch mesh sieve), with half to three-quarters as much cement. The sides of the cylinder may be parallel, or they may taper upwards, or the lower part may be made larger in diameter than the rest. This last arrangement has been found to give a greater output than the ordinary parallel-sided form, and also to decrease the tendency of the clinker to stick to the lining.

The cylinder is supported on several pairs of roller bearings, and is caused to rotate by a split toothed-wheel worked by a worm-wheel and reduction gearing. Generally there is a three-speed gear to regulate the velocity of rotation, which varies as a rule from 20 to 60 revolutions per hour, according to slope of kiln, character of the raw materials, and heating conditions in the kiln.

The upper end of the cylinder communicates through a flue with a chimney, or, where several kilns are worked together, they may be connected by dampered flues with a single large chimney. In all cases, the kiln gases, heavily charged with dust, are passed through a dust chamber before reaching the chimney. The deposited dust is removed either continuously or at intervals.

The well-dried, finely-ground bituminous coal mostly used as fuel has to be used as soon as it is ground, being too explosive to be stored. From hoppers above the lower end of the kiln it is blown into the cylinder (by means of a fan or compressed air, etc.) and at once becomes inflamed.

The clinker is discharged as little balls (ranging from the size of a pea to that of a walnut) into the cooler, which in Europe (including England) is usually an inclined rotating cylinder, shorter and smaller than the kiln, but operated in the same manner. While the clinker is cooled, the air is heated and passes on to the kiln. In America vertical coolers of various types are preferred. Several such coolers are sometimes used instead of only one.

Clinker can be stored with less risk of deterioration than ground cement, hence it is often ground only as required. Clinker from rotary kilns is often stored for a few weeks so that it may become softened, but the result depends on composition and degree of burning; clinkers low in lime easily fall to powder, and high alumina clinkers are more liable to crumble than more silicious clinkers. The rotary kiln not only saves much labour, but gives a large output—200 to 400 tons per kiln per week—and has other advantages.

A kind of blast furnace has been used with some success for burning Portland cement, and in spite of commercial difficulties due to the high temperature (about 1500° C.) necessary for sintering, the process has merits of its own which may eventually bring it into prominence.

Clinker properly burned is very dark-brown, or greenish-black, hard, but rather porous. Under-burned clinker (half-burned, slack, or pink as it is called) is softer and mostly greenish-grey, but sometimes yellow, pink, reddish, or purple. Over-burned clinker is hard, non-porous, and generally bluish-black, presenting a metallic appearance.

The grinding of cement clinker is done most frequently in a ball-mill and tube-mill successively, but sometimes in a Griffin mill or some other kind. Clinker from vertical kilns is first crushed before grinding. The small size of the lumps of clinker from rotary kilns renders preliminary crushing unnecessary in general, though their great hardness makes them more difficult to grind. Moreover, special treatment is necessary to regulate the time of setting of cement from rotary kilns, as the ground cement sets almost immediately if the clinker is merely ground as it comes from the coolers and then used. Even the clinker from vertical kilns has sometimes to receive special treatment for the same purpose. The setting time is mostly regulated by adding a little gypsum or plaster to the clinker, either before or during the grinding; sometimes moistening the clinker with water will have the same effect, or both may be used together; another method is to pass steam into the tube-mill (in which the grinding is being finished) through the hollow trunnion at the feed end, the setting time of the cement depending on the pressure of the steam.

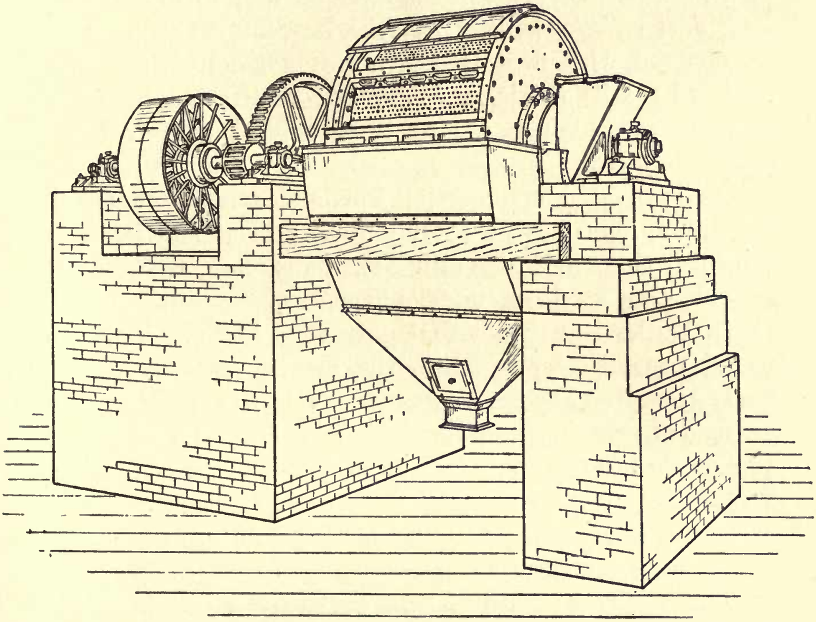

FIG. 10.—Ball-mill for dry grinding.

The finer material is separated from the coarser particles by means of sieves or air separators, a regulated current of air effecting the separation in the latter.

The finished cement is placed in storage bins or silos, and eventually packed into sacks or casks.

Much dust is produced at various stages in the manufacture of cement, and this is separated from gases at a high temperature in expansion chambers; dust is collected in this way from the air, from dryers, kilns, and coolers. Such dust chambers are also suitable for collecting dust from crushing and grinding mills, filters being also used; instead of filters are sometimes employed collectors which depend on centrifugal force for their effectiveness, but in most cases they do not answer so well as filters. The *Beth dust collector* is, perhaps, the best-known device; the air charged with dust is drawn through cylindrical sieves made of textile fabric, and the dust adheres to the inside of the sleeves, which are automatically cleaned from the deposited dust.

Well-prepared commercial Portland cement should be bluish-grey, and have a specific gravity of 3·10 at least. A brownish tinge indicates either excess of clay, unsuitability of the clay used, or under-burning of the cement. As D. B. Butler has shown that only very fine particles have useful cementing properties, the cement should be very finely ground. The modern tendency is towards increased fineness of grinding, and the proportion left on a sieve with 180 meshes to the linear inch rarely amounts to 10 per cent. The setting time varies to such an extent that cements are classed in this country as quick-setting, medium-setting, and slow-setting cements.

The tensile strength of neat cement after seven days is in most cases from 500 to 700 lb. to the square inch, and the crushing strength about ten times as great as a rule; both go on increasing for a year or more, and both decrease in proportion to the amount of sand mixed with the cement.

The composition of typical Portland cements varies only slightly, though it may be made from different raw materials. The essential components are lime, silica, and alumina, but oxides or iron, magnesia, and alkalies occur in smaller amounts, and a little sulphur is also usually present. It is only in old or badly burned cements that carbon dioxide and water occur to any notable extent.

In the British Standard Specification (1915) for Portland cement, it is laid down that the ratio of the chemical equivalent of lime to the total equivalents of silica and alumina—that is, the ratio of $n : (p+r)$ in $n\mathrm{CaO} : (p\mathrm{SiO_2}+r\mathrm{Al_2O_3})$ must neither exceed 2·85 nor be less than 2·0.

Ordinary free lime probably never occurs in modern Portland cement. The calcium hydroxide formed on hydration of tricalcium silicate would in the presence of trass or other suitable silicious material form a pozzuolanic cement. The addition of trass to Portland cement for this purpose (advocated by W. Michaelis) certainly increases the strength, but has not come into general use.

Magnesia is nearly always present in small amounts, combining with silica and alumina to form compounds resembling the calcium silicates and aluminates. These magnesium compounds hydrate much more slowly than the corresponding calcium compounds, and their presence would tend to cause disruption after setting. Messrs. Newberry consider that magnesium silicates and aluminates have no hydraulic properties. In the British Standard Specification (1915) the magnesia in Portland cement is limited to 3 per cent. According to tests made by the U.S. Bureau of Standards, increased magnesia was associated with a reduction in the clinkering temperature of the cements, and also (as shown by microscopic examination) with increased size of crystals, and appearance of new constituents—monticellite and spinel. Below 8 per cent. of magnesia, the physical properties of the cement were not seriously affected, and the mechanical strength of neat and mortar specimens and also of concrete, were comparable to those obtained with cements having normal composition. With more than 8 per cent. magnesia the early strength was less (though initial setting was quicker), but the gain was consistent with age.

Iron oxides are the chief colouring agents in Portland cement, which in the absence of colouring impurities is almost as white as snow. At the clinkering temperature iron oxides combine with lime to form ferrites, compounds which, according to Le Chatelier, slake and decompose in contact with water, but do not set. Sulphides (when present) act on the iron compounds to form ferrous sulphide, which later becomes oxidized to ferrous oxide and eventually to ferric oxide.

Alkalies in Portland cement include potash and soda in the form of silicates. They are derived chiefly from the clays and shales, but rarely amount to 1 per cent. As some alkaline silicates dissolve in water, they may serve a useful purpose in carrying silicic acid during the setting of the cement.

Sulphur in Portland cement originates from calcium sulphate and iron pyrites in clay and shales, from the fuel, and from the calcium sulphate usually added to retard the setting time of the calcined cement. Small quantities of calcium sulphate (1 to 2 per cent. of either gypsum or plaster), and also up to 2 per cent. of water, added after calcination, are beneficial for regulating the setting time. Larger quantities promote the formation of the highly expansive calcium sulpho-aluminate, and so are harmful; calcium sulphate is also softer than cement, and liable to be washed out by water. The maximum of sulphur trioxide allowed by the British Standard Specification (1915) is 2·75 per cent.

Typical analyses of good Portland cements show 60 to 63 per cent. of lime, 20 to 25 silica, 6 to 8 alumina, 2 to 5 ferric oxide, with about 1 per cent. (not more than 2) each of magnesia, sulphur trioxide, loss of ignition, and alkalies. The silica and alumina should saturate all the lime present.

CONSTITUTION OF PORTLAND CEMENT.

Though the composition of good cement varies only within narrow limits, the properties depend more on the way in which the constituents are combined than on the proportions. Numerous investigations have been made on the constitution of cement and on the processes of setting and hardening, including analyses of cements and careful study of their chemical and physical properties, microscopic examination of clinker and of hardened cement, study of reactions occurring during the formation and cooling of cement clinker (more particularly changes in electric conductivity), and synthetical studies of possible components of cements, with comparison of the properties of such synthetical products with those of cements.

Analysis of cements gives little information as regards constitution, though it serves to show the compositions of the best products. Study of chemical properties also throws little light on the subject.

Microscopic investigations have yielded important results, the microscope being used in two different ways. In one method, a thin section of the material is placed under a petrological microscope for examination by transmitted light. In the second method, a small piece of clinker or other material has one side only ground, polished, and etched, and then examined by reflected light. This second method is applicable to hardened cement, which is not hard enough for the preparation of the thin sections needed for the first method. A surface of cement clinker etched with a 1 per cent. solution of hydrochloric acid in alcohol is seen under the microscope to consist of crystalline grains embedded in a matrix, the only apparent difference between the clinker from vertical kilns and that from rotary kilns being that the latter is generally much finer grained. Le Chatelier, and also Törnebohm, distinguished four kinds of crystals, which were termed *alite*, *belite*, *celite*, and *felite* respectively.

Alite seems to be the chief component of Portland cement clinker, and forms the crystalline grains noticed in etched clinker. It occurs as nearly colourless crystals, and the amount increases with the proportion of lime in the clinker. Pure alite has been found to consist of lime, silica, alumina, magnesia, and ferrous oxide.

Alite is decomposed and hydrated by water.

Belite is not invariably present in cement clinker, but generally occurs in clinker poor in lime. It is not so light-coloured as alite, and usually shows fine striations.

Celite is the matrix between the alite grains, and must have been melted at the clinkering temperature. Alite and celite are the only essential components of Portland cement, and the amount of celite increases with the proportion of ferric oxide. The colour of celite is a deep brownish-orange, indicating the much larger proportion of iron present in it than in alite. Celite is only slightly affected by water.

Felite seldom occurs in cement clinker, but it occurs in blast-furnace slag. H. Kappen considers that high temperature calcination promotes the formation of felite in clinker. Felite and belite seem to be two varieties of the same solid solution.

C. Richardson compares cement clinker to an alloy. In pure cement the alite is a solid solution of tricalcium silicate in tricalcium aluminate, and the celite is a solid solution of dicalcium aluminate in dicalcium silicate, whilst in commercial Portland cement occur compounds of ferric oxide and lime corresponding to the aluminates; magnesia, alkalies, and sulphur trioxide are considered to be non-essential components.

Keiserman investigated the effects of certain dyes on the chief components of cement, and found that patent blue answered best for detecting alumina, anthropurpurin (in alcohol) for free lime, and methylene blue for silica—acetic acid solution for combined silica, and neutral solution for free amorphous silica. He concluded from his examination of cement in this way under the microscope that Portland cement clinker is mainly composed of dicalcium silicate and tricalcium aluminate, probably without alumino-silicates; the proportions of these components in cement clinker correspond to the formula $4(2CaO.SiO_2)+3CaO.Al_2O_3$.

Ditter and Jesser studied, with the aid of the microscope, the changes occurring during the sintering of Portland cement, and found that the electrical conductivity gradually increased up to 1375° C., at which point the process was endothermic. Between 1425° C. and 1450° C. the reaction was strongly exothermic, and at 1500° C. it became endothermic again. At about 1375° C. the sintering of the particles was observable by means of the heat-microscope and between 1425° and 1450° C. crystals of alite separated suddenly, with a little celite.

Janecke investigated the quaternary system $CaO—SiO_2—Al_2O_3—Fe_2O_3$, and concluded that ferric oxide only occurs combined with lime, and does not form solid solutions. He also concluded that a single ternary compound was produced, corresponding to the formula $8CaO.2SiO_2.Al_2O_3$, which he considered identical with alite, thus accounting for the necessity of alumina being present in Portland cement. He further concluded that belite, celite, and felite have compositions represented by $2CaO.SiO_2$, $3CaO.Fe_2O_3$, and CaO respectively. A little later, Janecke and Schumann arrived at the conclusion that the compound $8CaO.2SiO_2.Al_2O_3$ constituted the chief constituent of Portland cement clinker. Rankin and Wright, on the other hand, contended that Janecke's supposed compound is a mixture of calcium silicates and aluminates, the components at ordinary temperatures being tricalcium silicate, dicalcium silicate, and tricalcium aluminate.

W. and D. Asch assume the existence of a number of very similar cements consisting of calcium salts of complex alumina-silicic acids, which occur as various isomerides and polymerides, to which imposing constitutional formulæ are ascribed. These are highly speculative, and, though very ingenious, cannot be regarded as fairly established.

Le Chatelier, as a result of synthetic studies (1882 to 1887)—using definite proportions of pure lime, silica, alumina, etc.—concluded that the hardening of Portland cement is due to tricalcium silicate ($3CaO.SiO_2$), and that the initial setting is due chiefly to tricalcium aluminate ($3CaO.Al_2O_3$), but in some degree also to dicalcium aluminate ($2CaO.Al_2O_3$) and monocalcium aluminate ($CaO.Al_2O_3$), as all three aluminates set in water. Tricalcium silicate cannot be produced by the direct combination of lime and silica, but is formed in the cement clinker by combination of lime and another silicate. Dicalcium silicate ($2CaO.SiO_2$) forms twinned crystals, which separate on cooling because of unequal contraction of the opposite faces, and so give rise to the spontaneous disintegration of cement clinker. Monocalcium silicate does not react with water, and so cannot affect the hardening of cement.

S. B. and W. B. Newberry found later (1897) that powdered tricalcium aluminate after mixing with water cracked after setting and disintegrated entirely when immersed in water. They also claimed to have brought about direct union of lime and silica to form tricalcium silicate. They considered tricalcium silicate and dicalcium aluminate to be the chief components of Portland cement clinker.

Day, Shepherd, and Wright (1906) have shown that tricalcium silicate cannot be produced from lime and silica alone, and that the material obtained by the Newberrys was composed of an intimate intergrowth of crystals of calcium silicate (calcium orthosilicate) and lime.

The elaborate researches at the Geophysical Laboratory (Washington) have definitely established that the essential components of a pure and well-burned Portland cement are dicalcium silicate (the beta form only), tricalcium silicate, and tricalcium aluminate. In perfectly burned clinker there may be in addition some free lime and also the calcium aluminate, $5CaO.3Al_2O_3$; the latter may also arise from raw material low in lime and high in alumina. Commercial cement almost invariably contains ferric oxide, magnesia, potash, and soda, though none of these appears to be at all essential, and free lime is usually present in small quantities. Dicalcium silicate is the first silicate to be formed, and it is only with difficulty that this compound afterwards takes up more lime to produce tricalcium silicate. This latter exists in well-defined crystals in well-burned clinker with high silica, but such clinker is exceptional. The first aluminate formed is $5CaO.3Al_2O_3$, which later combines with more lime to form tricalcium aluminate. The alite of earlier investigators was apparently a mixture of $3CaO.SiO_2$ and $3CaO.Al_2O_3$, and celite was probably either $2CaO.SiO_2$ or an intimate mixture of this and $3CaO.Al_2O_3$ (or $2CaO.Al_2O_3$ according to some authorities).

The setting and hardening of Portland cement involves the formation of an amorphous hydrated material which subsequently partly crystallizes.

Le Chatelier explained the initial setting of Portland cement as being analogous to that of plaster, resulting mainly from the formation of a supersaturated solution of tricalcium aluminate, which immediately deposits hydrated crystals of $3CaO.Al_2O_3.12H_2O$. The solution can then dissolve some more anhydrous tricalcium aluminate, and again deposits hydrated salt, the process of solution and deposition proceeding at the same time at neighbouring points. The later hardening is attributed to decomposition of the tricalcium silicate, which reacts with water to produce hydrated monocalcium silicate, $(CaO.SiO_2)_2.5H_2O$, and calcium hydroxide; the former appears in very small needles, and the latter as hexagonal plates.

The initial set is probably due to hydration of tricalcium aluminate (with or without amorphous alumina). Sulpho-aluminate crystals (a combination of calcium sulphate and calcium aluminate) may be formed at the same time, and any free lime becomes hydrated. The formation of these compounds begins soon after the cement is gauged with water. Within 24 hours tricalcium silicate begins to be hydrated, and after a week or more the amorphous aluminate begins to crystallize, and calcium disilicate begins to hydrate. Calcium disilicate is the chief constituent of American Portland cements. The ideal cement should perhaps have an excess of dicalcium silicate, which would give a not too dense hydrated material, gaining strength later. Less of the tricalcium silicate would give the desirable early strength, and also remedy the excessive porosity of the dicalcium silicate.

The hardness and cohesive strength of Portland cement are due at first to the cementing action of the amorphous material produced by the tricalcium aluminate and of tricalcium silicate, and the gradual increase in strength is due to further hydration of these two compounds, together with the hydration of dicalcium silicate. Tricalcium silicate is apparently the essential eonstituent of Portland cement, probably because gelatinous silica is so readily liberated when it is mixed with water.

It may be added that a cement can be made having all the properties of Portland cement, and containing less than 0·5 per cent. alumina. But such a cement cannot be produced commercially, as it would require too high a temperature. In the manufacture of Portland cement, alumina is necessary for lowering the burning temperature to such an extent that a ternary system may be formed without too great an expenditure of heat, and from which the tricalcium silicate (the active hardening constituent) may separate.

POZZUOLANA CEMENTS.

Pozzuolanas are volcanic lavas modified by the action of superheated steam and perhaps other gases, so that they have become powdery, and have also acquired hydraulic properties. The name is derived from Pozzuoli, near Naples, where such material was found in early times. Similar material occurs elsewhere in Italy, and also in France and other places. The chief constituents are silica and alumina, with smaller proportions of iron oxides, lime, magnesia, and alkalies. The silica can easily combine with lime, when water is present, to form calcium silicate.

Pozzuolana may be white, grey, brown, black, yellow, etc., and is mostly amorphous, but contains crystalline mica, and other minerals. Sometimes it occurs as fine powder, sometimes in coarser grains, sometimes in the form of pumice, etc. The material is screened and ground.

Trass is a material of somewhat similar nature, found in the Eifel district by the Rhine, and is pale yellow or grey. It may be described as an altered volcanic ash, and is generally more compact than ordinary pozzuolanas, but is sometimes porous like pumice. As regards composition, it contains relatively less lime and more silica than pozzuolana.

Santorin earth is a light-grey volcanic ash, from the Grecian island Santorin (Thera), which has similar characters, but is more silicious. Pumice and volcanic tuff have also similar properties.

Pozzuolanic materials have in some cases resulted from alteration of sandstones and limestones by contact with eruptive igneous rocks. Even basalts and trap rocks, when crushed and ground, give similar results, but can scarcely be used in this way economically because of their greater hardness.

Natural pozzuolanic materials are rarely used in England for making mortar, and not very much abroad, owing to the better qualities possessed by the natural and slag cements, and especially by Portland cement.

Pozzuolanic (or trass) cements or mortars are made by mixing the materials with slaked lime (preferably in pasty condition except when very hydraulic lime is used), the pozzuolanic material being generally mixed with sand or other inert material to reduce shrinkage and prevent cracking, and also to increase the porosity, at the same time reducing the cost. Contrary practice notwithstanding, the lime paste should be stiff for materials consisting of hard and palpable particles, but thinner for fine-grained impalpable materials. The best proportions in the case of common lime are considered to be 1 of lime (powder) to 2½ of pozzuolana, to 2 of trass, or to 1 of sand with 1 of pozzuolana or trass.

The simplest pozzuolana cement would be a mixture of pure lime and hydrated silica, but the latter is too costly for use in making cement. The same is the case with kieselguhr, a natural active silica.

The name pozzuolana cement or Victoria cement, is sometimes given to a mixture of 3 parts of finely-ground slag (previously granulated by running into water) and 1 part by weight of slaked lime. If kept moist enough, the mixture sets slowly and becomes fairly hard and strong. Frost acts destructively upon slag cement structures. Slag cements also have a bad tendency to crack, which can only be obviated by not grinding the slag so fine, and they are not very strong. The initial hardness is not great, which is also the case with all natural and artificial pozzuolanic cements.

CONCRETE.

Concrete (or beton) consists of a matrix of mortar—either lime mortar or cement mortar—in which are embedded pebbles or broken stones forming what is called the *aggregate*. The aggregate may be gravel or broken stone, broken bricks, slag, clinker, coke, and ashes, etc. Rough angular pieces bond better with the mortar than rounded pebbles do. When strength is not essential, and a light concrete is desirable, a porous substance (such as pumice or coke) is used for the aggregate. Coke and ashes containing oxidizable sulphur compounds are liable to undergo expansion, and thus to cause rupture of the concrete; slags and clinker also contain such sulphur compounds, and are therefore also liable to expand.

Careful grading of the aggregate, using pieces of various sizes, enables the strength of the concrete to be nearly doubled. Some gravels need no grading, as they contain particles of proper sizes in correct proportions. The largest pieces of the aggregate should in most cases pass through a 1-in. hole, but they may be much larger for great masses of concrete; the smallest pieces should not pass through a $\frac{1}{4}$-in. hole, and all smaller material should be removed (preferably by washing), and the aggregate thoroughly wetted. The proportion of spaces between the pieces should not exceed 45 per cent. The sands used should be clean and roughly angular, and well graded—from about $\frac{1}{8}$ to $\frac{1}{24}$ in.

A very good concrete to set quickly in water is made from a hydraulic mortar (consisting of hydraulic lime, pozzuolana or trass, and sand) with which broken stones and gravel are mixed. A good concrete for water work may also be made by mixing mortar (produced from 3 parts of fine sand to 1 of hydraulic lime unslaked) with an equal quantity, or even half as much again, of broken stones or gravel.

For most purposes, including foundations, Portland cement concrete may be made from 1 volume cement, 2 volumes sand, and 4 to 6 volumes aggregate—that is, from an ordinary mortar with aggregate. Where weight rather than strength is required, much poorer concrete is sometimes used. For a watertight reservoir, it would be better to use 1½ to 2 volumes sand, and 2½ to 4 volumes aggregate. For ordinary operations, from 20 to 30 per cent. of water is used, but much less for quick setting, and much more when setting is to be retarded. When the water is sufficient to make the consistency like that of cream, and the particles of aggregate are very small, the mixture is termed *grout*. Clean rain water is preferable when available.

In making concrete the materials should be mixed dry, first the sand and cement, then the aggregate added to the mixture, and finally water added, and the mixing completed rapidly.

Reinforced Concrete, Ferro-Concrete, or **Armoured Concrete,** as it is variously termed, is a combination of concrete with steel, which has much greater strength than the concrete by itself, and the concrete also serves to protect the steel against corrosion, and from the expansion and contraction which might result from great changes of temperature. At ordinary temperatures the coefficients of expansion of concrete and steel are nearly the same. The steel (usually "mild") is used in the form of rods or bars, wire-netting, etc., but mostly rods are used to increase the tensile strength where it is most needed.

Reinforced concrete is extensively used in buildings, bridges, boats, railway sleepers, telegraph poles, gate posts, tiles, drain pipes, etc.

Mixed Cements are produced by mixing ground slags with ordinary Portland cement, but a good Portland cement cannot be improved in this way, and the added slag is to be regarded as an impurity.

SOME SPECIAL CEMENTS.

American Natural Cements are made from *cement rock*, a comparatively soft limestone containing 13 to 35 per cent. of argillaceous material and some magnesia. Those with the larger proportions of lime are called (in America) *natural Portland cements*, and are calcined at a higher temperature than those with less lime, but they contain 10 to 15 per cent. less lime than Portland cement does, and are also more variable in composition; a true Portland cement is obtained by mixing them with a suitable proportion of non-argillaceous limestone. Those with smaller proportions of lime are calcined at a lower temperature, and resemble Roman cement, but have a larger proportion of magnesia. **Rosendale Cement** is of the latter type, and contains about 15 to 18 per cent. magnesia, only 2 to 4 per cent. alumina, and only 18 to 25 per cent. silica. **Louisville Cement** resembles Rosendale cement, but contains less magnesia.

The great drawback of natural cements is that great care is needed in order to use them successfully; if such a cement be not used immediately after making, or if too little or too much water be added, it has a great tendency to solidify unequally, giving rise to cracks, and adhering badly to the materials.

Cements only need a little water to work them up to their greatest strength, about one-third the volume of the cement giving the best result, according to General Treussart. The more the cement is turned over before the setting begins, the harder it becomes. As the setting begins in a comparatively short time, the cement should only be prepared in amounts which can be used up at once.

Passow Cement is a more recent product, made by specially granulating blast-furnace slag of suitable composition, and then grinding finely, either alone or with an admixture of about 10 per cent. of Portland cement clinker. It is not (like ordinary slag cement) a pozzuolanic cement, depending on the interaction of granulated slag and lime. The slag for Passow cement is granulated so as to produce a material which itself sets, and attains a strength comparable to that of Portland cement. Passow cement has been successfully made from slags of different compositions in Germany, England, and America.

Aluminate Cements.—According to P. H. Bates (*Journal of the American Ceramic Society, 1*, 679, 1918), it is possible, by a method and equipment like that used for Portland cement, to make cements which give in 24 hours strengths as high as those usually developed by Portland cements in 28 days, either as mortar or concrete. This quick-hardening cement is not quick setting. It is a calcium aluminate (preferably with 55 to 75 per cent. alumina). The presence of silica or iron oxide is not desirable, but they may be present up to 15 per cent. if they replace lime and not alumina. The actual cost of manufacture would not exceed that of Portland cement, but the cost of the alumina would preclude the use of the product except for special purposes. Addition of 3 per cent. plaster markedly accelerates the setting of these aluminate cements (contrary to its action with Portland cement).

All the calcium aluminates have hydraulic properties except tricalcium aluminate, which happens to be the only aluminate present in Portland cement of normal composition and burning. But in the presence of hydrated lime and water the tricalcium aluminate forms a smooth plastic paste which hardens in air like Portland cement. In Portland cement, lime may either occur originally uncombined, or it may be liberated by water from tricalcium silicate.

Plastic Cements are adhesives applied to secure joints and connections of a more or less permanent character. J. B. Barnitt gave a fairly comprehensive collection of them in the *General Chemical Bulletin* for February, 1917, which was reproduced in the *Journal of the Society of Chemical Industry, 36*, 443, 1917. They consist of solids dissolved or suspended in suitable vehicles, the solids being little or not at all affected by the gases or liquids about them. The following include such as do or may contain silicious materials:—

Hydraulic Cement is used either alone or with sand, asbestos, etc., and is specially resistant to nitric acid. *Plaster of Paris* is often used alone as a paste for joints on gas and wood distillation retorts and similar places where quick setting is needed. A fibrous material such as asbestos is often mixed with it to give strength; stone, glass, and various mineral substances are used as fillers. Plaster and water, and wet plaster with asbestos, straw, plush trimmings, hair, or broken stone, are particularly suitable cements for oil vapours and hydrocarbon gases. *Clay* is often present in plastic cements as a filler. Clay and linseed oil are suitable for steam, the same two materials with fireclay added for chlorine, and clay and molasses for oil vapours. Preparations of linseed oil include China clay and linseed oil, lime and linseed oil (forming *putty*), and red or white lead and linseed oil; these mixtures become very strong when set, and are best diluted with powdered glass, clay or graphite. **Silicate Cements** for hot oil vapours include a paste of sodium silicate and asbestos; for gaskets for superheated steam retorts, furnaces, etc., sodium silicate and glass, or sodium silicate 50, asbestos 15, and slaked lime 10; metal cement consists of equal parts of sodium silicate with oxide of zinc, lead, or iron, or with mixtures of these oxides.

For insertion of glass tubes in brass or iron for high temperatures is used a mixture of alumina 1, sand 4, slaked lime 1, and borax $\frac{1}{2}$, with water. As a coating for glassware to protect from injury by direct flame is used a mixture of fireclay and plumbago made into a paste with water.

Of other adhesive cements the following may be mentioned. A strong cement for alabaster and marble, which sets in a day, is obtained by mixing 12 parts Portland cement, 8 fine sand, and 1 infusorial earth, and making into a thick paste with sodium silicate (water-glass); no heating is necessary in applying it.

Cutlers' Cement for fixing knife-blades in their hafts, is made of equal parts of brick-dust and melted rosin, or of 4 parts rosin with 1 each of beeswax and brick-dust. For covering bottle corks, a mixture of pitch, brick-dust, and rosin is used. A cheap cement, sometimes used to fix iron rails in stone-work, is melted sulphur (brimstone), or sulphur and brick-dust.

STATISTICS.

Cement manufacture is quite a modern industry. Some idea of its progress may be gathered from the following approximate figures relating to the production of Portland cement :—

	1890	1907
Great Britain ..	1,000,000 tons	2,750,000 tons
Germany.. ..	1,500,000 ,,	5,000,000 ,,
United States ..	50,000 ,,	8,000,000 ,,

Three years later the total production had reached something like 25,000,000 tons. The future demand for constructional purposes will be enormous.

LITERATURE.

"The Portland Cement Industry," W. A. Brown. London, 1916.
"Limes and Cements," E. A. Dancaster. London, 1916.
"Lectures on Cement," B. Blount. London, 1912.
Encyclopædia Britannica, 11th edition, vol. v., Article by B. Blount. Cambridge, 1910.
Thorpe's "Dictionary of Applied Chemistry," vol. i. Article by B. Blount. London, 1912.
"Modern Manufacture of Portland Cement," P. C. H. West. London, 1910.
"Portland Cement," D. B. Butler. London, 1905.
"Calcareous Cements," G. R. Redgrave and C. Spackman. London, 1905.
"Cements, Limes, and Plasters," E. C. Eckel. New York, 1905.
"The Mineral Industry," Articles by Stanger and Blount, and by Lewis. New York, 1897, 1898, 1905.
Journal of Society of Chemical Industry. Articles by B. Blount and others. London, 1894, 1905, 1906, and recent years.
Proceedings of Institution of Civil Engineers. Article by Stanger and Blount. London, 1901.
"Concrete" (No. 2, p. 101), C. H. Desch.
Also H. Le Chatelier's "Experimental Researches on the Constitution of Hydraulic Mortars" (in French).
"Cement," by Bertram Blount. London, 1920.

SECTION IV.—CERAMIC INDUSTRIES

Meaning of the word "Ceramic."—This word is frequently stated to be derived from the Greek *keramos*, "potter's earth" or "burned clay" products. Dr. J. W. Mellor suggests that it may be derived from the *Kerameis* or "potters" who lived in the part of ancient Athens called Kerameicus, and who worshipped Keramus—the son of Bacchus. Potters are called ceramists, and the potter's art is the ceramic art, and by a natural tendency the term came to be applied to clayworkers in general. Some consider that it should refer to pottery only, and not to such things as bricks, refractory materials, etc. On the other hand, in America the word has acquired a greatly extended meaning. Thus, in the *University of Illinois Bulletin*, vol. xiv., No. 12 (November 20, 1916), "ceramics" is explicitly stated to imply "the technology of nearly all mineral products except ores and minerals of organic origin. The ceramic industries thus embrace the manufacture of all kinds of clay products, such as stoneware, china, and porcelain ware, brick, tile, sewer-pipe, and terra-cotta; Portland cement, dental cements, lime, plaster, stucco, and a variety of gypsum products, and special cements; all of the many varieties of glass and glassware, fused silica, and magnesia ware; enamelled metals and sanitary ware; a variety of electrical and thermal insulating materials; talc, chalk, and slate products; abrasive materials, such as finely divided silica and carborundum and alundum products; rare earth products, such as mantles and tips for gas burners; bricks, crucibles, and other refractory articles manufactured from bauxite, magnesite, chromite, carbon, graphite, asbestos, talc, lime, porcelain, clay, alundum, sand, and many other materials." This is comprehensive indeed and the American Ceramic Society apparently adopts the same range. The chief continental technical journals, such as *Sprechsaal, Keramische Rundschau, La Ceramique,* etc., do not accept this wide interpretation of the term, so that it must be regarded as peculiar to America for the time being, though possibly it might prove convenient for adoption at some future period. Probably the least objectionable course just now is to follow Dr. Mellor's view (*Trans. Cer. Soc.*, *16*, 69, 1917) that "the word ceramic embraces the plastic or fictile arts in which objects are first shaped or moulded, and subsequently baked."

Clay the Basis of nearly all Ceramic Wares.—From the earliest period—extending back even to prehistoric times—the clays which form such a prominent feature of the readily accessible surface portions of the solid globe have been used for making earthen vessels. This no doubt arose naturally from observation of the plastic properties of clay, which enabled it to be easily shaped by hand. The simple pieces first made were for vast ages merely dried by the sun, which gave rise to sufficient hardness for grain and other dry materials to be stored in them. As the use of fire extended it was eventually discovered that clay after heating became much harder and stronger than when simply dried, and so in the course of time it became a settled practice to bake clay vessels in order to give them greater hardness, and therefore greater durability. Sven Odén, a Swedish investigator, defined clays as disperse formations of mineral fragments in which particles smaller than 2μ (*i.e.* 0·002 mm.) predominate. The mineral fragments may include quartz, felspar, mica, etc., as well as their decomposition products (kaolin, bauxite, hydrargillite, zeolites, allophane, clays, gelatinous silicic acid, iron oxide, etc.); but none of these is necessary to characterize a deposit as clay.

The difference in plasticity of clays, and the different degrees of hardness of the fired pieces, as well as differences in other properties such as colour and structure after firing, give rise to a great variety of products. Even in the same district, the clays would not all fire to the same colour, and this fact would indicate to the observant a means of producing rude colour decoration by smearing the surface of a piece with a different kind of clay (sometimes white), or some other earthy material. The application of glazes and colours later on modified the effects, but the production of wares on any large scale from purely local clays continued with very few exceptions until about the middle of the eighteenth century. Then the use of local clays was largely superseded by the introduction of white-burning clays, brought from a distance in most cases.

Clay of some kind continued to form the basis of ceramic wares in general. Exceptions included such abnormal products as those of the early Egyptians, who made objects from sand mixed with a little clay, or carved them from solid stone, and covered them with bright blue glazes, fired on in the usual way.

GENERAL AND SPECIAL CHARACTERS OF CLAYS FOR CERAMIC PURPOSES.

The most important characters of clays for ceramic purposes are plasticity and hardening when heated. The colour (especially after heating) is another important property in many cases.

Plasticity is the property by virtue of which clay, when mixed with a certain quantity of water, can be moulded by pressure into definite shape. This property is lost when clay is strongly heated, and attempts to restore it after the combined water has been driven off have met with little success, the quantity of water taken up—even on treatment with very hot water—being only small. Quite recently it has been announced by J. S. Laird and R. F. Geller (*Journal of American Ceramic Society*, *2*, 828, 1919) that although the plasticity of raw clays is little affected by the action of very hot water, clays which have been almost completely dehydrated by calcination at a moderate temperature (600° to 700° C.) can be rehydrated by heating with water to 200° to 270° C. (under great pressure of course) for 8 to 48 hours. The rehydrated material is generally plastic and seems to be colloidal. After being worked up and dried two or three times it resembles a raw clay, that is, its original condition. Clays which have been calcined at higher temperatures can be rehydrated only much more slowly and incompletely. The greater the plasticity of clay the more water is generally required to bring it to a given degree of softness for working.

Plasticity is not a simple measurable property, but according to Le Chatelier results from the union of two elementary properties which can be measured separately; these are deformability (or deformation before rupture), and tenacity (or resistance of the moist body to deformation). The body for ceramic pressed tiles may have very low deformability, and so may be very silicious or sandy. Delicate vases, if they are to be turned, have on the contrary to be made from a very deformable body. Resistance of the moist body is very important for large vases, but is of little consequence for flat articles fired horizontally. Each of the two factors of plasticity can be measured by the same methods as are used for metals, plasticity being quite comparable to malleability, though the magnitude is usually far greater in metals than in ceramic bodies. Tenacity of ceramic bodies may be expressed in kilogs. per sq. cm. and deformability as linear expansion (per cent. of original length). Both resistance to deformation and magnitude of deformation increase with speed of operation within very wide limits, and this serves to explain the differences often observed in results obtained from different workmen who may at first sight seem to be working in exactly the same way; probably the best results come from the workman who brings the body to its proper shape in the shortest possible time.

Plasticity depends on various factors, the more important being the proportion of mixing water, the size and shape of the solid particles, and the nature of the material dissolved in the water. Either too little water or too much gives no plasticity, owing to absence of deformability or absence of resistance respectively. A normal body mixture is taken as being the richest in water which can be worked without sticking too much to the hand; though the definition may seem rather vague it has been found (still relying on the authority of Le Chatelier) that different operators agree to within 1 per cent. on the water content of this normal body. Some clays give a normal body with 30 per cent. water. Coarser clay needs less water to give a normal body, and this applies also when sand, chalk, etc., are mixed with clay. Dissolved substances may greatly affect the plasticity of clay bodies. Alkalies (potash, soda, etc.), as also their carbonates or silicates, considerably reduce the amount of water necessary as compared with pure water, but alkaline earths (magnesia, lime, strontia, baryta)—and to a smaller extent their carbonates, sulphates, etc. (when soluble)—increase the amount of water necessary. Tannin and certain other organic substances act like the alkalies. Reduction of the mixing water reduces also the contraction in drying.

The plasticity of clay is due apparently to the extreme fineness of the particles and their lamellar structure. In fact, all very fine powders, whatever their chemical nature may be, possess some degree of plasticity, though much inferior to that of clay; they can be kneaded in the fingers, and acquire some hardness by drying.

The combination of lamellar structure with extreme fineness is very rare outside clays, but Le Chatelier has obtained it by grinding of mica and of glauconite, neither of which occurs naturally in fine powder. The material thus obtained was as plastic as clay, though prolonged grinding was necessary in the case of mica, owing to the elasticity of the lamellæ. Glauconite occurs naturally as a coarse sand consisting of nearly spherical grains. Ground glauconite can be treated like clay for making into a normal body or a slip. Plasticity is a direct consequence of the existence of a superficial tension in the liquid, the resultant of the capillary tensions in the many minute air spaces always present in a plastic body. As evaporation proceeds, water is concentrated more and more closely in the spaces, and the clay lamellæ become more strongly pressed against one another and so adhere together, the average force of adhesion increasing with the number of grains on unit surface, that is, with increased fineness of the clay particles. The degree of hardness when dried usually increases with the plasticity of the clay.

Some authorities ascribe the plasticity of moist clay to the presence of colloidal grains (or glue-like particles) composed of hydrated metallic oxides or salt in a peculiar non-crystalline condition. The water content of these particles varies continually with the temperature and with the vapour pressure of the surrounding atmosphere. The components of clay which might take a colloidal form include aluminium hydroxide, iron oxide, and hydrated silicic acid. Still other authorities refer plasticity to molecular attraction between the clay particles themselves, or between them and the water surrounding them. It scarcely seems likely that any of these suggested causes of plasticity is the sole cause, but that plasticity is rather dependent on a combination of them.

Contraction or **Shrinkage.**—During the evaporation of the water the grains or particles of solid material approach one another owing to capillary tensions, the effects of which increase as they come to act in narrower and narrower spaces. With very fine clays rich in kaolinite this contraction in drying may amount to 20 per cent. of the linear dimensions.

The further contraction during firing is never uniform, but is produced first towards the outside, and the resistance offered by the uncontracted central parts results in the formation of surface cracks, which gradually extend inwards and cause the piece to be broken into several parts. To remedy this trouble, the clay is mixed with non-contracting materials such as grains of sand or of grog (calcined clay). The presence of these materials does not prevent the contraction and cracking of the clay, but the distribution of the cracks is altered, so that they are rendered harmless. The less the proportion of clay used in the bodies the less the contraction, but also the less the final strength. In industrial clay bodies the proportion of true clay ranges from about 25 per cent. in bricks and other common articles to 50 per cent. or a little more in glass-house pots.

The contraction of a clay body helps to loosen it from the moulds.

Contraction is nearly finished when only half of the mixing water has evaporated, so the later stages of the drying may be carried out very rapidly without risk of producing cracks. In the case of bricks and other thick ware, the drying is commenced behind cloths so as to retard the drying, which is finished in full sunshine (or other heat).

The composition can be so adjusted that by using clays containing sufficient sand, and suitably regulating the firing temperature, bricks can be made which do not change their dimensions as the result of firing.

Porosity of a clay arises from the partial replacement of the water (after evaporation) by air; the contraction which accompanies the evaporation prevents complete replacement. Numerically the porosity is the total volume of the pore spaces expressed as a percentage of the apparent volume of the dry or fired material, depending on the shape and size of the particles; pore space generally increases as fineness of particles increases. When clay consists of particles of different sizes, the porosity is much lessened.

The possible rate of safe drying depends on the quantity of water absorbed and the facility with which it can escape; large pores permit rapid escape, but small pores retard both absorption and evaporation of the water.

At the moment of dehydration the volume of the pores increases suddenly about 10 per cent. by liberation of combined water. As the temperature is carried higher, the porosity decreases as contraction increases. The use of non-plastic materials to mix with clay, by reducing contraction, tends to increase porosity.

Expansion of clay bodies causes great difficulty in the application of vitreous glazes. Thus fine earthenware often develops very numerous fine cracks in the glaze. The expansion of glasses and glazes is generally greater than that of clay bodies, so on cooling the glaze remains in a state of tension, and finally proceeds to crack. This cracking of the glaze—termed crazing—takes place rapidly on exposure to considerable variations of temperature, as when domestic ware is washed in hot water. In exceptional wares the body may contract more than the glaze, and its cracking involves the destruction of the glaze; sometimes the body resists cracking, and the compressed glaze peels off.

Tensile Strength, or resistance of clay to rupture when air-dried, has importance in connection with the handling, moulding, and drying of ware. The tensile strength of clay ranges from a few pounds to over 400 pounds per square inch.

Fusibility.—The temperature of fusion or complete softening of clay depends on the amount of fluxes present and their nature, the size of the grains (especially of refractory particles), the homogeneity of the mass, the kind of atmosphere (oxidizing or reducing), and the mode of combination of the elements in the clay. Usually no reaction takes place between the grains until one kind melts, but it is not necessary for each to melt in order that reaction may take place.

The white-burning clays are characterized by the low proportion of iron oxide present, and the high percentage of alumina. In the China clays (kaolins) the alkalies are very low, and so are all oxides other than silica, alumina, and water, so that China clays are as a class highly refractory. Ball clays contain a greater percentage of alkalies, and of silica, which, in conjunction with the exceptionally fine state of subdivision of the particles, makes them distinctly less refractory than China clays. Ball clays are also characterized by the presence of fine particles of carbonaceous material, which gives them a dark blue or almost black appearance in their natural condition.

The best fireclays have strong points of resemblance with the white refractory clays, the chief difference being in the larger percentage of iron oxide present. This similarity is enhanced as the result of electro-osmosis treatment of such fireclays. The author had occasion a few years since, to prepare some small trials in which a South Staffordshire fireclay so treated was substituted for the ball clay constituent of an earthenware body. The only distinguishable feature in the resulting trials after the glost firing, was that they were slightly more yellow than normal pieces containing ball clay.

CORNISH STONE AND FELSPAR.

These are two important fluxing materials largely used in the ceramic industry. They are used in finely divided condition, chiefly in bodies and glazes, and the object with each is the same, that is, to assist in promoting more or less vitrification of the mixture under suitable heat treatment. But whilst complete fusion of the whole is aimed at in glazes, the intention in bodies is generally to produce a sufficient degree of vitrification to give the fired material a varying amount of hardness and strength according to the nature of the particular product desired. In the cases of stoneware and porcelain, the vitrification is carried almost to completion, and with porcelain especially great care has to be exercised to avoid distortion of the ware when softened by heat.

Cornish Stone or **China Stone** is largely worked in Cornwall and Devonshire. It was discovered by William Cookworthy, a Plymouth apothecary, in Cornwall, between 1745 and 1750, and was first used by him for making porcelain. A common type of granite consists essentially of the minerals quartz, felspar (orthoclase), and white mica (muscovite), with often small amounts of other minerals such as tourmaline, fluor spar, topaz, etc. Decomposition of the felspar of these granites gives rise to formation of China clay, and Cornish stone is a similar rock in an intermediate state, that is, with the felspar more or less decomposed. Cornish stone thus consists essentially of quartz, white mica, felspar in a more or less advanced state of decomposition, with possibly other minerals in small proportions. Felspar is light-coloured (whitish or creamy), quartz appears dark-greyish in the rock, though the individual grains are glassy and nearly colourless, mica is whitish, but sometimes dark. The different commercial varieties depend on the extent of the decomposition of the felspar, and the nature and amount of the accessory minerals. When the felspar is only in an early stage of decomposition, the stone is said to be hard—purple or white as the case may be. In medium white stone the decomposition may be sufficient to make the material friable, though the stone is fairly compact. In hard white stone decomposition of the felspar has just begun, and in hard purple there is little or no appearance of decomposition.

Cornish stone, as well as China clay, was first used by William Cookworthy (of Plymouth), who took out a patent (No. 898, March 17, 1768). This was taken over by Richard Champion of Bristol, who obtained an extension of the patent (No. 1096, September 15, 1775). In 1881 Champion sold his patent to seven North Staffordshire potters.

Jersey stone resembles Cornish stone, but is somewhat more fusible and contains rather more iron. It has been suggested that it would be very suitable for use in glazes.

Felspar, as used in this country, is mostly from Norway and Sweden. It is the potash felspar (orthoclase) and usually is salmon-coloured or pale reddish-brown. Felspar is hard and compact, but when finely ground it fuses rather easily to a colourless or whitish mass. On the other hand, some white felspars become grey after melting. At high temperatures felspar forms in thin layers a perfectly transparent glass or glaze.

For ceramic uses, felspar is crushed and afterwards ground.

VARIETIES OF POTTERY AND PORCELAIN.

It is impossible to assign sharp limits for the different kinds of ware, because the same materials may give different kinds under different conditions, but they may be conveniently (though rather broadly) grouped into three divisions.

I. Bodies made from only plastic materials (one or more clays), or such materials mixed naturally or artificially with a proper proportion of non-plastic materials (like flint or other form of silica, or ground pitchers, etc.), but without the addition of any fluxing materials. The firing is not carried to the fusing point, and the products are highly porous, opaque, fairly hard, and usually of a red-brown, yellow, or sometimes grey to black colour. In this group are included common bricks, flooring and roofing tiles, terra-cotta (mostly red or brown), refractory clay products, and common stoneware. Terra-cotta is made of common clay, always containing iron, and is not adapted for withstanding great heat; some special terra-cottas are white or nearly so. Refractory clay products are made from clays containing comparatively small amounts of impurities, free especially from iron, lime, and alkalies, and which can therefore resist high temperatures; they include firebricks and special shapes for use in connection with heating apparatus (as furnace linings, etc.).

Terra-cotta is sometimes covered with a transparent lead glaze or an opaque lead and tin glaze, which makes the surface impermeable to liquids, and often also masks the colour of the body; the tin glaze is usually white, but the transparent lead glaze is often dark-coloured.

II. Bodies containing plastic, non-plastic, and fluxing materials (which help to make the mixture fusible); the bodies after firing are white or light-coloured, compact, hard, and usually opaque. They include fine earthenware (or faience), fine stoneware, and mortar bodies. Fine earthenware has an opaque white body fired to incipient fusion, and covered with a transparent colourless (alkali-lead or sometimes alkali-boracic leadless) glaze adapted for underglaze decoration. Stoneware has an opaque body including clay mixed with a suitable proportion of flux, and heated to the point of complete softening, so that it becomes hard and very impermeable. Mortar bodies are only specially hard white stonewares.

III. Bodies containing only plastic and fluxing materials, the fired bodies being translucent, white or cream-coloured, hard, and durable. They include porcelains (hard and soft, the latter both natural and artificial), parian, jasper, etc. Sometimes the body is coloured by material specially added.

Ceramic bodies are often divided primarily into permeable and impermeable bodies. The permeable bodies include those in Class I. with the exception of common stoneware, and those in Class II. excepting fine stoneware and mortar bodies; impermeable bodies include these exceptions along with the bodies grouped in Class III. Impermeable pottery has a vitreous fracture, is smooth to the tongue, and cannot be scratched by steel. Permeable pottery has an earthy fracture, is rough to the tongue, is generally soft, and can in nearly all cases be scratched by steel. This distinction into permeable and impermeable bodies is largely a matter of firing, as permeable bodies become impermeable if heated strongly enough (though the ware may then lose its shape), and impermeable bodies are always permeable during the earlier stages of the firing.

PROCESSES IN THE PREPARATION OF EARTHENWARE.

GRINDING AND MIXING.

Clays do not require grinding. China clays are purified at the pit or mine, by washing and successive sedimentations, the impurities being mostly deposited in the earlier stages, and nearly pure clay in the later stages. Ball clay is not subjected to any special treatment at the pit, but should always be weathered before being used; for this purpose it is most advantageous to spread it out for exposure with the long slope facing the south (so as to get maximum solar radiation), the superficial portions being raked off from time to time after it has weathered sufficiently.

Flint is the non-plastic material mostly used in England for mixing with clay and fluxing material to make earthenware; in other countries ground sand or ground quartz is often used instead. The flint used is generally obtained from chalk flints, which are very hard and solid. Before grinding, flints are calcined to serve two useful purposes; they become much more friable (and so are more easily crushed), and the flint substance undergoes a certain beneficial change in its structure, rendering it better adapted for use in ceramic bodies. If calcined at about 800° to 900° C., the quartzose flint changes to tridymite, the specific gravity being reduced at the same time from about 2·6 to possibly about 2·33 (or a little higher) with a corresponding change in volume. If the heating be carried to about 1300° C. or higher, the tridymite in its turn changes more or less completely into cristobalite, with a further small reduction in specific gravity and increase in volume. If such changes took place during the firing of ware containing flint they would be likely to cause serious trouble.

Flint makes the fired earthenware body more open and porous, reduces the excessive plasticity imparted by ball clay, and so promotes quicker drying. It makes the body whiter and stronger, and enables it to resist a high temperature without becoming deformed. An addition of flint to an earthenware body is a good remedy for crazing (that is, formation of fine cracks in the glaze), but an excess of flint is liable to cause peeling (scaling of the glaze from the body).

It is interesting to note that from the commencement of its use for pottery in Staffordshire, flint was pounded or beaten dry, followed by sifting, until 1726, when Thomas Benson took out a patent (No. 487, dated November 5) for wet grinding by means of iron edge-runners worked by a water-wheel; the grinding was finished on iron pans with large iron balls. In 1732, Benson obtained a patent (No. 536, January 14) for an improved process, the improvements consisting in the substitution of stone edge-runners and pans, with large stone balls, to take the place of iron; wind and horses are mentioned as additional sources of power to work the wheels.

It may be noted that calcined and ground flint was used as early as 1689 by Dwight of Fulham, but the flint proved more expensive and troublesome than the white sand which it replaced. It was about fifty years later that it came into use to improve white stoneware in Staffordshire.

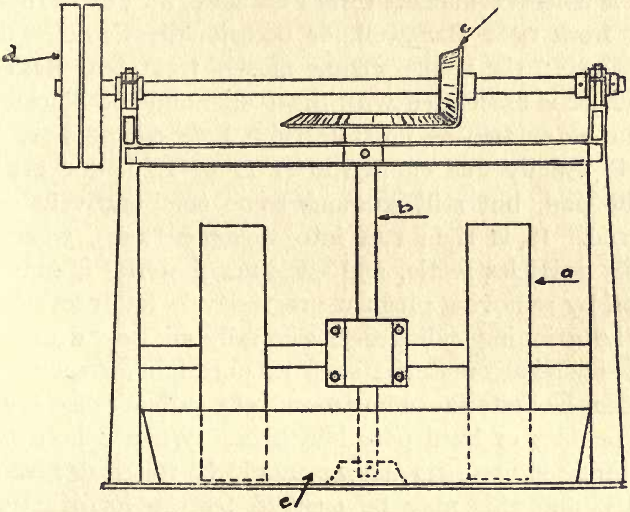

FIG. 11.—Pulverizing mill with solid bottom. (Manor Engineering Co., Fenton.)

Wedgwood (in a letter to Bentley, dated July 19, 1777) attributed the discovery to a Shelton potter named Heath, but Simeon Shaw and Parkes, writing much later, credit Thomas Astbury (the younger) with the invention.

The calcined flints are graded, the finer material being removed and the remainder crushed ready for grinding on a pan or in a cylinder. The crushing is usually done in a jaw crusher.

The grinding pan is usually circular in section, but sloping a little outwards from below upwards. The bottom of the pan is formed by a thick pavement consisting of blocks of hard chert, and over the top of this pavement larger blocks of chert (called runners) are carried by arms fixed on a revolving central shaft. The crushed material is charged on to the pavement, some water is added, and the material is gradually reduced to a fine state of subdivision, the time required depending on the weight of the runners. Excess of water tends to prolong the time of grinding. This form of pan was once exclusively used for the fine grinding of all pottery materials. For the pavement is used Welsh chert from Flintshire, etc., or Derbyshire chert from near Bakewell, or occasionally Scotch granite from Skye; the runners come mostly from near Bakewell. The chert is associated with limestone, and the blocks used should be as free as possible from lime compounds. The flint is usually fine enough after 11 or 12 hours' grinding on the pan, but still contains some comparatively coarse material. It is then run into washing tanks, where the coarser particles settle, and the finer material is gradually run off by removing plugs at progressively lower levels.

The grinding cylinder is generally an iron drum lined with some hard material such as porcelain or quartz, etc. Besides the material to be ground, the cylinder also contains flint pebbles or hard porcelain balls. When a hard porcelain lining is used, its surface should be rough to give good results, and this may be ensured by the introduction of sharp pieces of flint. As the cylinder revolves (on a horizontal axis), the pebbles or balls exert a crushing and grinding action on the material, which is caught between the pebbles and the sides, and between the pebbles themselves. The size and number of the pebbles need adjusting, and also the number of revolutions per minute.

An important difference between the pan and the cylinder is that in the latter either wet or dry material can be ground. It is claimed that a cylinder can grind much more material than a pan in a given time, and with much less expenditure of power. On the other hand, it is objected that cylinder-ground material varies less than pan-ground material as regards sizes of particles, that in particular it contains relatively much less of the very fine particles, so that the packing is not so close, that the particles are less irregular than when pan-ground, that ware made from it is more liable to dunt (or develop fine cracks in the body), that flat ware made from it is less able to support its own weight when arranged in bungs in the warehouse, and that generally ware made from it gives more pitchers (or broken articles).

There is, however, evidence to show that with due care and proper regulation of the grinding process, cylinder-ground materials can be produced fine enough to give as satisfactory results as pan-ground materials—at any rate for earthenware, though for china it does not seem to have proved successful hitherto, possibly because of the lower degree of plasticity and tenacity of unfired china bodies. Part, at least, of the difference between pan-ground material and cylinder-ground material is due to the fact that the former is washed, but the latter is nearly always sieved without washing, as otherwise the output would be very much reduced.

Stone is not calcined, but after crushing is put on the pan, and under proper conditions is well ground in 11 or 12 hours. As in the case of flint, the ground stone needs washing to take out the coarser particles.

Felspar is treated much like stone, but usually takes longer to grind, and when ground it should be run direct on to the drying kiln, as it cannot easily be kept in a slop state owing to its strong tendency to set.

Bone is calcined before grinding. The grinding usually takes about 10 hours, and the ground product has to be carefully washed like ground flint and stone.

Clays are prepared by simply blunging or slipping, that is, agitating with water in a sort of tank called a blunger, which is octagonal or hexagonal in cross section, having iron sides, with usually a paved bottom, and a wooden cover. The central vertical shaft carrying obliquely set flat arms is caused to rotate, the arms serving to lift the material to the top of the blunger, where it is received by iron splash boards fastened to the sides, and the slip falls to the bottom, the slip thus becoming thoroughly mixed.

The clay in the blunger is mixed with suitable amounts of water—adjusted when necessary by adding more clay or more water—to give a slip of definite standard weight, which is usually 24 oz. to the pint in the case of ball clay, and 26 oz. to the pint for China clay. Water alone weighs 20 oz. to the pint. The writer once had the singular experience of meeting with ball clay "slip" which weighed less than 20 oz. to the pint—actually less than the same bulk of water. It had another peculiarity in that it would not flow, even when a containing vessel was turned upside down. Continued blunging caused no improvement, and the sliphouse operations became somewhat disorganized. Close examination of the ball clay slip under a lens revealed the presence of innumerable minute bubbles of gas, probably air entangled in the slip owing to the presence of some oily liquid which had got into the water. The most obvious remedy was the application of heat in order to expand the bubbles, and this was successfully accomplished by

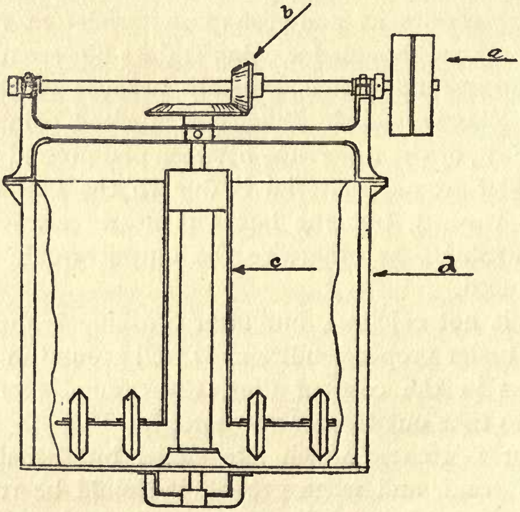

FIG. 12.—Over-geared slip blunger. (Manor Engineering Co., Fenton.)

temporarily fixing a branch steam-pipe with its open end near the bottom of the blunger.

The dry material in a standard pint of ball clay slip averages about 6½ oz., and China clay slip contains 9 to 10 oz. of dry solid in the standard pint.

Dry Mixing.—The mixing of dry materials by measuring (as in boxes) is not practised for any of the finer wares, and the method could not give very consistent results unless the materials were uniform as regards size of grain. Careful weighing of finely divided dry materials is commonly resorted to for the finest bodies (allowance being made for moisture, etc.), and the mixture is then blunged or slipped, that is, well agitated with water to form a slip or slop. The dry method of mixing requires less power and less space; it needs no mixing ark, and only one blunger. The wet method requires more power and machinery, and more space. The dry method is more expensive as regards labour and raw materials, for the flint and stone have to be dried after wet grinding.

Wet Mixing.—In this method, which is most commonly employed, the materials (finely divided) are first blunged separately, and the resulting slips (of definite pint weights) are run separately into a mixing ark or large vat, where they are well mixed together by agitation with revolving arms. The usual means of getting the right proportions is to fill up to successive marks on an upright stick with the several slips—in the case of earthenware, ball clay, China clay, flint, and Cornish stone, in the order named. Sometimes the stick is marked in inches (instead of the four special marks), and sometimes the side of the mixing ark is similarly marked, a specified height being filled up in either case with each of the several slips. A small but definite amount of stain—also in slop state—is added to each mixing to correct the slight creamy or yellowish tint which the ware would otherwise have after firing. The blue stain consists of cobalt oxide mixed with flint, stone, and other white substances, calcined, and then finely ground. Sometimes solution of cobalt chloride or sulphate is used instead for staining. A certain amount of blunged "cuttings" (or scraps of clay from broken unfired ware, odds and ends of plastic clay, etc.) is added to each mixing of slip. Such material by itself would give a more plastic clay than that freshly prepared, and so increases the plasticity of the full mixing.

This usual method of blending or mixing slips or slop materials cannot be regarded as very reliable, because it is practically impossible to gauge accurately the materials passing into the large mixing arks, and it is also difficult to make proper allowance for slight deviations in pint weights or densities of the prepared slop materials. Ordinary earthenware body slip is about 26 oz. to the pint, including about 9½ oz. of dry material.

It should have been mentioned that in running the different slops into the mixing ark, coarse sieves are generally used to catch any lumps of clay or dirt, etc. A fine sieve is used for the stain to ensure that none but very fine particles pass into the mixture.

The slip when properly mixed is passed through a series of lawns or sieves to intercept any coarse particles which may accidentally get in the slip. Such particles may include iron pyrites, lignite, quartz, sand, small lumps of clay, coarse flint or stone particles, and occasionally other foreign material. Very coarse material generally settles at the bottom of the blunger, which should be cleaned out from time to time. Iron pyrites if not removed would cause specks in the ware, or even blisters. Lignite would either burn away and leave surface holes or black specks, according as the supply of oxygen were adequate or not. Sand grains would also be liable to cause specks, as sand grains often have thin coatings of iron oxide.

The lawns for sifting are made of silk, brass, or phosphor bronze, and should be kept clean so that the slip shall not splash over the sides. There are three main types of lawn or sieve used in the pottery industry, the three-decked lawn, the cradle lawn, and the revolving lawn or rotary sieve. The two last named are self-acting as regards removal of the dirt and other rubbish, whereas the three-decked lawns need to have the rubbish removed at frequent intervals.

The sieved slip is passed over a series of magnets to remove any specks of iron or magnetic iron compounds. Commonly horseshoe magnets are fixed in the trough through which the slip flows to the stock ark, but sometimes special contrivances are used, often with electro-magnets.

The prepared slip was formerly converted into clay suitable for use by the potters by running it to a depth of 6 to 8 ins. over shallow drying kilns (" slip kilns ") made of brickwork or fireclay quarries or tiles with fires burning beneath. The fireplace is at one end, and the products of combustion pass along a flue to a chimney at the other end. In this way the water is slowly removed by evaporation, and the clay is obtained in workable condition. This method is now only used for comparatively small quantities of the clay mixtures, partly because of its slowness and the expense for fuel, partly because it requires very careful beating to make it as homogeneous as it should be, especially in view of the possible presence of hard lumps of clay which had been against the hot brickwork. The second method, now in general use except for small quantities of material, is to remove the excess of water by means of a filter press. A third method sometimes convenient for very small quantities of material, but much too slow and expensive for use on a large scale, is to pour the slip into plaster moulds, when the water is gradually absorbed by the plaster.

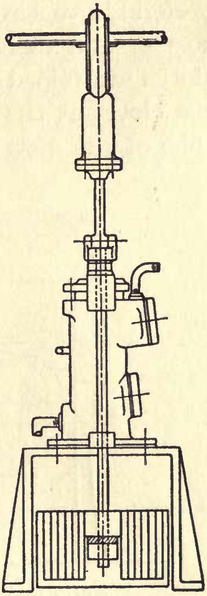

FIG. 13.—Patent automatic deadweight pump (for clay slip). (Gosling & Gatensbury.)

The filter press was invented by William Needham and James Kite (Eng. pats. No. 1669, July 14, 1853, and No. 1288, 1856; also Kite, No. 1300, June 15, 1854). It consists of a number of strong trays standing on edge side by side. These trays are grooved, and when placed together each adjoining pair encloses a space about an inch across. Within these spaces are arranged strong cotton press cloths, which are placed on the trays and carefully doubled over, the edges overlapping the bottoms and sides of the trays being folded up flat, so that each cloth forms a kind of bag. It is preferable to have two cloths, of which the outer is much coarser and merely serves to protect the inner; the two cloths are folded together in the tray. Near the middle of the cloth, at the point where it is first doubled, is fitted a tube of gun metal, through which the clay slip finds its way into the press. A stand-pipe, in communication with the supply-pipe from the press pump, passes along above the press, and nozzles fixed to this stand-pipe are connected with the tubes from the press cloths. Each nozzle has a tap, so that any chamber can be disconnected in case a cloth bursts. The clay slip being pumped with considerable force into the cloth bags, the water passes away through the cloth, and the clay remains. Pumping is then stopped, the nozzles are disconnected, the press taken apart, the cloths unfolded, and the clay taken out. The cloths are folded again immediately for another operation of the press.

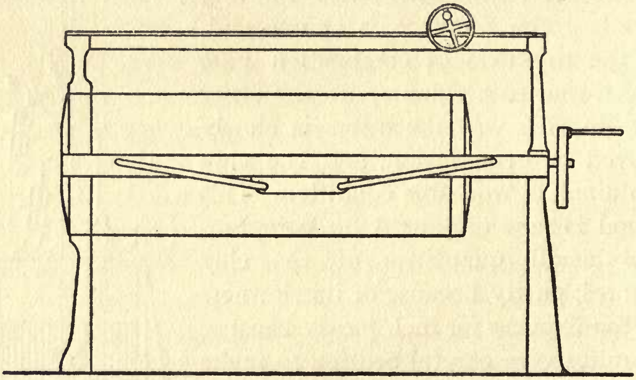

FIG. 14.—Iron filter press. (William Boulton, Ltd.)

The corrugated thick sheets or cakes of clay are rolled up and removed. The outer portions are always harder than the inside parts. The cloths need washing from time to time to keep the pores open, for if the water cannot escape readily the cloth may be burst. With reasonable treatment a press cloth ought to last four months or more. As the cloths contract when wet, they should be wet when folded in the trays, otherwise there is great risk of bursting. The trays and most other parts of clay presses were formerly made of wood, but there is a growing tendency to use iron presses because of their strength and greater regularity through absence of warping, etc. The only serious objection to iron presses is the risk of contaminating the clay, but with proper working this danger can be reduced to very narrow limits.

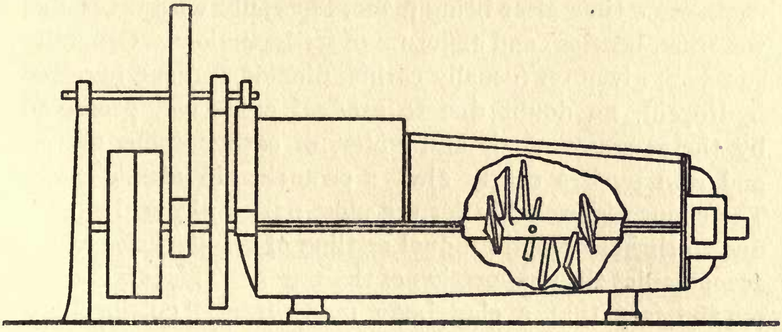

FIG. 15.—Pug mill. (William Boulton, Ltd.)

The clay from either the clay press or the slip kiln will rarely be of uniform consistency and free from air bubbles. This was formerly remedied by "wedging" the clay, that is, repeatedly cutting off a piece of clay with a wire and dashing it with great force against another piece placed on a block with plaster surface. The same result is now generally obtained by passing the clay through a pug mill. The essential parts of a pug mill are a cylindrical passage traversed by an axle to which are fixed iron blades set in such directions that they not only cut the clay, but they are always forcing it onward. The clay is charged into one end of the pug mill, and at the other end it is forced out as a solid block (usually square or rectangular in section) through an aperture at the other end, generally placed laterally (not terminally), at least in the ordinary horizontal pug mills. Some pug mills act vertically, notably those used for china bodies. The clay as it comes out is cut with wire into suitable lengths, and afterwards distributed to the workpeople, except when required for preparing casting slip.

Ageing.—It is often found advisable to set the prepared clay aside for "ageing" or "rotting." It has long been known that ceramic bodies become more plastic, more solid, and better as regards working qualities, by keeping them some time after being made, especially with occasional watering, beating, and exposure of fresh portions. Generally gases are given off (usually carbon dioxide and sulphuretted hydrogen), no doubt due to gradual oxidation, promoted by the presence of air and water, of carbonaceous matter and iron pyrites nearly always occurring in plastic clays. The change is probably for the most part a physical change due to shrinkage and gradual settling of the particles which accompanies the evaporation of the water. This is indicated by the fact that a clay body made from "cuttings" is always more plastic than freshly-made body, as already mentioned. Advantage is taken of this fact, in the case of certain bodies having only slight plasticity, to improve that quality by partly shaping the material on the potter's wheel, then shaving it down on the lathe and making up again, these operations being repeated several times.

Shaping.—The method employed for shaping articles depends on a variety of circumstances, such as the nature of the clay, the size of the piece to be made, and the shape of the piece. When the clay body is very plastic, and articles of rounded form are required, the method of throwing on the wheel is very suitable. For other shapes (oval, angular, or irregular), and for all shapes when the clay body is not sufficiently plastic, methods such as pressing or casting must be used.

Throwing.—The use of the potter's wheel dates from very remote times. The simplest (and probably the earliest) form of it is a disc of wood fixed on the top of a vertical spindle, which can be rotated by hand by the potter himself —known as a "thrower"—or by an attendant. The addition of a wooden wheel attached to the lower end of the spindle enabled the rotation to be produced by working with the foot or a stick on this lower wheel. A subsequent development was the introduction of an independent large wheel which an attendant turned round by means of a handle, and the motion was communicated by a cord or strap passing round this large wheel, and also round a small pulley fixed on the spindle to which the disc was attached. In modern times the potter's wheel has been turned by water power or steam power, and by means of cones and brakes the speed of rotation can be regulated to meet the thrower's requirements.

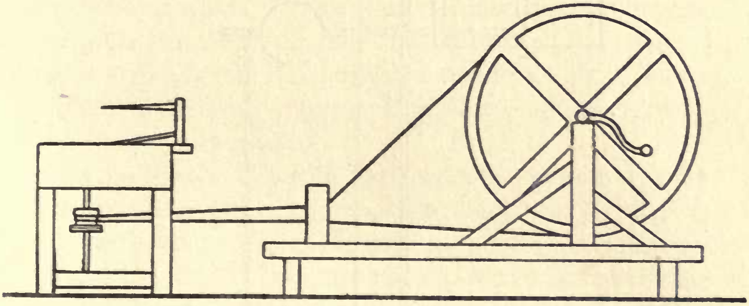

FIG. 16.—Hand-power throwing wheel. (William Boulton, Ltd.)

The thrower takes a ball of prepared clay of the proper weight, throws it on the rotating disc, and works it up and down with his fingers until it is quite uniform in texture and freed from air bubbles. He then places his thumbs in the middle of the clay, and by pressure between thumbs and fingers gradually works the piece into the correct shape. During this operation, his fingers and thumbs are kept moist by dipping in water at intervals, partly to prevent the clay from sticking to the skin, and partly to prevent a partial drying of surface parts of the clay through contact with the warm hand. The finished piece is cut off by a wire from the disc, and left in the drying stove until it is stiff enough for the turner (except in rare cases in which it is finished by the thrower himself).

In recent times the thrown and turned ware has greatly lessened in amount, the great bulk of articles other than artistic pieces being now made by machinery.

The turner finishes the shaping begun by the thrower, using mostly a horizontal lathe such as is used for wood and metals, etc. The excess clay should be turned off in shavings and not in dust, for in the latter case it would be almost certain to split before being finished. Artistic pieces are turned on a vertical lathe.

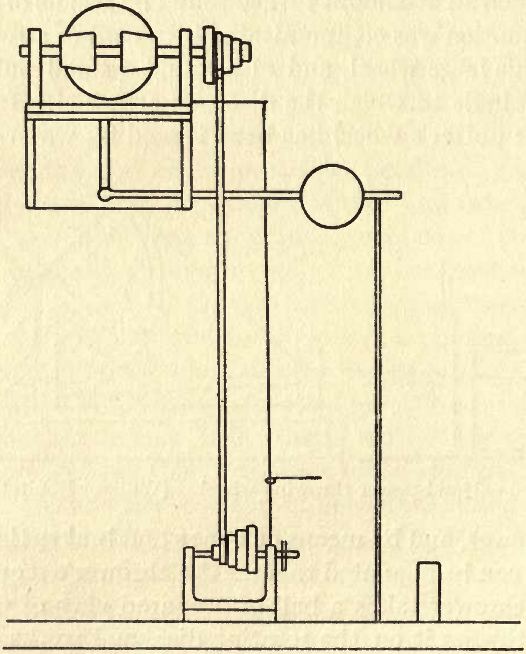

FIG. 17.—Power-driven potter's lathe. (William Boulton, Ltd.)

Pressing.—This is the operation of pressing clay on or into moulds, so that the clay takes the form of the mould. The presser formerly made most of the ware that could not be made with machines, as ewers, soup-tureens, sauce boats, teapots, etc., and the process may be said to be older than any other modern shaping process except throwing. In ordinary or plastic pressing, the clay is first flattened into a thin cake or bat, on a square plaster block, by beating it with a round plaster block to which a handle is attached. Sometimes batting machines are used for preparing large bats. The moulds, also usually of plaster, are mostly made of several parts. Each part of the mould receives a bat of clay, which is well rubbed down into it, the different parts are fitted together and tightly strapped, and the joints (or seams) are then well rubbed so that the clay shall form a single piece. When left to stand, the clay begins to dry, at the same time contracting slightly and becoming freed from the mould. When the clay is firm enough to be handled, the parts of the mould are removed, the clay piece has its seams and edges trimmed and sponged smooth, and finally the clay article is dried in a stove before being fired. Moulds of pitcher (fired clay), metal, sulphur, wax, etc., have been used.

Casting.—This method is used mainly with body compositions which are not very plastic, as in the case of ordinary porcelain and parian ; it is also used for pieces which cannot be properly pressed. The prepared slip is not in these cases necessarily obtained in the stiff plastic condition, but is concentrated so as to reduce the proportion of water. This concentration was formerly effected either by avoiding the addition of too much water or by letting the slip settle for a time, and drawing off the excess of water from the top. This procedure is now obviated largely by the use of certain alkaline substances in small proportions, those in practical use being sodium carbonate (soda ash), or sodium silicate (ordinary water-glass), or preferably both together. Caustic soda would also be effective in keeping the slip heavy without sacrificing fluidity, but it is not so convenient in use because of its strong corrosive action on the skin. The proportion of alkali to be used depends on the nature of the material, but the more plastic the material the more alkali is necessary to maintain the same degree of fluidity, or a given pint weight of slip, and the less readily does the piece come away from the mould. In case of trials where there is nothing to indicate the amount of alkali needed, a convenient starting point would be about $\frac{1}{8}$ of 1 per cent. (half sodium carbonate and half sodium silicate or water-glass) of the dry weight of the body.

It is advantageous in using very plastic bodies for casting to either substitute calcined clay (or kaolin) for part of the corresponding raw material, or to add 10 per cent. (or even more) of ground pitchers. Some earthenware manufacturers have added ground pitchers to their ordinary casting slip for some considerable time past.

The casting slip is poured into plaster moulds, which are then left to stand until the absorption of water by the porous mould has produced a sufficiently thick coating inside the mould. The remaining fluid slip is then poured off, the mould along with the clay cast being left to drain, after which it is transferred to a drying stove. The clay cast shrinks away from the mould in drying, and can then be removed from it, trimmed up, and thoroughly dried preparatory to firing it. Addition of a little salt or soda to the slip facilitates quicker delivery of the cast from the mould, but this would be very destructive to the moulds.

Casting is specially suitable for very thin ware. It also gives more uniform thickness to the piece of ware than could be got by pressing, and gives a very clear impression of the mould—especially of elaborate details; the contraction is also uniform, so there is less liability to splitting in the firing. A disadvantage is that as the body after casting is very porous, cast ware is more liable to craze (or form fine cracks in the glaze) than ware made in other ways. Greater drawbacks of cast ware are the excessive contraction it undergoes, and the great number of moulds required.

Handles of mugs, chambers, etc., are made separately by forcing clay out in long strips from a wad box (or squeezing box) through a hole in a metal plate, which gives the clay the desired shape; the strips are cut off in suitable lengths, bent into the proper shape, the ends being then trimmed, and the handles fixed by means of a little slip on the mugs or other articles. For the more ornamental handles small round rolls of clay are first produced with the aid of the wad box; these rolls are cut into suitable lengths, one of which is placed in one-half of a two-piece plaster handle mould, the other half being then fitted on, and the two halves pressed well together. The handle is removed after a short time, and placed on a board to dry, after which it is trimmed and fixed in its place by slip. In a similar way spouts are fixed on teapots, feet on soup-tureens, knobs on dish covers, etc. Pieces which are made in several parts are also stuck together in much the same way. Certain of these articles, teapots, for instance, are sometimes made complete by casting, special contrivances being employed.

Most dishes which are not round (but oval, etc.) are made by hand, a prepared bat of clay being carefully pressed on a mould; the mould is then placed on a whirler (or round block of plaster fixed at the top of a spindle), and the inside surface of the clay smoothed carefully. When dry enough, the dishes are fettled, and then placed face downwards on perfectly flat plaster slabs, so that they cannot go crooked in further drying.

The processes of throwing, pressing, and casting, subject to slight differences in detail when working with different bodies, are essentially all that are used for making the various types of pottery. For the purpose of saving labour much machinery has been introduced, though very strong opposition was offered by the workmen at the outset.

In pottery, as in other manufacturing industries, production is much increased by the proper application of suitable machinery. The motive power is largely derived from steam or water power, which is transmitted by shafting in the case of the heavy machinery of the slip-house and grinding mills, and by ropes or belts for the machines concerned in the making of the ware. In recent years electric motors have been increasingly brought into use in pottery works, especially for situations remote from the boiler. Rotary motion is produced in nearly all the machines, generally by means of a spindle, of which the lower end works in a socket, and the upper part in some kind of collar; a grooved wheel is fixed to the spindle, so that it can be turned by a running rope. The top of the spindle ends in a screw, on which heads or other appliances can be placed.

For making flat and hollow ware, an automatic batting machine is used, which has a spindle such as that just referred to, with a circular plaster block fixed (by means of an iron part) on the screw forming the top end of the spindle. A fixed iron upright supports an arm which works up and down on a pivot. This arm carries at one end a tool or spreader, which is a flat piece of iron, one end of which is just over the middle of the plaster block. The tool varies in size according to the size of bat required. An iron rod connects the other end of the arm with a lever attached to a cog-wheel which is moved by means of a screw on the spindle. Thus movement of the spindle sets the cog-wheel going, and that pushes up the lever and the arm, and so brings the tool down to or towards the plaster block. The workman places a lump of clay in the middle of the plaster block, and then starts the machine by setting the spindle in rotation. As the tool descends, the clay is spread out in a round flat bat of the thickness determined by the setting of the tool. On the tool reaching its lowest point, the lever is automatically released, the tool rises again, and the machine stops. In the absence of the machine the workman would have to beat out every clay bat by hand with a batter on a plaster block.

Jolleys (or plate machines) are special machines for making plates, saucers, bowls, etc., a different tool being used for each different size and shape. Each machine has a frame and bed fixed to a working bench, and has also a spindle ending above in a screw by which can be adjusted various heads into which moulds are made to fit. When in use, a mould is firmly fixed in the head, and should run quite true when the spindle is turned. Fixed to the bench (or bed) behind the spindle is an upright support, which works in a socket, and is kept at the proper height by a set pin. The upright support carries an arm and handle, capable of moving only vertically (up or down); the exact position of the lower end of the arm is regulated by a screw, and the tool-holders are firmly attached to this arm. A tool or profile is fixed to the tool-holder in the required position, and in working is held down by the handle connected to the arm. The other end of the arm (behind the upright) has a counter-weight which causes the tool-holder and tool to swing up when not held down by the workman.

In plates, saucers, and other flat articles, the mould forms the face or normally upper surface, and the profile or tool forms the outside or back of the piece. On the other hand, in hollow-ware (cups, bowls, chambers, soup-tureens, etc.), the mould forms the outside, and the tool gives the inside shape. Special modifications are used in making certain articles, and some of them have special names—such as the Monkey or Upright Jolley (for making chambers, jugs, jars, and pieces with large bodies and small mouths), the Automatic Cup-making Machine, the Automatic Chamber and Basin Machine, etc.

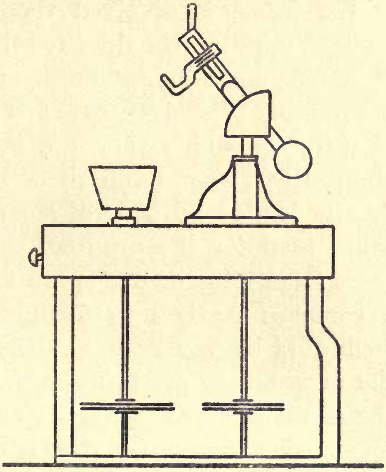

FIG. 18.—Rope-driven jigger and jolley (William Boulton, Ltd.)

Machines were introduced for making earthenware about eighty years ago, and the innovation met with such determined opposition from the workmen that considerable delay took place before the regular employment of machines for the purpose got well established. (See Eng. pats. 8339 and 8340, January 11, 1840, John Ridgway and George Wall. Also 9901, October 5, 1843, George Wall.)

Drying Stoves are used for removing as much as possible of the moisture before firing the ware. In some lands the sun's heat can be utilized for the purpose, but in this country at least that would not be practicable. The plaster moulds also need drying periodically in order that they may be worked to their full capacity. The stoves should be arranged so that the carrying to and fro of the ware shall be reduced to a minimum. Each stove is constructed about a central upright shaft resting in a socket below and in a bearing above. The shaft supports iron arms and ties forming a frame which divides the stove into compartments (mostly six). Each compartment is occupied by shelves on which the ware and moulds are placed, and the doors are made of the width of a compartment, so that as the frame is revolved the compartments are in turn brought opposite the door for the removal and introduction of moulds and ware. The size of the stoves, and especially the number of shelves, depends to some extent on the class of ware for which they are intended; a common size is about 12 ft. across and 10 or 12 ft. high. The stoves are usually heated by beds of steam pipes, the exhaust steam being used for the purpose. Sometimes hot air or waste gases from kilns or ovens are used in like manner; this is a common method in Germany. The drying is greatly facilitated by ventilation at the top of the stove to enable the moisture to get away readily. For large hollow-ware, the revolving stove is not suitable, shelving round the stove room being preferable; the heating is effected in the same way. In a recent American invention, the ware travels through the stove, alternately upwards and downwards in passing along. Two endless sprocket chains are connected with a series of sprocket wheels, and boards to support the ware are suspended from the chains. It is very efficient and very adaptable. (See *Trans. Ceramic Society, 19*, 26, 1920.)

After the ware has been dried, it is fettled and cleaned, and the edges of plates are polished. This is done on a whirler with a plaster head such as is used by a presser, but smaller and lighter. Very simple tools are needed.

The ware is then ready to be fired, unless decoration in the clay state is intended.

Decoration in the clay state is effected, before the ware is too dry, by applying figures, flowers, etc. (previously made in moulds) to the surface of the piece, fixing them by means of slip; by pressing (stamping) small dies, etc., on the ware; by modelling with the hands; by building up (as in the case of basket work or flowers); by perforation; by marking with scratched lines, dots, etc., or by the use of coloured slips, or by both these means jointly. Decoration by scratched lines is termed "sgraffito." Coloured bodies have also been used, the colour arising from the presence of certain mineral substances, mainly colouring metallic oxides. Such colouring of the body is applicable to all the best ceramic bodies, such as fine earthenware, porcelain, jasper, etc.

During the drying of clay ware, contraction or shrinkage takes place. A slight contraction takes place in the mould because of absorption of some moisture by the plaster. After the piece of ware has been removed (still somewhat moist) from the mould, it gradually loses all the water added to the materials for mixing purposes, etc., and also part of the moisture originally present in them, especially in the clays. As the water passes away, the solid particles draw closer and closer together. During the subsequent firing, all the remaining water is driven out—slowly and very gradually to avoid cracking—including the combined water in clays, and further contraction takes place in a similar way. After that, the particles begin to enter into chemical reaction, and the more fusible components become vitrified, and these changes are accompanied by a different kind of contraction, the amount of which increases as the clay body becomes more vitreous.

In earthenware bodies the proportion of fusible material is very low, so the contraction in such bodies during the finishing stage of firing is very low in comparison with that of vitreous bodies. The contraction in earthenware bodies is commonly about 8 per cent., or 1 in 12, but will vary according to the composition of the body (especially as regards the fusible constituents), and the temperature and duration of the firing. The contraction is also dependent on the method of manufacture, increased pressure being associated with reduced contraction. Cast ware contracts most, thrown and turned ware contract more than pressed ware, and tiles and other articles made with metal dies under great pressure will contract least. Hence special care is necessary in uniting parts made by different methods, particularly when the clay is very plastic. The same thing —difference of pressure—accounts for the fact that seams of a piece (where the parts of a mould fitted together) are always evident.

Sometimes—especially in tall pieces and in cast ware—contraction is greater vertically than horizontally, doubtless partly owing to the compressive action of the weight of the upper part on the lower part.

FIRING WARE.

The firing may be said to be the most important operation of all, for nothing done in other operations can make up for unsatisfactory firing. It is equally true that for satisfactory results good firing is necessary for glost (that is, glazed) ware as for the first or biscuit ware. The general type of oven used for firing earthenware is circular in section, with a dome or crown on the top. All consist essentially of mouths (fire-places), flues, and the single large firing chamber, but with differences in different parts of the oven. The mouths are arranged regularly round the outside of the oven, near the bottom. In the old-fashioned **Hob-mouthed Ovens,** which are still much used, the mouths project outwards (1½ to 2 ft.) from the sides, coal being fed in through a hole in the top, which can be covered with a slab of fireclay. The stack generally springs from the shoulder of the oven. It is assumed that cold air cannot easily be drawn into the flues while "baiting" (feeding with coal). In **Hovel Ovens,** the oven proper is surrounded by a circular hovel, which rises vertically to about the level of the shoulder of the oven, and then gradually narrows in the same way as the shoulder and neck of a bottle, the neck forming the stack which carries off the smoke, etc. The space between oven and hovel is barely enough for the distribution of the coal. These ovens have mouths protected from air currents, and repairs to the oven can easily be made, but the space round the oven is very limited for firing, and the draught is sometimes imperfect.

Stack Ovens have the ovens and stacks built together. They are solid and compact, but when the mouths are first lighted they are liable to smoke, and deposit dirt in the adjoining shops. They are also somewhat more difficult to repair, and are slow in cooling. **Down-draught Ovens** are much used for biscuit firing, and for firing firebricks. They can be worked with less fuel, and with better distribution of heat, owing to special arrangements of flues. Several kinds of down-draught oven have been extensively used. In the **Up-draught Ovens**, which are still mostly used for glost firing, the flames and gases from the mouths pass partly along horizontal flues below the floor of the oven to the central well-hole, from which they pass upwards through the middle of the firing chamber, and partly up short chimneys (called "bags") just inside the oven, and thence to the top of the oven. A pipe bung of fireclay rings, or saggars with holes in the bottoms, is often built up from over the well-hole to near the top of the oven. The crown has a central hole, controlled by a damper, which regulates the discharge of gases, etc.

In **Robey's Down-draught Oven** (patented by C. Robey, E. Banks, and T. Forester, No. 970, March 15, 1873), flues pass under the floor from each mouth to a central well-hole, and between each pair of these flues a passage runs through the floor of the oven down into a vaulted chamber below. This vaulted chamber is connected by a flue with the chimney stack, which either passes up the outside of the oven, or is quite separate from it and communicates with several ovens. On commencing to fire the oven, the damper on the crown-hole is opened, and the chimney flue shut off, but after the fires are well started the damper is gradually closed and the chimney connected. This oven is economical in fuel, but the distribution of the heat is by no means perfect.

Minton's Down-draught Oven (T. W. Minton, No. 1709, May 10, 1873) has very much thicker walls than those of ordinary up-draught ovens, and the mouths, which are only half the usual size (though slightly taller and narrower) and are built entirely in the walls, open into the interior of the oven only through bags. The only flues communicating with the well-hole are horizontal 9-in. flues passing under the flat floor to vertical flues situated in the oven walls between the bags. These vertical flues run up above the shoulder of the oven and open into a hood or hovel built on the top of the oven, and forming an upper chamber where printed ware can be hardened on, or certain kinds of pottery can be fired at a low temperature. The damper for the crown-hole is an essential feature of the oven, but there are no clearing holes round the shoulder like those in up-draught ovens. When the upper chamber is dispensed with, the vertical flues are omitted, and the gases then pass on from openings in the floor to a central opening leading to an outside chimney. The advantages of Minton's ovens are economy of fuel (often 30 to 40 per cent.), better distribution of the heat, and better control of the firing. Disadvantages are the greater cost (as much as 40 per cent. more) in building, greater wear and tear, and irregularities of firing unless the flues and air-spaces are properly proportioned. The greater wear and tear might probably be largely obviated by a suitable selection of refractory materials for lining the flues, etc. The crown-hole damper is raised to promote cooling of the ware after firing the oven, but if raised too quickly, some of the ware would certainly be dunted (that is, cracked), for dunting takes place between red heat and dull heat.

Wilkinson's Down-draught Oven (A. J. Wilkinson, No. 4356, March 20, 1890) has two sets of flues under the floor of the oven, the products of combustion passing through one set to the central well-hole, and thence into the oven—as also another portion directly upwards through the bags—

and the other set, receiving the gases, etc., through openings in the floor, and conducting them to dampered vertical flues running in the walls; sometimes the gases are allowed to pass away by openings in the crown. The heat of the oven is regulated by admission of air above.

Generally speaking, down-draught ovens are found advantageous for biscuit firing, because of the slower, steadier, and more uniform development of the heat, and up-draught ovens are mostly preferred for glost firing, because of the more rapid development of the heat and the more ready escape from the oven of the products of combustion and any other fumes—so that the liability to "sulphuring" (generally arising from partial reduction of lead compounds in the glaze) is lessened.

The hovel built over (and in some cases about) a pottery oven serves the useful purposes of creating a draught, facilitating the escape of smoke and other products of combustion, and screening the mouths from winds which might cause inequalities of burning—the fires in some mouths burning up fiercely, whilst in those on the opposite side the flame might be blown back out of the oven mouths. When the hovel starts from the shoulder of the oven, the latter is more or less surrounded by placing sheds (or saggar-house) and warehouses which screen the mouths from winds.

The so-called **Skeleton Oven**, which has come into extensive use, apparently combines in itself the best features of the various up-draught ovens, being simple to work, clean, easy to repair, quick to cool, and also giving satisfactory results, whilst occupying a comparatively small space. In a skeleton oven the stack is supported round the oven by a number of arches, leaving the oven separated from the shell or arches by a few inches only; the first three feet or so (up to the top of the mouths) of the oven and outside brickwork are built together, but above this level the oven stands quite free from the shell.

It may be noted that while very large ovens are economical as regards fuel, great attention is needed to get anything like a regular distribution of heat; they also take longer to set and draw, and longer to cool; ovens that can be rapidly and progressively filled, fired, and emptied, answer best for trade purposes.

Various other types of oven have been devised for firing pottery, including various forms of gas-fired ovens, and continuous ovens, but have been only partially successful in practice, except for comparatively low temperatures, in this country. They have been much more extensively used in the United States, Germany, and France, and it seems quite likely that in the not very distant future the use of some forms of continuous ovens and kilns may spread considerably, even in the United Kingdom.

In firing bricks, common flooring tiles, some kinds of terra-cotta and stonewares, the exclusion of smoke and flame is not necessary, but for firing earthenware, china, parian, white stoneware, or other white or artificially coloured bodies, it is necessary to employ saggars to protect the wares from the direct action of flame, etc.

Saggars are fireclay boxes of various sizes and shapes, but mostly round or oval. They are made of mixtures of fireclay (commonly termed marl) and grog, the latter being crushed or ground material from old saggars, firebricks, broken biscuit ware (earthenware or china), or any refractory material which owing to previous firing or in other ways is not liable to any considerable amount of contraction. For special purposes the ordinary grog has been advantageously substituted by comparatively expensive materials such as emery, corundum, or carborundum. The most important qualities of saggars are that they should be sufficiently refractory to resist the heat of the ovens without losing their shape, and that they should bear sudden changes of temperature without fracture, and should have strength enough to stand whatever pressure they may be subjected to in the oven. These properties may be secured by using a fireclay (or marl) rich in silica, and as free as possible from ironstone nodules. Flying off or scaling of bits of saggar may be caused by [illegible] particles of quartz, iron compounds, or lime, or by imperfect mixing. Local fireclays (marls) with about

55 to 60 per cent. of silica are refractory enough for making saggars to be used for earthenware and tile bodies, but for the harder china bodies, etc., the more refractory fireclays from the Stourbridge, Dudley, and Ironbridge districts are used for saggar making. As all such fireclays are massive, and usually hard in their natural condition, the marl for saggars is first pulverized by passing through chilled iron rollers or by grinding on a heavy roller pan. It should then be left to weather, and after addition of the grog the whole is well mixed and turned over, then left for some time before being used. Better mixing is secured by passing it twice through a pug mill. The coarser the fireclay the less grog is required, and the more plastic the fireclay the more grog is required. The greater the proportion of grog the more open the mixture and the better the resulting saggars, providing the working qualities of the mixture are not unduly lowered. The less water and the stiffer the mixture the better the saggars, though it is harder work to make them. Heinecke states that the best saggars are obtained by mixing the dry clay and grog, and afterwards moistening, and that they have been made very successfully in this way in several German factories. As the sides of saggars have mostly to bear considerable weights (due to saggars above them with contained ware), whilst bottoms have only to support the ware actually in the respective saggars, the bottoms need not have the same strength, and so the bottoms should have relatively more grog than the sides. For the sides 6 to 8 cwt. grog, and for the bottoms 10 to 12 cwt. grog, to each ton of fireclay, are sometimes used. Some fireclays can be worked with two parts only to three or more parts of grog. In general, a larger proportion of grog is used on the Continent and in America than in Great Britain; from 40 to 60 per cent. grog is mostly used in Germany, the clay being half fat and half lean. Sometimes 5 to 10 per cent. charcoal powder or saw-dust is added. In practice it is found to be better to use a mixture of clays rather than a single kind of clay. For small saggars fine and medium grog are most suitable (say 1 : 3), and for

larger saggars medium and coarse grog are best. Increase in either size or proportion of grog decreases strength in both the green and fired states, and also increases porosity.

According to F. A. Kirkpatrick (*Trans. Amer. Cer. Soc.*, *19*, 268, 1917), with the use of equal weights of grog and plastic fireclay (the latter ground to pass a 20-mesh sieve) the best mixtures for resistance to repeated heating and cooling contain grog of 4–8 mesh, 8–12 mesh, and 12–20 mesh in the proportions 1 : 2 : 2 and 1 : 3 : 1 respectively, and grog of 8–12 mesh, 12–20 mesh, and 20–40 mesh in the proportions 1 : 1 : 3 and 1 : 1 : 1 respectively; the best mixtures for giving strength to the saggars are grog of 12–20 mesh, 20–40 mesh, and 40–80 mesh in the proportions 2 : 1 : 0, 3 : 1 : 1, 2 : 2 : 1, 1 : 2 : 0, 1 : 3 : 1, 0 : 2 : 1, and also the 12–20 mesh or 20–40 mesh alone.

Saggar marls and bonding fireclays fall into two classes, vitrifying clays (which vitrify at a comparatively low temperature, and keep their low porosity over a wide range of temperature without swelling or being overburned), and open-burning clays (which remain porous and highly absorbent up to a comparatively high temperature). With proper size and proportioning of grog particles, proper proportioning also of vitrifying clay and open-burning clay (for combined strength and porosity), and with uniform mixing and tempering, saggars of the desired strength in the cold can be obtained. Good proportions (recommended by G. H. Brown in *Journal of American Ceramic Society*, vol. *2*, 1919) are 50 grog, 20 vitrifying clay, and 20 open-burning clay. Low-grade China clay would be very good for the open-burning clay.

It is good practice to grade the grog particles, and to include definite proportions of different sizes in the mixture for making saggars, as this gives a more complete skeleton of grog particles, united by the bonding clay. Addition of sand to the mixture makes the saggars more liable to crack, since the saggar as a whole may be unable to resist the effects of the volume changes of the sand grains. For mixing and tempering saggar mixtures, a wet pan has been found to give better results (in the United States) than a soaking pit followed by pug mill. The wet pan develops maximum plasticity of bond clays, so that more grog can be added, and this involves less contraction. Saggars made from wet pan mixtures also mould better, and have smoother surfaces. With the mullers of the wet pan slightly raised the grog particles can slide under without being crushed. The use of a low-grade ball clay as bonding clay would enable more grog to be used in the mixture.

Small saggars may be made by expression from a press in the same way as ordinary drain pipes are made. The tubes so obtained are cut into lengths, and bottoms are stuck on with clay slip.

The sides of saggars are commonly made by beating out the mixture of marl and grog. The flattened cake is cut up into pieces of suitable size, and each such piece is then placed round a wooden drum or mould. The drum with its attached side is then fitted to a beaten-out piece of mixed saggar marl for the bottom, and the two are well worked together. The drum is then withdrawn, and the inside of the saggar made good, after which the saggar is taken away on its shord (wooden support) to dry. The pieces for the sides of saggars are sometimes prepared by pressing under rollers. Hydraulic and other machinery have also been employed for making saggars complete, but have not come into anything like general use. The same statement applies to casting processes. There seems no valid reason why such processes should not be commercially successful, provided they are properly carried out with suitable materials.

It may be added that in many factories the saggar-making department receives less attention than almost any other, with the result that enormous losses occur. The opinion seems to be widely prevalent that it is not worth serious attention or that no great improvement is practicable. This is a costly heresy, for great economies could be effected by competent supervision. It should be realized that a considerable increase in outlay for better raw materials (as, say, low-grade China clay and ball clay, or even high-grade fireclay, instead of common saggar marls, with carefully selected material for grog) would be handsomely compensated in the greatly extended average life of the saggars, and consequent saving in making costs. Probably the best materials for general use would be inferior ball clays (as bonding clays), inferior China clays (as open-burning clays), with grog in the form of crushed biscuit pitchers—either good white earthenware or china, though for china biscuit ovens it might be advisable to use a more refractory grog material. As an extreme case it may be recalled that K. Eleod reported saggars cast from corundum (fused bauxite) or carborundum, mixed with a little English ball clay, as having been repeatedly raised to white heat and thrown into cold water without showing even cracks.

Another point to be borne in mind in connection with saggars is that the thinner the walls and bottom the better, providing they have sufficient strength. This gives advantage as regards both heating up and cooling, as well as in carrying by the placers. In this connection it may be mentioned that in Germany smaller saggars are much used, and it has been even contended very plausibly that saggars for single pieces of ware (as a teapot, etc.) would be economical as regards space in the glost oven. The thin bottom is often strengthened by two ribs crossing at right angles in the middle outside.

Broken saggars—in not more than three pieces—can generally be profitably mended by using a rather stiff paste, made with water-glass and water, of dust grog, alone or mixed with some China clay or fireclay. The paste should be made as required, for it soon sets. Too much raw clay should not be used.

Placing or Setting is the arrangement of the ware, usually in saggars, for firing in the ovens. The details differ according to the classes of ware, various devices being employed for supporting the ware in position so as to avoid distortion, etc., and glost placing differs in some respects from biscuit placing, for in the latter there is no glaze to melt and stick together pieces which may be in actual contact; in glost placing, pieces must not be allowed to touch one another, and to prevent this, pointed and sharp-edged supports are used, so as to leave as little marking as possible when (for commercial reasons) a number of pieces have to be placed in the same saggar. Saggars are piled up in "bungs" or columns, and these bungs are arranged in successive "rings" in the ovens. The products of combustion (including flames) pass along the interspaces between the saggars.

Effects of Firing.—The effects of firing ceramic wares appear in regular sequence when the temperature is not raised too rapidly. In the biscuit firing, water (which may contain sulphuric acid, derived from sulphur in the fuel) is often deposited on ware below 100° C. Between 100° and 120° C. this water evaporates, along with the other water present in the ware as moisture. From 200° to 480° C. organic matter is burned away, water is driven off from hydrated oxide of iron, and certain hydrated silicates may possibly also lose their water. In the next stage, between 480° and 600° C., the essential substance of clay is decomposed, and loses its combined water. At still higher temperatures, between 800° and 900° C., calcium carbonate (when present) is decomposed into lime and carbon dioxide. Finally, with further rise of temperature, the various oxides recombine to form double silicates, or alumino-silicates, etc., from 900° up to about 1300° C. In the case of hard porcelain, sillimanite is formed at the higher temperatures. The iron speck which often appears on ware after a sharp firing of a biscuit oven, probably arises from reaction between iron compounds, water vapour, and organic substances, when the firing is carried on too quickly between 400° and 500° C., that is, when the whole oven is just getting red. Before contraction commences, there is generally a small though distinct expansion, probably due mainly to the physical action of the escaping gases and vapours. In the case of earthenware, contraction proceeds very rapidly between 900° and 1300° C., and in a body like parian containing a much larger proportion of alkali, contraction takes place similarly between 840° and 1160° C. or thereabouts. The limits are similarly modified in other cases, according to the proportion of alkali present. The action of the alkali is modified in china bodies by the presence of the bone-ash, and though china undergoes great contraction, the upper limit is higher than for parian and other bodies high in alkali.

Besides the contraction and changes in chemical composition of bodies, caused by biscuit firing, there are also usually changes in colour, hardness, tenacity, and density. Hardness is always associated with contraction, and increases along with the latter.

Colour Changes depend on the amount and nature of the iron compounds present, on the presence or absence of certain other impurities which may affect colour, and on the firing atmosphere (whether oxidizing or reducing). A creamy tint is given by ½ to 1½ per cent. of iron oxide, as in ball clays; 2 to 4 per cent. of iron oxide gives shades of yellow (cane or buff); more than 4 per cent. iron oxide gives salmon, bright red, and chocolate tints, terra-cotta containing about 7 to 8 per cent. iron oxide.

Clays containing iron oxide are generally yellow or red in their natural condition, and the colour becomes deeper after firing. Iron sulphide (pyrites) and iron carbonate give clays a dark-grey colour, inclining to bluish or greenish; these tints are as a rule completely changed after firing. Lime or magnesia usually lightens the colour of a fired clay containing iron, owing to the formation of nearly colourless double silicates. This is well exemplified by the yellow London malm bricks, made of chalk and a red brick earth. Carbonaceous matter in clay also tends to bleach it, because of the reduction of ferric oxide to ferrous oxide during the firing. In the case of Staffordshire blue bricks, a ferruginous marl is fired to a high temperature, and the fires are then damped down with slack. The colour of the bricks is due to formation of magnetic oxide (Fe_3O_4).

General Course of Biscuit Firing.—The temperature should be raised slowly to about 120° C. all through. Then it should rise more quickly to about 450° C. (when the bags appear just red), then more slowly up to 600° C. (the oven being then a solid red throughout); then it should rise very quickly to 950° C., and finally it should rise steadily to the finishing temperature, followed by a soak according to the size and thickness of the ware. Mr. Joseph Burton suggests, for the best course of earthenware biscuit firing, about 15 hours up to 120° C., 20 hours from 120° to 450° C., 16½ hours from 450° to 600° C., 16 hours from 600° to 950° C., and 20 hours from 950° to 1140° C. (a total of 87½ hours), followed by, say, 3 hours' soak, and then cooled down to 660° C. in 16 hours. In some works the total firing period from starting to reaching top heat is 20 to 30 hours less than this. For china, the biscuit firing can be taken on more rapidly up to 600° C. than with earthenware.

For the control of the firing, thermo-electric pyrometers or electrical resistance pyrometers are sometimes used, with or without recording apparatus. But more commonly other contrivances are employed, such as pyrometric cones (or Seger cones, which soften and bend over or collapse at fairly definite temperatures), Holdcroft's bars (which bend under their own weight at corresponding temperatures), Buller's rings (which indicate temperature, etc., by the measured contraction), and small "bits" made of certain other clay mixtures (sometimes the regular body composition used at the factory), the contraction of which is measured by means of a gauge. The last-named represents the old Wedgwood pyrometer. Within recent years Messrs. Wengers, Ltd., have introduced trial pieces termed "calorites," which are short rods or bars somewhat resembling Holdcroft's thermoscope bars, but only one end is supported in a socket, the other end standing out free to bend as the proper firing conditions are approached. The rings and "bits," depending on contraction, have to be drawn from the ovens at convenient intervals for measurement, but the cones and bars are placed so as to give their indications, whenever required, by simple inspection through spy-holes. For ascertaining the maximum temperature reached in certain parts of the oven, other means are sometimes employed, such as Watkin's Heat Recorders, which consist of refractory rods, each with a number of pellets melting at different temperatures; the maximum temperature in this case is the melting temperature of the pellet which was the last to show distinct indications of fusion.

GLAZING OF EARTHENWARE, ETC.

Most ceramic bodies are more or less porous after being fired, and in order to render the surface impervious to water and other liquids a glaze (or glassy coating) is applied. This glaze when properly fired on the ware has also a decorative effect, for the sake of which it is commonly applied also on vitrified bodies which are themselves practically impermeable to liquids. The essential qualities of a good glaze are: (*a*) suitability to the body, as regards both composition and behaviour when heated and cooled, that it will neither craze (form very fine cracks) nor peel (chip off from edges of ware); (*b*) sufficient hardness to resist wear, especially when used for cooking or other domestic purposes; (*c*) power of resisting water or acid vapours and (in many cases) all acids other than hydrofluoric acid; (*d*) clear transparency and brilliance following prolonged exposure to gradually increasing temperature. It should not be thick enough to obscure the modelling. The melted glaze should have sufficient tenacity not to run off vertical or sloping surfaces, but should not be too stiff to flow smooth on flat surfaces. It should dissolve colouring materials (metallic oxides) without forming unsightly separations. It should not act too strongly on underglaze colours. The same purposes are served by an enamel, which differs from a glaze in being opaque and not so completely vitrified. Enamels are, in fact, often nothing more than lead glazes containing some tin oxide, which makes them opaque. Both glazes and enamels may be variously coloured by the addition of certain oxides of metals, etc.

These stipulations are met by the salt glaze on stoneware, and the glaze on hard porcelain, and—though not quite so completely—by the glaze on the best English bone porcelain. Most other glazes regularly used are more or less defective in the respects indicated, though they may answer for most purposes which a glaze is intended to serve.

Glaze is applied to pottery, etc., in most cases in one of the following ways:—

(1) By **dipping** or **immersion.** This is the usual method for fine earthenware, china, etc., and is the quickest and cheapest way of glazing large quantities of ware. The finely ground materials are mixed with a suitable proportion of water (as previously ascertained by actual trials, and afterwards checked by finding the weight of a pint) in a dipping tub or trough, and the dipper plunges the articles singly into the glaze for a very short time, taking precautions to get an even coating of glaze on the ware. The excess of glaze is allowed to run off while the ware is resting on a lawn or fine netting. The porous surface of the biscuit ware absorbs water, and a deposit of glaze accumulates. This causes the glaze left in the tub to get gradually heavier, and water has to be added from time to time to restore the original strength approximately, which may be checked either by weighing a pint or by means of a gauge in the form of a simple hydrometer. Most dippers can judge by the feel of the glaze on putting a hand in it. Adjustments have also to be made for marked differences in porosity of the biscuit ware (due to differences in the biscuit firing), and for various other circumstances, as differences in thickness of ware, different shapes, etc. Cleanliness is particularly necessary throughout.

(2) By **sprinkling** (or watering) the ware with glaze of creamy consistency. This method is resorted to in the case of ware which is vitreous in the biscuit state, so that it has practically no power of absorption. The glaze is allowed to run over the piece while it is moved to and fro until it is entirely covered, when a slight jerk causes any superfluous glaze to drop off. The same plan is adopted for glazes of different colour used on the same piece, the outside being glazed by dipping and the inside by means of glaze ladled in.

(3) By **volatilization.** This is effected by first raising the biscuit ware to a suitable temperature, and then putting the glazing material (preferably damp) in the oven through special openings in the crown, and through the mouths. This is the method used for salt glazing, the salt volatilizing and penetrating to the ware in the saggars (which are not—like those in which dipped ware is placed—practically closed to fumes and gases by wads, that is, rolls of clay carefully fixed all round where one saggar rests on another). Mutual chemical action takes place, and, it is often stated, with formation first of soda and hydrochloric acid gas, the soda then combining with silica on the surface of the body to form a hard and insoluble sodium silicate. As has been pointed out by Dr. J. W. Mellor, among others, it is more probable that the salt, steam, and body materials react together forming a double silicate of soda and alumina as a coat of glaze both inside and outside. The salt glaze is also liable to contain small amounts of other bases, especially lime. The salt-glazing process is only suitable for bodies containing a considerable proportion of uncombined silica. The process of **smearing** is essentially the same, but in this case the saggars are washed with the glaze, and powdered glaze in cups is put in the saggars. The glaze at a certain heat volatilizes, and the ware in the saggars becomes glazed. The advantage of smearing is that all cavities and incisions, however deep or fine they may be, are glazed without losing any sharpness of outline. Smears consist of two or more (rarely only one) of the following: red lead (or sometimes litharge), Cornish stone, salt, potash, nitre (saltpetre), bone-ash, flint, lime.

Flows are similar to smears, and were introduced (about 1840) with the object of making the cobalt blue and some other colours spread or flow. The same substances are used as for smears, and sometimes whiting, alum, sal-ammoniac. The flow in small biscuit cups is put in the saggars with the glazed ware, and the fumes produced when firing cause certain colours to flow slightly into the melted glaze.

(4) By **dusting** the ware with dry powdered glazing material (as red lead or litharge). This method is generally used in the clay state, while yet somewhat moist, and the ware undergoes a single firing, in which both body and glaze are matured together. Such dry dust is very injurious to the health of those who have to use it.

(5) **Painting** with a brush, employed in a few exceptional cases.

(6) **Spraying, Blowing, or Aerographing** is rather a decorative process than mere glazing, colours or coloured glazes being chiefly used.

Glazes fall conveniently into four classes, according to composition:—

(1) **Alkaline Glazes,** which are mainly silicates of the alkalies (potash and soda, more particularly soda) or of the alkalies and lime. Examples are salt glaze, and the remarkable ancient Egyptian turquoise glaze.

(2) **Felspathic Glazes** (consisting of silica, alumina, alkaline and alkaline earthy bases), which contain a large proportion of felspar or felspathic rock, sometimes softened to a certain extent by admixture of more fusible materials. Examples are the glaze of hard porcelain and brick glazes, as well as some glazes of English porcelains, borax being added in the latter cases to increase the fusibility.

(3) **Lead Glazes,** consisting mainly of silicates and boro-silicates of alkalies and alkaline earths, with some alumina, and softened by addition of lead oxide (introduced either as red lead or white lead, the latter being practically a combination of carbonate and hydroxide of lead). They often contain felspathic materials. Examples are all ordinary transparent glazes for English earthenware, and those for most English porcelains.

(4) **Enamels** or opaque glazes, which generally have the composition of lead glaze, but are rendered opaque by the addition of tin oxide, oxide of arsenic, bone-ash, or zirconia, etc.

Lead glazes may be either raw (unfritted) or fritted.

In raw glazes the components are merely ground together, the harder materials being put on the mill to be partly ground first, and the softer materials being added later.

In the case of fritted glazes, all the substances soluble in water—including soda ash, borax, boracic acid, potash (pearl ash), nitre (saltpetre), etc.—with some of the others (as whiting, flint, etc.), are first fritted together, and the frit (or imperfect glass) is afterwards ground like the harder components of raw glazes, the softer ingredients being added at a late stage. Fritting is necessary for glazes containing much lime, magnesia, or baryta (which are not themselves fusible) in order to promote combination which might otherwise need a high temperature to start. For fritting small quantities of glaze materials, clean flinted saggars or crucibles are used, and for large quantities, special reverberatory furnaces called frit kilns are employed.

The composition of glazes varies within wide limits according to the duration, maximum temperature, and other conditions of firing. Their composition is conveniently represented by the molecular formulæ employed by Seger, which show the relative molecular proportions of the different oxides present, the alumina and silica being kept separate, and the basic oxides—collectively termed the fluxes and represented as RO—being taken as constituting one molecular proportion jointly ; boron, when present, is calculated separately as B_2O_3.

According to Seger, the glazes in actual use fall within the limits indicated by the glaze formulæ for the respective classes. Ordinary earthenware and fine French faience, $RO : 1{\cdot}5SiO_2$ to $RO : 3SiO_2$. English and German white earthenware, $RO : 0{\cdot}01Al_2O_3 : 2{\cdot}5SiO_2$ to $RO : 0{\cdot}4Al_2O_3 : 4{\cdot}5SiO_2$. Hard porcelain glazes, $RO : 0{\cdot}5Al_2O_3 : 5SiO_2$ to $RO : 1{\cdot}25Al_2O_3 : 12{\cdot}5SiO_2$.

The SiO_2 often includes boric acid in proportions from 0·25 to 0·05 of the silica. RO = potash, soda, lime, magnesia, baryta, lead, and the colouring oxides. The corresponding firing temperatures range from below the melting point of silver (cone 010) to cone 18.

Glazes containing no alumina tend to become devitrified, and are also liable to run off or soak into the porous body. Alumina in glazes removes these risks, and at the same time raises the melting point. The composition of ordinary glasses can be represented by $Na_2O.CaO : 5SiO_2$, or $RO : 2{\cdot}5SiO_2$, which comes within the first pair of the above limits; a larger proportion of silica causes the glass to be easily devitrified, whereas a lower proportion of silica causes loss of ductility and viscosity; in each case it becomes worse as regards working qualities. Devitrification consists of a separation of silicic acid, or of silicates, in crystalline forms which cloud the glass and destroy the surface lustre, producing a mass resembling porcelain if heated for a long time at softening temperature. Such separations can only be removed by heating the glass up to a very liquid condition.

The silicates of magnesia, lime, baryta, and strontia alone are stony or slag-like in appearance, and therefore do not form transparent glasses.

For the same acidity, it is found in practice that the fluidity increases with the number of fluxes (basic oxides) present.

The leadless glazes mostly contain lime and alkali (potash or soda, or both). Sometimes magnesia, baryta, or zinc oxide is used, or more than one of these.

The alkali-lime glazes have a much more limited application than lead glazes, and much more care is necessary in order to get good results from them. The permissible proportions range between 0·2 equivalent of potash or soda to 0·8 equivalent of lime, and 0·6 equivalent of potash or soda to 0·4 equivalent of lime. As regards the alkalies it appears to be of no consequence whether potash or soda be used, except that soda gives a slightly more fusible glaze than potash, and both present together make it still more fusible. Glazes high in alkali are better suited for bodies rich in quartz, glazes low in alkali are better suited for a high alumina body. A great peculiarity of lime glazes is that they require a high content of alumina to produce transparent glasses at all on slow cooling, as otherwise they always give dim and milky glasses—excepting glazes corresponding to ordinary glasses, and these would craze badly on bodies high in alumina. A silica content of 4 equivalents is needed to give a sufficient gloss, and at least 0·5 equivalent of alumina is necessary. With lead glazes the alumina seems to tend always to make glasses or glazes more dim and milky, and in the lead glazes used the alumina is much less than the minimum amount necessary for the lime glazes. More than one equivalent of boric acid in these lime glazes tends to produce a milky appearance, but at least 0·5 equivalent is necessary to give sufficient fusibility. Hence with lime-alumina glazes to mature at a temperature not exceeding the melting point of gold, the frits to be used (with addition of 10 per cent. kaolin) must be kept within the limits $0{\cdot}6K_2O(Na_2O).0{\cdot}4CaO : 0{\cdot}5Al_2O_3 : 4SiO_2.0{\cdot}5B_2O_3$, and $0{\cdot}2K_2O(Na_2O).0{\cdot}8CaO : 0{\cdot}6Al_2O_3 : 0{\cdot}5SiO_2.1B_2O_3$.

Such formulæ enable the percentage composition of a glaze or frit, etc., to be calculated, and conversely the formula can be obtained from the percentage composition. With fritted glazes, allowance has to be made for the loss of weight (CO_2, H_2O, etc.) sustained on fritting.

Working out a suitable glaze for a particular body would be difficult and tedious by haphazard trials, but by starting with a mixture based on a definite chemical formula within known limits, an experienced investigator, even without much knowledge of practical potting, need not take long in reaching the desired result.

Similar calculations may be made in the case of body compositions, but with them it is usually preferred to take the alumina (instead of the fluxes jointly) as 1 molecule.

Some approximate values—accurate enough for all ordinary calculations—of combining weights for certain ceramic materials are appended :—

Substance.	Formula.	Molecular or combining weight.
Alumina	Al_2O_3	102
Barium oxide (Baryta) ..	BaO	153
,, carbonate	$BaCO_3$	197
,, sulphate	$BaSO_4$	233
Borax	$Na_2B_4O_7.10H_2O$	382
,, anhydrous (Borax glass)	$Na_2B_4O_7$	202
Boric acid	H_3BO_3	62
,, oxide	B_2O_3	70
Calcium oxide (Lime) ..	CaO	56
,, carbonate	$CaCO_3$	100
,, sulphate (Gypsum) ..	$CaSO_4.2H_2O$	172
Ferric oxide	Fe_2O_3	160
Lead oxide (Litharge) ..	PbO	222
Red lead (Minium)	Pb_3O_4	683
White lead	$2PbCO_3.Pb(OH)_2$	773
Magnesia	MgO	40
Magnesite	$MgCO_3$	84
Potash (Potassium oxide) ..	K_2O	94
Potassium carbonate (Pearl-ash)	$K_2CO_3.2H_2O$	154
Nitre (Saltpetre)	KNO_3	101
Potash Felspar (Orthoclase)	$K_2O.Al_2O_3.6SiO_2$	559
Silica, (Flint, Quartz, etc.) ..	SiO_2	60
Soda (Sodium oxide) ..	Na_2O	62
Soda ash (Sodium carbonate)	Na_2CO_3	106
Soda crystals	$Na_2CO_3.10H_2O$	286
Sodium chloride (Salt) ..	$NaCl$	58·5
Sodium nitrate (Cubic nitre)	$NaNO_3$	85
Tin oxide	SnO_2	150
Titanium oxide (Rutile) ..	TiO_2	80
Zinc oxide	ZnO	81
Kaolinite and Clayite (Clay substance)	$Al_2O_3.2SiO_2.2H_2O$	259

It should be borne in mind that any given formula or recipe for a glaze is practically useless in itself, inasmuch as it is suitable only for a particular body or bodies, and even with them only under fairly definite conditions of firing. Such a formula or recipe, however, may serve as a convenient starting point, providing the investigator has the requisite knowledge and experience to make good use of it.

Seger deduced the following general conclusions as regards the chemical and physical relations between the composition of the body and that of the glaze. By increasing the clay bonding material in a body, its expansion with a given rise of temperature is decreased—and crazing increases with the same glaze—but addition of a plastic clay decreases the coefficient of expansion in a less degree than the less plastic kaolin or China clay. Increase of felspar also reduces the contraction (or expansion) of the body. Increase of quartz (free silica) increases the coefficient of expansion—and peeling increases with the same glaze—and this increase is more rapid with increasing fineness of grain. The coefficient of expansion is also increased by increasing hardness of the biscuit firing, so that very easy biscuit firing promotes crazing, whilst very hard biscuit firing promotes peeling and cracking of the edges. Seger gives the following as practical means of adjusting defects arising from differences in contraction of body and glaze on cooling :—

I. To remedy crazing. (1) Reduce the plastic bonding material (clay) in the body, and at the same time increase the silica. (2) Replace part of the clay substance used as kaolin by an equivalent quantity in the form of plastic clays (such as ball clay). (3) Reduce the felspar (or Cornish stone). (4) Use quartz (free silica) in a more finely ground condition. (5) Fire harder for the biscuit.

II. To remedy peeling, or cracking of the edges, or breaking away of attached parts such as handles, spouts, etc. (1) Increase the plastic clay substance, and at the same time decrease the quartz (free silica). (2) Replace part of the clay substance used as plastic clay by an equivalent quantity as kaolin. (3) Increase the felspar (or Cornish stone). (4) Use quartz (free silica) less finely ground. (5) Fire easier for the biscuit.

Seger also points out that the coefficient of expansion of the glaze decreases with increase of silica, and increases with increase of fluxes (bases). The tendency to crazing decreases—and tendency to peeling increases—by increasing the content of boric acid to replace part of the silica. Hence boric acid decreases the coefficient of expansion of a glaze. The relative fusibility of lead-soda glaze, lead-potash glaze, barium-soda glaze, lime-soda glaze, and lead-magnesia glaze, is in the order named, the lead-soda glaze being the most fusible. The tendency to crazing is least in the magnesia-soda glaze, and greatest in the lead-soda glaze, the others being intermediate as regards fineness of the network of cracks. In case peeling should take place, it would be most pronounced with the magnesia-soda glaze, and decrease in the order indicated above. If alumina to the extent of $0{\cdot}1Al_2O_3$, $0{\cdot}2Al_2O_3$, $0{\cdot}3Al_2O_3$, be introduced into a glaze of the composition $0{\cdot}5PbO$, $0{\cdot}5Na_2O : 2{\cdot}5SiO_2$ (which represents a normal glass), the melting point rises rapidly, and at the same time the product becomes clouded and enamel-like. The added alumina appears to exert no perceptible influence on the expansion or contraction of glazes with temperature changes.

Seger gives the following as practical means to remedy crazing by alteration of the glaze. (1) Increase of the silica content, and decrease of the fluxes, but the ratio of silica to fluxes must not exceed that of a trisilicate. Further increase of silica would involve addition of more alumina as well—and also rise of the melting point—or otherwise a tendency towards devitrification would be developed. (2) Increase of boric acid at the expense of the silica, the melting point of the glaze being lowered thereby. (3) Substitution of a fluxing oxide of high combining weight by one of lower combining weight, thereby raising the percentage of silica, and also raising the melting point of the glaze.

Increase in thickness of the glaze layer increases the tendency to crazing. A glaze which crazes after a short or easier fire may adhere to the body without crazing after a long and hard glost firing. This is explained by mutual chemical action, the glaze becoming richer in alumina by taking up some from the body.

Seger gives the following as practical means to remedy peeling, cracking of the edges, etc., by altering the glaze: (1) Lowering the silica content and at the same time increasing the fluxes, but the ratio of silica to fluxes must not fall below that of a bisilicate. Below this ratio silica can only be reduced by reducing alumina at the same time, which would also have the effect of lowering the melting point of the glaze. (2) Increase of silica at the expense of boric acid, which without other changes would raise the melting point. (3) Substitution of a fluxing oxide of high combining weight (as lead oxide or barium oxide) for one of low combining weight (as lime or soda), which lowers the percentage of silica and also lowers the melting point of the glaze.

Seger's rules for increasing the fusibility of a glaze are the following: (1) Decrease the silica content, and thus raise the percentage of basic fluxes, keeping within the limiting ratios of trisilicate and bisilicate in order to avoid devitrification or a tendency to run off the ware respectively. (2) Substitute a more energetic flux for a less energetic one, but retain the same acidity. (3) Increase the number of fluxes present, keeping the same acidity. (4) Decrease both alumina and silica, keeping within the limits of acidity mentioned in (1) above. (5) Increase the boric acid, with or without corresponding reduction of the silica. In (1) the same effect would obviously result from increase of fluxing oxides, especially of lead oxide. The brilliance of the glaze also increases with the fusibility. When increased fusibility is produced by boric acid, the resulting glaze is also more brilliant, but has less hardness (being more easily scratched), and also has much greater action on underglaze colours.

All these general statements of Seger apply strictly for a particular range of conditions as regards composition, firing, etc. Nevertheless they serve as useful guides, if allowance be made as far as possible for any important differences.

Coloured Glazes are prepared by the addition (in suitable proportions) of certain mineral substances—chiefly metallic oxides—to a white glaze. Thus Salvétat gives a white glaze of wide adaptability consisting of 4 parts red lead, 2 parts flint, and 1 part calcium borate; this gives with addition of 2 or 3 per cent. of cobalt oxide a blue glaze, with 8 or 9 per cent. of copper oxide a bluish green glaze, with 4 per cent. of ferric oxide a yellow glaze, or with 3 per cent. manganese oxide a brown or purplish-brown glaze. Different shades would be obtained by increasing or decreasing the amount of colouring oxide added. Similar proportions might be tried with other glazes, but it should always be borne in mind that different glazes may react differently on colouring oxides. Many of the colours applied on the glaze are not available for underglaze decoration owing to the destructive action of the melted glaze. All the colouring metallic oxides, with the single exception of copper oxide, form compounds with a lower expansion than that of lead oxide. That is why it is so difficult to obtain satisfactorily certain colours (especially turquoise) from copper.

Crystalline Glazes are produced as the result of the devitrification of the glassy composition. The crystals most readily produced are those of zinc silicate, which can be obtained of a size easily visible to the naked eye, by the slow cooling of a leadless glaze containing zinc oxide and potash. They tend to form in rosettes distributed irregularly. The crystals can be coloured by adding nickel oxide or cobalt oxide to the glaze. The author has himself obtained in this way fine blue crystals by addition of commercial oxide of nickel. Titanium oxide also favours crystallization, but the crystals are minute. Manganese oxide may likewise give crystallization.

The **drying, placing,** and **firing** of glazed ware, are carried out in much the same way as the corresponding operations for unglazed ware, with the important difference that special precautions have to be taken that the pieces shall not touch each other, for otherwise they would become stuck together at points of contact by the melting and subsequent solidification of the glaze. In the biscuit firing this is not necessary, except in the case of vitrified wares like porcelain, parian, or stoneware, though some care is needed to prevent deformation of such articles as dishes (open and covered), cups, and similar pieces; in most cases smaller pieces may be put inside the larger hollow-ware. Another important difference is that for the glost firing wads (small rolls of clay) are laid round the upper edge of each saggar, so that when covered the saggars become practically dust-tight and air-tight, or at any rate sufficiently so to prevent smoke, etc., from entering them. As there is little water to be driven off, and the clay body has been previously fired, the early stages of gradual heating are much shorter in glost than in biscuit firing, with the result that the whole firing lasts usually, in the case of large ovens, 20 to 25 hours, as compared with 45 to 55 hours commonly allowed for firing a large biscuit oven.

DECORATION.

Decoration may be under the glaze or over the glaze (on-glaze), and may be applied by painting or printing, etc. Excluding decoration in the clay state, which has already been alluded to, pottery decoration may be roughly classed as **underglaze decoration,** including painting and printing, and **enamel** or **on-glaze decoration,** including painting, printing, lithography, gilding and silvering, lustres.

Some eight or nine years ago, the author conceived the idea that bright-red crystals (in outline at least) might possibly be obtained by the use of copper compounds. With this object in view, an aqueous solution of a copper salt (sulphate, nitrate, or chloride) was applied to the white glazed surface of a small earthenware vase, and when crystals had been deposited over the surface, the vase was dried, and afterwards fired under suitable reducing conditions. Two trials only were made, and red crystal forms were actually obtained, but unfortunately they were so very small and so crowded as to possess only slight decorative value. The trials were abandoned for a time, but no favourable opportunity has since occurred for further testing the idea. In passing, it may be mentioned that the author had previously discovered that, with proper firing, a good plain copper-red colour—giving the effect of a fine red glaze—can be readily obtained by similar application of a solution of a copper salt to the carefully cleaned surface of a white glazed piece, then drying and firing as in the case just referred to. It was further ascertained that very satisfactory liquid for this purpose is a solution of copper chloride or copper nitrate in alcohol (ordinary methylated spirit answering very well instead of alcohol). One advantage of this method is that little or no cleaning (or polishing) is necessary after the firing. It may be added that the quality of the colour apparently does not depend on strength of solution, for solutions of several different strengths were used, and comparatively weak solutions gave as good a colour as the stronger solutions. It cannot be too strongly emphasized that the conducting of the firing is the decisive factor in these copper reds.

Before leaving the subject of crystalline glazes, it may be pointed out that the foregoing experiences suggest a general method of perhaps wide application for obtaining various crystalline glazes, coloured or uncoloured, and in most cases without necessitating reducing firing conditions. For instance, it seems possible with proper precautions to get coloured crystals containing zinc by the use of a solution of zinc sulphate containing some isomorphous nickel sulphate or cobalt sulphate, etc. Such crystals, of course, would not be zinc silicate, and perhaps might not take up the colouring material easily. It would seem possible that the application over the crystals of rather dilute silicate of soda solution before firing might result in the formation of silicate, though on the other hand too high a temperature might be necessary to effect that change. The author regrets he has not been able to explore this extensive field himself, and as he sees no early prospect of doing so he has decided, after careful consideration, to give others the chance of taking up the quest.

The very earliest decoration consisted in ornamentation of the clay by scratched lines (sgraffito), etc. The next decorative device (at any rate in this country) was the application of white and coloured slips to the surface of the clay before glazing; barbotine or slip painting is a modern style of decoration of the same character. This naturally led to painting with colours when the common clay bodies, often dark-coloured, were replaced by materials which, after firing, yielded a lighter ground of more or less yellowish tint (cream-coloured), and finally white. The immediate object of painting was imitation of the decoration of Chinese porcelain. Printing on pottery, etc., is of purely English origin, dating from early in the second half of the eighteenth century. Lithography is a comparatively recent development.

Printing on pottery is generally believed to have been introduced by John Sadler, at Liverpool, in or before 1756, that year being the first which has been verified with certainty; it was used on Bow porcelain in the same year, and in both places was on the glaze. Sadler took Guy Green into partnership. Printed enamels (on copper) are known to have been made at Battersea three years earlier. Underglaze printing is first known at Worcester (on porcelain) in 1757. The familiar willow pattern was first produced by John Turner in 1780 at Caughley, close to the present Coalport. About 1783 James Robinson and Thomas Lucas introduced the use of "oils" and the method of washing the transfer paper off the biscuit ware, and the process of hardening on the colours before glazing. Later improvements have been chiefly in matters of detail, as regards colours, paper, presses, etc.

The design is engraved on a copper plate (often in the form of a cylinder or roller), and the colour, mixed with a special oily composition known as printers' oil—which enables the colour to adhere to the biscuit ware—is spread over the plate and well rubbed into the lines and hollows. Excess of colour is then removed by means of a large flexible knife, and the surface of the plate is cleaned. A sheet of special paper is saturated with a size consisting of water and soft soap, and is then spread over the engraved plate. By working the press, which is only a modification of an ordinary printing press, the pattern is fixed on the paper. The paper is next detached from the plate, the waste paper cut from it, and the pattern is placed on the ware and rubbed well with a roll of flannel, when the colour is absorbed by the porous surface of the biscuit ware. The paper is easily washed off after soaking in water, and the ware is then dried. The oily matter is in most cases removed by a special firing (termed "hardening on") in a muffle kiln, at a comparatively low temperature. After this the ware is ready for glazing.

Enamel Printing is done in the same manner as underglaze printing, but usually with the special enamel colours. It is often employed to print outlines which are then filled in by painting. It is also much used for badges, lettering, etc.

The chief mineral colouring oxides used for decoration in ceramics include cobalt oxide (giving blue and black), nickel oxide (green, etc.), copper oxide (green, red, brown, and blue), chromium oxide (green), manganese oxide (brown, violet, and black), iron oxide (red, brown, yellow, green, black), titanium oxide (yellow), antimony oxide (yellow and orange), uranium oxide (yellow, orange, or black), iridium oxide (black), tin oxide (opaque white), besides certain substances such as chromate of iron and other chromates, silicates, etc. The so-called native chromate of iron, consisting essentially of ferrous oxide and chromic oxide, is not a true chromate, but in practice acts like the artificial chromate obtained by precipitation; it gives browns. A few oxides such as alumina, zinc oxide, tin oxide, lime, which alone do not give rise to characteristic tints, powerfully modify the colouring effects of other substances. A notable example is the pink or crimson, produced by tin oxide and lime with a small proportion of chromium oxide; the olive green produced by iron in presence of lime is another instance. Black is produced by various combinations of oxides, especially the oxides of iron and chromium (or the equivalent chromate of iron), manganese, and cobalt. One manufacturer at least was in the habit of obtaining black by simply mixing samples of various colours. Various substitutes for tin oxide have been tried to get opaque white, but the only one to approach it is zirconia or preparations based on it, such as the "terrar" used for that purpose in Germany. Several comparatively rare oxides, as those of tungsten and vanadium, have been used for the preparation of ceramic colours (yellow).

It may also be noted that cobalt oxide alone always gives a strong blue either to a body or glaze, inclining to violet in the latter case; mixed with oxide of zinc it gives an ultramarine blue, and mixed with alumina it gives a fine sky-blue colour, whilst any other shade of blue can be obtained by mixing with other colouring oxides. In like manner the effect of manganese oxide depends on the nature of the glaze; alkaline glazes are coloured violet, boracic glazes brown, and lead glazes intermediate tints. So, also, with copper oxide, in boracic or lead glazes it gives a green colour, but in alkaline glazes a turquoise blue; under reducing conditions alkaline glazes are coloured a fine purplish red, but boracic or lead glazes are more inclined to orange or brown.

Underglaze Colours.—These are derived from a limited number of mineral products, which are capable of resisting the action of the melted glaze, and consist mainly of oxides of cobalt, chromium, iron, manganese, and antimony, as well as certain compounds such as chromate of iron.

To assist in protecting the underglaze colours from the action of the glaze, certain other materials are also mixed with the colouring substances, such as flint, China clay, etc. The main points to attend to are to get the materials thoroughly well mixed together, and after calcining the mixture (and washing when necessary) the preparation should be ground very finely to get the best results. As pointed out by A. Granger, intimate admixture can be easily secured by using soluble substances, preferably salts which when heated yield the colouring oxides. The solutions are mixed in proper proportions, and then evaporated to drive off the water. An alternative method is suggested by the usual way of preparing purple of Cassius, of which gold and tin are essential components; two or more oxides may be precipitated together from a mixed solution, and the precipitate is washed, etc., as may be necessary. This plan is followed, with good results, in at least one well-known British factory.

Enamel or On-glaze Colours.—These are in reality nothing more than coloured glasses, fusible at a comparatively low temperature, which at a red heat become fixed on the glaze. As the action on them at that temperature is only slight, a much greater variety is available. These colours consist of the colouring substance mixed with a suitable flux. All are fired in muffle kilns, and are classed as regular kiln colours and hard kiln colours, according to the lower or higher proportion of flux they contain. Nearly all the enamel colours are prepared by grinding the components, then melting the ground mixture, and grinding very finely the fused product. The only exceptions are the colours prepared from gold (largely in the form of purple of Cassius), and the iron-red. The gold colours are prepared by well mixing the components, and gently calcining the mixture below a red heat; the colour produced in the kiln ranges from rose through carmine and marone to purple, at temperatures between a clear red heat and almost white heat. The red from iron contains red ferric oxide, obtained by careful calcination of dried copperas (ferrous sulphate) at temperatures of 400° to 420° C., the colours obtained outside this range being very inferior; a suitable flux consists of 6 parts lead oxide, 2 parts flint (or other form of silica), and 1 part borax glass; 3 parts of this flux may be mixed with 1 part of red oxide. Some colours, as the uranium black and the copper red, can only be produced under reducing conditions. From the author's experience it may be stated that the production of fine reds from copper depends much more on careful attention in the management of the firing than on the materials used, and for this reason it seems very unlikely that such effects will ever be produced cheaply.

Lustre Decoration.—This style of decoration, so well illustrated by the Hispano-Moresque pottery (produced by the Moors in Spain during mediæval times), has been revived of late years. The colouring components of the lustres, which are applied to surfaces already covered with glaze or enamel duly fired on, are essentially preparations of silver and copper. The lustre is fired on the ware in a kiln at a red heat, the kiln being filled with smoke when the full temperature is reached. The cuprous oxide formed by reduction provides a fine red background, and on this is often formed an iridescent film of copper or silver. In this case also practically everything depends on the management of the firing.

Decoration by Coating with Metal.—Gold, silver, and platinum are the only metals used for this purpose, the two latter being often employed to modify the effects produced by gilding. Details as to application will be found in Sandeman's "Notes on the Manufacture of Earthenware," and in books devoted to the decoration of ceramic wares.

STONEWARE.

The distinguishing features of stoneware are impermeability combined with opacity, though the degree in which these properties are possessed depends on the firing as well as on the composition. Several varieties come under this heading.

Ordinary Stoneware (often termed "common" stoneware).—This has usually a coloured argillaceous body, though sometimes only slightly blue or yellow, and is prepared in a pasty or dry manner, and may be with or without glaze. For its production are used vitrifiable clays containing fluxes (alkalies, lime, magnesia) and ferric oxide. In a reducing atmosphere the iron oxide would be reduced to ferrous oxide, which would then act as a flux. A medium vitrifiable clay suitable for making stoneware contains about 68 to 75 per cent. silica, 20 to 25 alumina, 2 to 10·5 lime and magnesia, and 3 to 5 alkalies, with sometimes 10 to 15 per cent. iron oxide. Sometimes a fusible clay is made more refractory by addition of a proportion of fireclay, with also some silica, if necessary, to give a composition similar to that of a normal stoneware clay. Sometimes, again, a similar result is obtained by adding fluxes to a fireclay, preferably finely powdered felspar or pegmatite (or similar material—Cornish stone for example); from considerations of economy, calcareous clays, marls, and calcium carbonate are used, or (better) blast-furnace slag, which is an impure calcium silicate. Bodies thus prepared contain about 51 to 55 per cent. silica, 19 to 22 alumina, and 22 to 25 lime, together with small amounts of iron oxide, magnesia, alkalies, and manganese oxide. The difference between the action of alkalies and of lime as a flux is noteworthy. Lime, when the temperature of decomposition of the carbonate is attained, has a tendency to form rapidly throughout the mass a double silicate of lime and alumina, with perhaps aluminates of lime also, so that it softens soon after vitrification commences, and the ware may easily lose its shape. On the other hand, alkalies, in the form of mica or felspar, act quite differently; the minerals melt, and the flux only gradually acts on the surrounding silica and alumina, and a comparatively long interval after the beginning of vitrification precedes deformation. In such bodies, the alkalies are about 2 per cent. and the lime 6 to 10 per cent. The colour of stoneware is due (apart from the very rare presence of manganese oxide) to iron oxide and to the firing conditions. Grey or bluish-grey colours are produced in a body containing a little iron, and fired under reducing conditions—best above 800° C. Yellow colour is due to very little iron, or to iron along with lime, fired under oxidizing conditions, and in like circumstances a larger proportion of iron oxide without lime gives a brown or even black colour. A regular black can only be produced, without the use of manganese oxide, by firing under reducing conditions and the deposition of carbon in the pores before the body vitrifies; for this it is best to put the ware in saggars filled with powdered charcoal or coke.

Drain Pipes of true stoneware may be made from a thinned vitrifiable clay, or from a mixture of fireclay with felspar or pegmatite, etc. On economical grounds a slightly vitrifiable clay or a fireclay is sometimes mixed with a fusible calcareous clay, and in that case the ware is rarely fired to vitrification owing to the great risk of deformation, and so it does not acquire the full degree of impermeability. The same result would follow from the use of fireclay alone, but in this case owing to want of flux to promote complete vitrification.

Straight pipes can be made from the plastic material either on the potter's wheel or by expression; in the latter case, the socket is made separately from part of a similar but larger pipe, and joined on by hand, or is made by machine. The last of these three methods is the most extensively used.

The firing takes place in round down-draught kilns, or in semi-continuous kilns, or continuous kilns with several burning spaces. When the maximum temperature is reached, sea-salt is thrown into the kiln; it volatilizes a little above 800° C., but only decomposes towards 1200° C. in contact with silicious material, with the result previously mentioned in connection with the glazing of earthenware, a superficial coating of glaze being formed. To avoid excessive lowering of temperature the salt should not be introduced all at once, but in several portions at intervals.

Culinary and Chemical Stoneware is mostly made from a fairly pure vitrifiable clay, which does not need washing. It is chiefly made on the wheel, and rarely by expression (as cylindrical parts of bottles or pots, to which the other parts are joined on); where necessary, moulds are used. This ware is usually rough or salt-glazed, but sometimes a cheap glaze is applied by dipping, or brushing on, or powdering on, the unfired body; only alkaline-calcareous glazes are available, and for cheapness are used in the form of blast-furnace slag, or a mixture of cinders, lime, and sand.

Fine Stoneware.—This was an English invention, and is still extensively made in this country. It is made of ball clay, China clay, and Cornish stone, with sometimes addition of flint, and occasionally without the China clay, though the latter makes it whiter. These white bodies contain about 70 to 75 per cent. silica, 20 to 25 alumina, 0·5 to 1 lime, and 3 to 5 per cent. alkalies. The preparation of the body and the shaping are as described for earthenware, and the firing is also conducted similarly.

Mortar Body (sometimes called Wedgwood ware after the inventor) is a specially hard fine stoneware used for making mortars and pestles for grinding.

Jasper (also invented by Wedgwood) is a fine stoneware in which Cornish stone is largely replaced by cawk or heavy spar (barium sulphate). This body is variously coloured—blue by cobalt oxide, green by chromium oxide, etc.

Black Basalt, or Egyptian black (another of Wedgwood's inventions), is a variety of fine stoneware consisting of ball clay, calcined ochre, and manganese oxide.

Fine stoneware is often left dull. It is sometimes glazed by smearing—a mixture of sea-salt with red or white lead, etc., being put in the saggars with the ware. The lead volatilizes, probably as chloride, and this in contact with the surface of the ware forms lead silicate, which glazes it. Glazes similar to those for earthenware are often used, containing alkalies, boric acid, and lead oxide (besides alumina and lime).

ENGLISH PORCELAIN, OR BONE PORCELAIN.

This, as the name implies, was invented in England (towards the middle of the eighteenth century), and is still made there almost exclusively. Its firing temperature is much below that necessary for hard porcelain, and this not only reduces the cost of manufacture, but also makes it easier to decorate, and permits a much wider range of colours to be employed. It is, of course, not so hard as the chief continental porcelains, but the chief reason why it is not made to any great extent elsewhere lies in the inherent difficulties associated with the manufacture, for the range of possible composition of a satisfactory body is very limited, and extreme care is necessary to avoid heavy losses in the firing. John Dwight, of Fulham, who took out patents (Eng. pats. 164, April 23, 1671, and 234, June 12, 1684), made excellent stoneware, some of which approached porcelain in character, but the origin of English porcelain was probably not long before Heylyn and Frye's patent (No. 575, July 15, 1741), and that of the same Thomas Frye (No. 649, November 17, 1749). Frye was for some years manager of the famous old china works at Bow (London).

It is only quite recently that it has been definitely established—by Dr. J. W. Mellor and his collaborators at the Stoke-on-Trent Pottery Laboratory—that the practical limits of composition are so very narrow. The normal constituents are China clay, bone-ash (ground calcined bones), and Cornish stone, the best proportions being apparently 44 or 45 per cent. of bone, with equal weights of the clay and stone. Any material departure from these proportions, or at any rate from the relative proportions of clay and stone, invites trouble. An increased proportion of clay (whether introduced as such, or associated with the stone) tends to produce blue or brown china, which coloration is known to arise through transfer of some of the phosphorus from the bone to the iron, which occurs to the extent of about 1 to 1½ per cent., in a bone china body. This may be otherwise expressed by stating that the presence of a high proportion of alkalies (in the stone) prevents the transfer of phosphorus from the bone-ash to the iron. An attempt to steer clear of this difficulty by increasing the stone (or using the same proportion of a softer stone which contains relatively more alkali) would involve serious risk of blistering or bloating of the body. The composition is so nicely balanced that a change only from a softer to a harder variety of Cornish stone may cause a perfectly white body to become blue (and possibly brown later through oxidation, or conversely a softer stone instead of a harder one may make a perfect body liable to blister. Even a variation in the proportion of water present in the same variety of stone, or in the China clay, may cause similar effects. Indeed all three varieties—blistered, blue, and perfect china—may arise from the same body through irregular mixing. It is remarkable that the proportion of bone may be varied considerably—and variation of the water present in it is accordingly of less importance than in the case of clay or stone—providing the amount of China clay and Cornish stone are kept nearly equal. Other important facts concerning English china will be found in papers by Dr. J. W. Mellor and Mr. Bernard Moore respectively, in vol. 18 and vol. 5 of the *Transactions of the Ceramic Society*. It may be added that small proportions of flint or of ball clay are sometimes used in the body.

The body for bone china is usually prepared by the wet method as for earthenware (though with some differences in detail), but it is much less plastic than earthenware. Vertical pug-mills are generally used. As regards shaping, much of the ware is made on the potter's wheel, and a comparatively small amount is produced by hand pressing in plaster moulds. Within the last few years a considerable proportion has been shaped by casting.

The glaze usually contains alkalies, lime, boric acid, and lead. China biscuit being at most only slightly porous, the glaze is used much thicker than for earthenware, and is applied by dipping. Colour decoration may be applied underglaze or on-glaze, including lithographic printing.

FRENCH SOFT PORCELAIN.

This is sometimes called "fritted" porcelain or Réaumur porcelain, and was the first type of porcelain made in France. It is strictly a glass (the composition being very like that of a plate glass, except the relative proportions of the several bases), but is made like pottery, and has similar appearance and usage. It was superseded by hard porcelain, but its manufacture has been revived from time to time. The body consists of a mixture of 75 per cent. of a glassy frit, with 17 chalk and 8 chalk marl. The glassy frit contained

60 per cent. silica, the remainder being chiefly potash and soda, with small amounts of alumina and lime. The plasticity of the body was so slight that it was mixed with water, soft soap, and parchment size, before it could be shaped in plaster moulds by compression with a plaster chuck. The piece was finished (when dry) by turning. The firing resembled that of bone porcelain and earthenware, consisting of a biscuit firing at a relatively high temperature, and an easier glost firing. The glaze consisted of silicates of lead, potash, and soda, and was applied by pouring on. Owing to excessive contraction of the body, the pieces had to be supported by suitable props made of the raw body. Colouring was on-glaze only.

New Sèvres Porcelain (introduced in 1884) has a body somewhat like the preceding, but even richer in lime. The biscuit firing is to cone 9. The glaze differs from the previous glaze in having lime instead of lead oxide, and also in being much richer in silica ; it is applied by dusting or by dipping. The decoration may be either underglaze, on-glaze, or with coloured glazes, and can include the use of copper blues and iron reds.

SEGER PORCELAIN.

This is an argillaceous soft porcelain, and is an imitation, both as to body and glaze, of Japanese porcelain. It is made of 30 per cent. felspar, 35 to 40 quartz sand, and the remainder clay or kaolin or both. The glaze has the same composition as Seger cone 4 ($0{\cdot}3K_2O.0{\cdot}7CaO.0{\cdot}5Al_2O_3.4SiO_2$, prepared from 35 parts whiting, 83·5 felspar, 26 China clay, and 54 flint). The biscuit firing is very easy, and the glost firing is to cone 9. Though composed of the same materials as hard porcelain, the greater proportion of felspar enables it to be fired at a much lower temperature, but in hardness and some other important properties it is very much inferior to hard porcelain.

PARIAN.

Parian is really a variety of soft porcelain which is generally left without glaze. Any soft porcelain could be so employed, but in most cases the appearance would not be satisfactory, the surface being too dull or otherwise deficient.

In England, bone porcelain for this purpose has been replaced by a special composition (first prepared by Copeland in 1848), which fires to a slightly yellowish tint and with a waxy surface; the name parian is derived from its resemblance to marble from Paros. The body is prepared mostly from a mixture of China clay (kaolin) and felspar or Cornish stone, with or without small proportions of glassy material. It may be coloured to imitate various natural stones. **Carrara** is less translucent than parian, and is thus intermediate between the latter and stoneware; it is so called from its resemblance to the famous Tuscan marble. Parian is often shaped by casting, because of its slight plasticity. It is fired in England at the same temperature as for bone porcelain, and owing to great contraction, as well as softening, projecting parts are kept in position by supports made of the same raw body. Parian is much used for statuettes.

HARD PORCELAIN.

This constitutes the main type of porcelain made on the Continent, and also in China and Japan. The terms "hard" and "soft," as applied to porcelain, indicate that the former requires a greater heat in firing, and also offers greater resistance to heat; they also indicate a corresponding relationship as regards the effective mechanical hardness of the glaze on the surface of the porcelain.

Hard porcelain is generally made of kaolin (sometimes two, or even three kinds), quartz, and felspar, the quartz and felspar being often introduced as pegmatite (or similar granitic rock), and in some cases a small proportion of lime (as carbonate) is included. In strong contrast with soft porcelain, hard porcelain has a very easy biscuit firing (in an upper chamber of the oven, at about 800° C.), followed after glazing by a hard firing at a temperature ranging from about 1300° to 1400° C., or even higher, to mature the body and glaze together. The biscuit firing in this case is only intended to enable the ware to bear manipulating for glazing, etc. As the firing is conducted under reducing conditions, the porcelain acquires a faint bluish white tint. The glaze of this hard porcelain cannot be scratched by steel.

Messrs. Mintons at Stoke-on-Trent, about 70 years ago, made hard porcelain from a mixture of 100 parts by weight of China clay, 5 ball clay, and 20 felspar, according to (W. G. Turner and Herbert Minton's) Eng. pat. 8124, June 22, 1839. This manufacture was under the superintendence of the late Mr. Arnoux, who was the son of a French hard porcelain manufacturer, and the ware produced was of good quality. The loss in firing was excessive, however, mainly owing to defective saggars—though they were made of ball clay from Dorsetshire mixed with grog from similar saggars—and the production was discontinued.

Probably China clay would have answered much better for the saggars, if the difficulty of shaping could have been surmounted (as by use of a proportion of ball clay to give greater plasticity).

Long before this brief effort of Minton's, hard porcelain was made in this country (first at Plymouth) by William Cookworthy, the discoverer of China clay and Cornish stone. Cookworthy took out a patent (No. 898, March 17, 1768) for his porcelain, and after a few years sold it to Richard Champion, of Bristol, who obtained an extension (No. 1096, September 15, 1775) and made hard porcelain at Bristol until 1781. The patent was then sold to seven Staffordshire potters, who for a number of years (until 1810) made an inferior hard porcelain at the New Hall Works, Hanley. The moulds and trained artists from Bristol were not taken to Staffordshire.

During the last two or three years an experimental investigation of continental types of porcelain has been in progress at Stoke-on-Trent under the direction of Dr. J. W. Mellor and Mr. Bernard Moore, and early in 1919 an excellent assortment of products manufactured from British materials was exhibited locally, and it is understood that several

North Staffordshire firms agreed to take up the manufacture. These products are of an intermediate type, which has been developed by the use of materials and methods at hand, with such modifications as were necessary for attaining the object in view.

The glaze used for continental hard porcelain is felspathic or calcareous, consisting either of pegmatite, with or without addition of calcium carbonate—as in Germany and Austria—or similar compositions made up from other materials (felspar, quartz, and kaolin). Quartz is sometimes added to the pegmatite to regulate its fusibility. The glaze is generally applied by dipping, but very fragile pieces are glazed by spraying or powdering. The glazed ware is fired in the lower chamber of the oven, the waste heat being to some extent utilized for baking the biscuit ware in the upper chamber.

TOBACCO PIPES.

Clay tobacco-pipes are made from pure white pipeclay, which is practically free from such impurities as sand, iron compounds, and calcium carbonate. They are white after being fired. In some places clays are used which contain a little iron, but the colouring effect of the iron is counteracted by the presence of some lime. The clay does not need washing, but is made into a pasty mass by hand, and the body so obtained is moulded into pipes by hand. A small piece of the clay is well kneaded, and then rolled out to nearly the form and size of a pipe, a small lump being left at one end to represent the bowl. After a short time the stem part of the roll is bored by means of a needle fixed in a wooden handle and ending in a small rounded enlargement. The head or bowl portion is bent to the proper angle, and the whole is next placed in one-half of a copper mould, the other half being then put on. The two parts are pressed together by means of screws and nuts, the surfaces of the mould being previously oiled to facilitate delivery. The head or bowl is partly shaped by the finger, and completed by introducing a chuck and turning it round. The bottom of the bowl is pierced by means of a point so as to communicate with the bore in the stem. The pipe is removed from the mould, any excess of clay is cut away, and the pipe is smoothed by an iron or copper blade. The best pipes are polished on the outside by rubbing with perforated flints, and the needle is withdrawn. The shaping is usually done by women or children, who acquire great dexterity. The pipes are dried very slowly, and finally fired either in muffle kilns, or in saggars in small round or square kilns.

For pipes made in two pieces, the bowl is made of a plastic ferruginous clay, thinned when necessary with grog made of the same clay. The bowls are shaped by throwing and turning, and the part for fixing the pipe in—which is turned separately—is then stuck on. The firing is done in saggars. The chief English localities for pipe making are London and Broseley (Shropshire).

COMMON POTTERY.

This includes the most ancient wares made in most countries, and such wares were for a long period almost entirely used for all domestic purposes. The body consisted of a fine-grained fusible clay, or of clay mixed with fine-grained sand when no suitable natural clay was available. The body was prepared by treading and kneading, and shaping was done by hand (without moulds) by using pellets for large pieces, or else by turning (when round). The ware was fired in horizontal kilns with a single fire-place, or in square kilns with rising flames. The very fusible clays, usually both ferruginous and calcareous, employed for making these wares, are still referred to as potters' clays.

TERRA-COTTA.

This term is generally applied to fired, unglazed, yellow and red clay wares. Vases, statues, and other decorative objects were made from a very early period, especially by the Greeks, but during the Renaissance the manufacture disappeared owing to the introduction of faience, and it was only from the nineteenth century that the manufacture of such decorative objects was resumed, though with refinements. For modern terra-cotta the clays are washed, and only very fine sands are mixed with them to give them an open texture, so that the surface may be very smooth. The pieces are made by turning or moulding by hand in plaster moulds. Statues are made in several pieces, which are afterwards carefully stuck together; in this way all the thicker parts (head, trunk, etc.) are kept hollow, and possible evils in drying and firing parts of very uneven thickness are largely avoided. The surface may be decorated by stamping or beading, etc. Uniformity of colour is important, and according to the clays used the colour may be yellowish-white, yellow, pink, orange, or red, and by mixing manganese oxide with the body, grey or brown colours can be obtained. The uniform tint is more easily obtained by applying to the ware thin body slip. Coloured slips can be used for barbotine painting. The goods are usually fired in saggars or in a muffle. Terra-cotta wares are made in some tile works and potteries, and also in special works as at Watcombe (near Torquay). Architectural terra-cotta is made from similar materials, which in this case are particularly required to be fine-grained to render the ware better able to withstand weather influences.

TILES.

Decorative Tiles are really earthenware slabs variously decorated, but are prepared by dry pressing (as distinguished from plastic pressing). The body is prepared in the same way as for ordinary earthenware. The clay from the filter press is dried in a steam shed until quite white, and is then reduced to a fine powder in a disintegrator or by passing between rollers. The dust is slightly damped (so that if squeezed in the hand it sticks together somewhat loosely), and is then put in a metal mould, covered with a die, and subjected to great pressure in a screw press. In this way a tile is stamped or pressed out of dust, and can be safely manipulated until it becomes fired, after which it is hard and sonorous. The glazing of decorative tiles is sometimes effected automatically by means of special machines, instead of ordinary dipping. The decoration is applied in the same way as for earthenware objects.

Decorative tiles are largely used for walls, and domestic hearths and fire-places; they are sometimes framed like pictures, or mounted to serve as stands for teapots, etc.

Roofing Tiles.—These require a more plastic body than is needed for bricks. Formerly they were exclusively moulded by hand. Some are now made by expression of a semi-stiff body, which is then cut into tiles of definite size and shape by special cutting machinery. Some are moulded in a press from semi-stiff material or from stiff material. The drying of the tiles generally takes place in large ventilated buildings over the kilns, waste heat from which is thus utilized. In rare cases independent drying sheds are used.

During the firing of roofing tiles, the fuel or ashes should be kept out of contact with the tiles.

The colour of black tiles may be produced by mixing manganese oxide with the body, by applying black slip on the body, by dipping the heated body in hot tarry material, by "blueing" or firing the tiles in a reducing atmosphere charged with hydrocarbons, or by firing the tiles in saggars containing powdered carbon. "Blueing" is done by introducing tar or other liquid hydrocarbons into the kiln after it has reached its highest temperature. In the absence of iron, or if iron be present combined with lime, the colour is a more or less dirty greyish black, but under other conditions ferric oxide is reduced, giving a fine blue metallic gloss.

Paving Tiles.—Paving tiles or floor tiles may be terra-cotta or stoneware. Terra-cotta paving tiles are usually square or hexagonal, and they are made from the same body as roofing tiles, and are shaped in the same way—by hand, or expressed and cut to size. The firing is also done as for roofing tiles.

Stoneware paving tiles are also hexagonal, square, rectangular, etc. They may be white, red, brown, black, or yellow; or they may be decorated with inlaid coloured slips (encaustic tiles). As in the case of other stoneware products, they are made of vitrifiable clay, etc. They are moulded either from plastic or dry body, in the former case as for terra-cotta paving tiles, but re-pressing them after partial drying. Thick tiles are almost exclusively made by pressing more or less dry dust, and this is also the case with inlaid tiles (encaustic tiles). The body for encaustic tiles may be a vitrifiable clay, or a fireclay mixed with felspar (or Cornish stone), some silica being added when necessary. It is decorated by coloured slips made by mixing colouring oxides with the body; the slips are applied in the form of powder at the time the tile is made. For this purpose a copper template is put in the bottom of the mould, and work-people then in their turns put the different coloured slips (powdered) into the proper places; the template is then removed, and the mould is filled up with ordinary body. The whole tile is then subjected to pressure in the usual way. After drying, the tiles are placed in saggars and fired.

BRICKS.

Bricks constitute a variety of terra-cotta used for building walls, just as tiles are mostly terra-cotta used for roofs, floors, etc. The word brick has been variously derived from Anglo-Saxon *brice* ("a fragment"), or the Teutonic *brikan* ("to break"), through the French *brique* (which originally meant "a broken piece," especially of bread, but afterwards also of clay).

Bricks were made by all ancient civilized nations. Well-fired bricks were made by the Babylonians more than 6000 years ago, and enormous mounds of bricks mark the sites of the walls, towers, and palaces of Babylon. The Babylonians and Assyrians are known to have made bricks coated with coloured glazes or enamels. The Chinese do not seem to have made fired bricks when they were made by the Babylonians. The great wall of China was made of bricks which had apparently been only sun-dried, as the material turned red when ignited. J. C. Witt (*Philippine*

J. Sci., *12A*, 257, 1918) found that samples of brick gave on analysis 73·02 silica, 18·96 alumina and iron oxide, 5·73 alkalies, 1·29 lime, 1·05 magnesia, with 0·10 loss on ignition, and the mortar gave 48·83 lime, 4·03 magnesia, 0·85 alkalies, 2·12 silica, 0·44 alumina and iron oxide, with 43·88 loss on ignition, so that no sand had been mixed with the mortar. The bricks made in Egypt by the Israelites were probably also only sun-dried; they were made of Nile mud (clay) mixed with chopped straw or reeds and water to a stiff paste. The chopped straw (or reeds) was added as a binding material, but it also increases the plasticity of clay, especially after standing a few days. Sun-dried bricks—called "adobes"—are still made from Nile mud mixed with chopped straw and water; the material is trampled to effect thorough mixing, and the bricks are shaped in moulds or by hand. The Greeks seem to have used bricks only to a limited extent, but the Romans took up the manufacture of bricks on an extensive scale, selecting and preparing the clay with great care, and they introduced the process of firing bricks in kilns, After the withdrawal of the Romans from Britain, bricks did not come into general use again until the fifteenth century, and then only for buildings of importance. Even to the time of the Great Fire of London (in 1666), the less important buildings, as well as shops and dwelling-houses, were made with a timber framework in combination with lath and plaster work. When London was rebuilt after the fire, bricks were used extensively, and from the later years of the seventeenth century onward they have been generally used in all ordinary buildings except where building stone is abundant and good clay for bricks is not readily available. Since 1625 the sizes of bricks have been regulated by statute, the standard adopted being $9 \times 4\frac{1}{2} \times 3$ in.

The clays used for making bricks until modern times were only the alluvial and drift clays found at or near the surface, which are easy to work, and do not need much preparation. Alluvial clay is merely accumulated river mud which is soft and plastic. Within comparatively recent times, hard clays, shales, and slates have been brought into use for making bricks, with the aid of heavy machinery. These hard clays or shales, etc., may be rendered plastic by prolonged weathering—exposure to rain, frost, and sun—or by crushing and grinding in water; they then closely resemble ordinary alluvial clays.

Brick earths or clays fall into two chief classes: (1) non-calcareous clays or shales, with little calcium carbonate (carbonate of lime), composed mainly of true clay substance with sand, felspar grains, and iron compounds (chiefly oxide or carbonate), and which when fired usually become buff, salmon, or red; (2) calcareous clays, containing (besides the substances just mentioned) a considerable amount—up to 40 per cent.—of calcium carbonate; these latter are called marls, and when fired they assume a characteristic pale yellow tint. It may be noted here that the term "marl" is often wrongly applied to fireclays, but should be confined to natural mixtures of clay and chalk, such as those found in parts of the Thames valley, and in other regions where chalk or limestone formations occur.

Brick clays of the first class are very widely distributed. Many natural clays are unsuitable for making bricks unless mixed with some clay of a different kind or with sand.

All clays contain more or less free silica as sand, and generally also a little felspar. Next in importance to the clay substance and the sand is iron oxide, for the colour of the fired bricks depends on this component. The iron oxide in the clays ranges from about 2 to 10 per cent., and the colour of the corresponding bricks varies from light buff to chocolate brown. It should be borne in mind, however, that the colour produced by the same proportion of iron oxide may be modified by the presence of alkalies or other substances, and also may be very different according to the manner of firing. Thus red bricks are ordinarily produced from clays containing 5 to 8 per cent. of iron oxide, but if the bricks are fired too hard, or if the clay contains also 3 to 4 per cent. of alkalies, a darker colour (more purplish) will be produced. Excess of alumina, on the other hand, tends to produce lighter and brighter colours. The composition of such clays varies widely, the clay substance being from 15 to 80 per cent., sand (free silica) 5 to 80, iron oxide 1 or 2 to 10, calcium carbonate (including magnesium carbonate) 1 to 5, and alkalies 1 to 4 per cent. There is always some organic matter present, and often calcium and magnesium sulphates, sodium and potassium chlorides and nitrates, and iron pyrites, all except the organic matter and the iron pyrites being soluble in water. Iron pyrites, when present in sufficient quantity, leaves iron sulphide after the firing, and this soon changes to sulphate, which before very long weathers out, and makes the brick brittle. The organic matter increases the plasticity of the clay, but sometimes it is present in excessive amount. The soluble substances are objectionable because they form a superficial scum, which causes patchy colour and pitted faces of the bricks. The most frequent of these soluble impurities is calcium sulphate, which causes a whitish scum on the brick's face when drying; this scum is fixed by the firing, and makes the brick fit only for common work. When a clay containing calcium sulphate has to be used for making high-class facing and moulded bricks, a suitable amount of barium carbonate is mixed with the wet clay, resulting in the formation of insoluble calcium carbonate and barium sulphate; the impurities thus remain distributed through the brick instead of the soluble substance collecting on the surface. Magnesium salts are also undesirable in clays, as they mostly remain in the fired bricks as magnesium sulphate, and this may later cause an outgrowth of fine white crystals on the surface. Mica and felspar, with iron oxide, act as fluxes, and if not in excess are useful rather than injurious in brick clays.

Strong or plastic clays are often termed "fat" clays; they are always rich in clay substance, and contain little sand. Fat clays take up a relatively large amount of water when tempered; they then dry slowly, show great shrinkage. and so are very liable to lose their shape and to crack during the drying and firing. The addition of coarse sharp sand much improves fat clays, by reducing the time required for drying, by reducing also the shrinkage, and by enabling the bricks to stand more firmly during the firing. Coarse sand is practically not changed during the drying and firing, and, if not absolutely necessary, is a desirable component of all brick clays. Hence the best brick clays feel gritty, but should be plastic enough to be shaped, and strong enough for safe handling after drying. Weathering or ageing—by being turned over and thoroughly exposed to the weather, or by being left to stand several months in a damp state—greatly improves all clays by increasing plasticity and making them more uniform.

Calcareous clays or marls are not so common as ordinary brick clays, and natural deposits of them in England have been mostly used up. A very fine "malm," as the chalky clay was termed locally, was obtained from the alluvium about London, and an artificial malm is now made by mixing an ordinary brick clay with ground chalk. For making best London facing bricks, the chalk is ground on pans, and the clay is mixed with water to a creamy consistency ; the mixture of the two is run through a grating or coarse sieve on to a drying kiln or "bed," and when stiff enough the mass is covered with fine ashes, after which it is turned over and mixed by a spade, and tempered by adding water.

Where clays containing limestone are used, the marl is simply mixed with water on a wash-pan, and the creamy mixture is passed through coarse sieves on to a drying bed. When necessary or desirable, coarse sand is added to the marl in the wash-pan. The plastic marls are sometimes squeezed (by machinery) through iron gratings, which separate pebbles. Alternatively the marl is passed through a grinding-mill with solid bottom and heavy iron rollers, the limestone pebbles being thus crushed and distributed through the whole of the material. If not removed, the limestone pebbles would be converted by the heat into quicklime, and this would be liable to cause shattering of the brick on exposure.

As already intimated, these marls—usually containing 15 to 30 per cent. calcium carbonate—after firing exhibit a distinct pale-yellow colour, though with over 40 per cent. calcium carbonate the colour becomes grey or very pale buff. Marls generally show little or no contraction on burning, and as a rule produce strong bricks possessing fine texture and good colour; when the marls are rich in calcium carbonate they produce good durable bricks at a very low temperature. Underfired marl bricks have a strong tendency to disintegrate when exposed to the weather; hence care should be taken to avoid underfiring.

Making Bricks.—The tempered clay may be made into bricks by hand moulding or machine moulding, and the machines may be worked by hand or by mechanical power. The clay after weathering is mixed with water to the proper consistency, and any sand or sandy substance used is then added and mixed well with the clay. Pug-mills are sometimes used for the mixing. The moulds may be of wood, of iron, or of wood strengthened by iron bands, and may be open above and below or may have a bottom in addition to the four sides. To prevent sticking, the mould before being used is either dipped in water or dusted over with sand, though in the former case they are more liable to split in drying.

The moulding by hand is done in all cases by knocking a piece of the prepared clay body sharply into the mould, taking care to fill the corners, and afterwards levelling the upper surface with a scraper or strip of wood called a "strike"; the brick is then turned out of the mould on to a board and afterwards carried away to be dried. The mould may be placed on a piece of wood (called the stock-board) to form the hollow or "frog" in the bottom of the brick.

A soft body is moulded best and most economically by hand. Though the ware cannot be handled, it requires extensive drying space, and shrinks very much, and being very porous it has little strength. Machines are only of advantage with stiffer bodies, which produce goods that can be handled more readily, piled up, and dried easily. In nearly all cases the direct expenses of working with machines will always be higher, but the total expenses of manufacture can be reduced by well-considered arrangements, by using suitable raw materials, and by charging extra for better quality. To improve the shape, and sometimes to modify it, bricks are partly dried until they are leather-hard, and are then re-pressed, the machines used for the purpose being worked by hand or by power.

Machine-made bricks may be classed, according to the method of making, as plastic or semi-plastic, but the same type of machine is often used for both. Bricks made of semi-plastic clay—ground clay or shale damp enough to stick together under pressure—are generally machine-made throughout. Machine-made plastic bricks are made of tempered clay, but the clay is generally prepared by grinding-mills and pug-mills, the grinding-mills being either a series of rollers or an ordinary edge-roller pan. Shales are sometimes crushed before exposure for weathering. For ordinary plastic brick clay, grinding-mills are only used when pebbles larger than a quarter of an inch in diameter occur ; otherwise

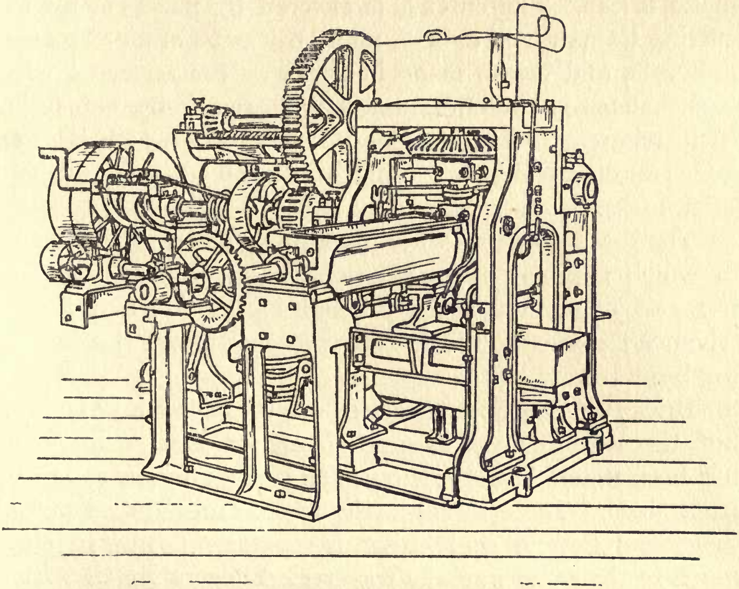

FIG. 19.—Stiff plastic machine for brick-making. (C. Whittaker & Co., Ltd.)

it may be passed at once through the pug-mill (and a second time if necessary). A pug-mill is essentially an iron box with a central shaft carrying knives or cutters, arranged so that when the shaft revolves, the clay fed in at one end is cut and kneaded, and also impelled towards and through a delivery hole at the other end, and as the delivery hole has a cross section approximately equal to that of a brick (9×4½ plus the amount of contraction for ordinary bricks), the issuing clay has only to be cut at proper intervals to make bricks. The cutting is effected by means of a wire-cutting frame which cuts off many bricks together at regular intervals, and bricks made in this way are termed "wire-cuts." These wire-cuts may be improved by subjecting them to great pressure under a brick-press, which is often done automatically by using a combined pug-mill and brick-press.

The essential parts of a brick-press are a box or frame in which the clay is to be moulded, a plunger or die at the end of a ram which transmits pressure, and a contrivance for discharging the pressed brick from the moulding-box.

Bricks pressed from tempered or plastic clay are the best, but the manufacture of semi-plastic or dust-made bricks has been much developed, especially where bricks are made from shale. These semi-plastic bricks are stamped out of moistened ground shale (that is, coarsely powdered clay) much in the same way as dust-pressed decorative tiles from prepared powdered white clays. The method is applicable for certain hard clays or shales that it would be impracticable to use for making plastic bricks; weathering, tempering, and ageing may be wholly or in great part omitted. The necessary plant is heavier and more costly, but the processes are simpler than with plastic clay.

The **drying** of bricks generally takes place in a special shed heated by flues leading from the kilns to the chimney. Ventilation is necessary to keep the drying-shed fairly dry. Too moist an atmosphere causes brick surfaces to keep damp, so that water comes from the inside to the surface in the liquid state, and dissolved salts are left on the surface as the water evaporates slowly, thus giving rise to scum.

Drying in the open air is only used for hand-made bricks.

Plastic bricks dry much more slowly than semi-plastic bricks; they also show more shrinkage, and a greater tendency to warp.

The **firing** of bricks is very important, the strength and durability of bricks depending in great measure on suitable firing. Ordinary bricks should be fired in an oxidizing atmosphere, and the finishing temperature, which (according to the nature of the clay) may range from about 900° to 1250° C.—and is usually about 1050° C. for ordinary bricks—should be adjusted so as to produce hard, strong, well-shaped bricks, not too porous, and resistant to frost. Calcareous clays generally require a firing temperature of about 1150° to 1200° C. to bring about chemical combination between the lime and other substances present.

Wherever bricks are made, the old plan of firing in "clamps" is followed in the smaller works, though the Romans used permanent kilns before the Christian era commenced. Clamps are formed by building up the unfired bricks into a series of walls arranged rather close together so as to constitute a rectangular stack; channels or fire-mouths are formed at the bottom of the clamp, and during the building of the stack, layers of fine coal are spread horizontally between the bricks. In the fire-mouths fires are kindled, and the clamp is left burning until all the fuel is burned away, after which it is left to cool. The cooled clamp is then taken down, and the bricks are sorted. Under-fired bricks are built up again in the next clamp to be re-fired. In some cases the outside of a clamp is built of fired bricks with clay plastered over them, and the fire-mouths are made larger and better. The method of building up the clamps varies as regards details in different localities, but the aim is always to produce a large proportion of well-fired bricks. Clamp firing has the disadvantages of being slow, irregular, and imperfectly controlled, wherefore it is not economical, and is only resorted to where the output is small.

Brick kilns are of many forms, but all are included in two main groups, intermittent kilns and continuous kilns.

Intermittent brick kilns are usually round with a domed top; sometimes they are rectangular in shape. Each kiln consists of a single firing chamber in which the dried bricks are arranged, and around the wall are placed a number of fire-mouths, in which fuel in the form of coal or wood is burned. The kilns may be up-draught or down-draught. In up-draught kilns (which represent the earlier type) the combustion products pass from the fire-mouths through flues below the floor to holes in the floor, and so into the bottom of the firing chamber, whence they pass upwards and escape at the top. In the modern down-draught kiln there is a short chimney or "bag" connected with each fire-mouth, and this bag directs the flames and hot gases to the upper part of the firing chamber, whence they pass downwards among the bricks and through holes in the bottom leading to flues connected with an independent chimney. The bags are sometimes run together so as to form a continuous passage bounded by an inner circular wall all round the firing chamber except across the doorway. A single chimney may serve for a group or row of kilns. Down-draught kilns are more economical as regards fuel consumption than up-draught kilns, and usually fire more regularly and give a larger proportion of well-fired bricks; some of the waste heat may be utilized for drying purposes by taking the flues under the drying shed floor on the way to the chimney.

Continuous kilns may have one or several firing chambers. Those with a single firing chamber may either have the goods carried gradually past fixed fire-places, or the fire-places can be put in the middle of goods which are fixed in position. The first of these methods, after many trials, has been given up so far as bricks are concerned. In the second kind, the fires can be spread about in the firing chamber.

A chambered continuous kiln really consists of several kilns or firing chambers, built in series, and connected with the main flue to the chimney, so that the combustion products from one kiln may be made to pass through other kilns before entering the main flue. The first continuous kiln of this type was invented by Hoffmann and Licht, in 1858, and had an annular firing chamber with twelve charging doors, and a central chimney, the latter communicating (through the agency of a smaller annular chamber surrounding it) by twelve passages or flues with the firing chamber. A movable damper can be placed near any door so as to quite shut off the firing chamber. The whole kiln consists of twelve chambers, each with a charging door at one end and a draught passage at the other, though there is no actual separation of the chambers except by the one movable damper. In normal working, two adjoining chambers are being charged and emptied respectively, only the door of the second of these being open; the four chambers next to the latter are cooling after firing, the next two are getting their final heating from the fire, and the last four are being gradually heated up. The air for combustion enters through the only open door, travels towards and past the fire, and so all round

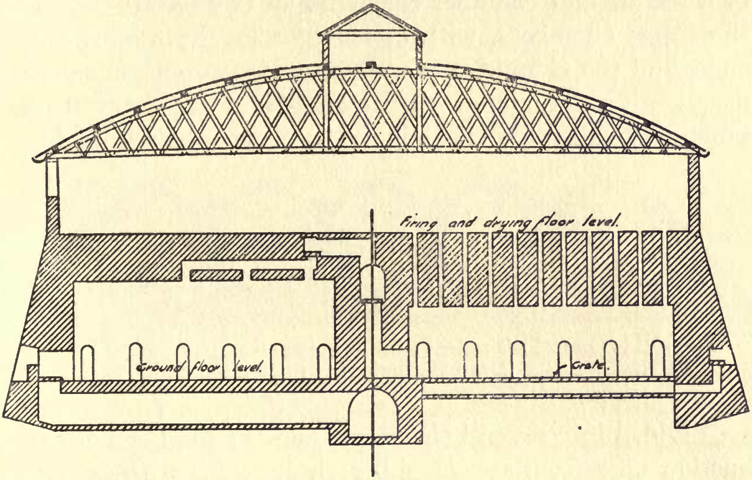

FIG. 20.—"Staffordshire" kiln. Cross section showing interior of chambers, arrangements of flues, and grate fire. (Dean Hetherington & Co.)

the firing chamber, first helping to cool chambers which have been fired, and afterwards assisting in the heating of the other chambers; from the last compartment it makes its way through the smoke flue or draught passage (all the others being shut off) to the chimney. As the firing of each chamber is finished, the movable damper is shifted to the next door in the direction of the cooling ware, and so on in turn all round, with corresponding adjustments for the draught, etc. Numerous modifications have taken place, the chief being the substitution for the circular firing chamber of a rectangular chamber consisting of two parallel rows of the single chambers, with communicating flues at the two ends, and the chimney generally outside. Continuous kilns usually give more uniformly fired products than intermittent kilns, and are economical in fuel. Some continuous kilns are divided into several chambers, and the products of combustion pass from one chamber through flues beneath the floor into the next, and so on successively.

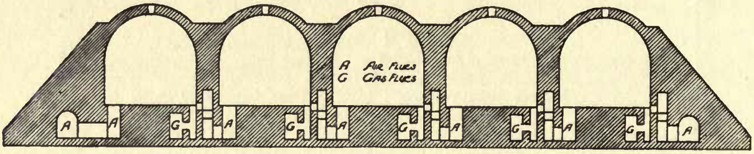

FIG. 21.—Dunnachie's patent continuous regenerative gas-fired kiln. (Dean Hetherington & Co.)

Gas firing is now frequently applied to continuous kilns. In Mendheim's gas-fired continuous kiln, a good distribution of the heat is obtained by a special arrangement of the gas and hot-air passages.

Where pyrometers are used to control the firing, the products are much more constant in quality.

Blue Bricks are very strong vitrified bricks with a dark slaty-blue colour. These blue bricks are made in the same way as other bricks, but of clay containing 7 to 10 per cent. iron oxide, and when during the firing the kiln has reached its highest temperature, a smoky (and therefore reducing) atmosphere is produced by throwing small bituminous coal on the fires and shutting out air as much as possible. The red oxide of iron is thus reduced to ferrous oxide, which combines with silica to form a fusible ferrous silicate, the latter partly filling up the pores, forming a vitreous, impermeable layer the thickness of which is dependent on the duration and other features of the smoking, on the finishing temperature of the kiln, and on the texture of the bricks. In the earlier stages of the smoking, carbon particles penetrate the brick, and tend to darken the colour.

Floating Bricks were made in ancient times, but the method of making them was lost for centuries. Fabroni rediscovered it in 1790, and made them from the kieselguhr (diatomaceous earth or fossil meal) of Tuscany. Besides being light, these bricks are fairly strong, and are poor conductors of heat. This last property enabled them to be used in building powder magazines on ships, etc.

The **Moler Bricks,** much used in Norway, are of this class. They are made by mixing the (diatomaceous) Moler earth with a little water, passing through crushing rolls, and then tempering in a pan-mill. The bricks are moulded by machines or by extrusion presses. Some have been made so light that a cubic foot of the material only weighed 350 oz., and these very light bricks are excellent insulators.

Mortar Bricks, which are not fired, are really blocks of artificial stone made in brick moulds. They are made of a mixture of sand and slaked lime, which is moulded, and the blocks are left to harden in the air. The hardening results partly from evaporation of the water, but chiefly by the action of atmospheric carbon dioxide (carbonic acid gas) on slaked lime to form calcium carbonate. A small proportion of the lime combines with silica and water to form a hydrated calcium silicate, and probably a little hydrated basic calcium, carbonate is formed as well; both these latter have cementitious properties. The natural hardening was found to take 6 to 18 months. The bricks were eventually improved in strength by adding some cement (or certain ground blast-furnace slags mixed with lime), and by using hydraulic presses for moulding, afterwards treating the bricks with carbon dioxide under pressure. Some of the mixtures and improved methods are still used, but sand-lime bricks have latterly practically superseded the old mortar bricks.

SAND-LIME BRICKS.

These were first made according to the patent of Michaelis nearly forty years ago in Germany. Blocks made of a mixture of sand and lime were hardened by subjecting them to the action of high-pressure steam for a few hours. They are now made very largely in many countries, especially in districts where clays suitable for ordinary bricks are not available. Subject to many differences in detail, the general method of making the bricks is the same everywhere. Dry sand is well mixed with about one-tenth of its weight of slaked lime, and after slightly moistening with water, the mixture is moulded into bricks under strong pressure (about 60 tons per square inch). From the press the bricks are at once placed in large steel cylinders (called autoclaves) about 7 ft. diameter and generally 60 to 80 ft. long, where high pressure steam (100 to 150 lb. per square inch) acts on them for 10 to 15 hours (in America 7 to 12 hours). Chemical action results in the formation of a hydrated calcium silicate, which acts as a strong bond between the larger sand grains. About 15 per cent. of the sand should pass through 100-mesh sieve, in order to be able to combine with the lime to form the bond. The other grains should be of assorted sizes, so as to give the greatest density, but should not include pebbles larger than half-inch. The sand-lime brick, which is usually light-grey or nearly white, is much stronger than an ordinary mortar brick. It may be stained by adding suitable colouring oxides or pigments which are not affected by lime, etc.

FIREBRICKS.

The term "firebrick" is employed to distinguish such bricks as can be used in fire-places, furnace linings, flues, etc., where ordinary bricks would be liable to melt. Sometimes the term is made to include also bricks made of silica, magnesia, etc., but in a more restricted sense firebricks are understood to be made of fireclay or other refractory clays, such clays being rich in alumina and silica, but low in ferrous oxide, lime, and alkalies. The clay is never used alone—being liable to excessive contraction and consequent cracking—but is mixed with grog or with sand, coke, graphite, etc. Apart from the direct fusion effects of temperature, firebricks have to withstand other destructive influences, especially the action of fluxing materials such as flue-dust, slags, alkaline vapours, melting alkalies, and certain metallic oxides; they must also be able to resist great temperature changes, and be strong enough to bear considerable pressure at temperatures which would soften ordinary bricks. Beyond the difference in raw materials, there is no essential point of difference in the manufacture of firebricks from that of ordinary bricks, except that more care is used, the material is stiffer, and the firing takes place at a higher temperature. At temperatures not exceeding 1000° or 1100° C., finely divided silica (only) tends to combine with bases and thus promotes fusibility. At higher temperatures the coarser-grained crystalline silica acts similarly. Excess of silica, beyond what can combine with the ordinary bases and alumina, acts as a refractory constituent.

In the absence of bases or other fluxes fusibility increases with increase in the proportion of silica to alumina, until the composition nearly corresponds to $Al_2O_3, 16SiO_2$, after which further increase in the proportion of silica increases the refractoriness. Grog acts as a refractory at temperatures below vitrification, but from that point onwards it no longer affects the fusibility. The presence of grog, fairly coarse-grained (according to the thickness of the articles) is particularly advantageous for resisting rapid changes of temperature, and with very plastic clays the amount may be as much as 2 parts by weight of grog to 1 of clay; part of the grog may be fine-grained, as the fine grains can get between the larger grains, and so allow a larger proportion of grog to be used. For resisting chemical action, as of fluxes and vapours, it is better to have fine-grained material, and to fire to incipient vitrification.

A strongly-marked feature of fireclay bricks when heated under load is that they gradually soften with rise of temperature until the brick finally collapses. This behaviour characterizes aluminous (fireclay) and zirconia bricks.

CRUCIBLES.

Crucibles are required to withstand very high temperatures, and sometimes other severe conditions as well. Good crucibles can be cooled rapidly without cracking, and can also resist the action of various fluxing materials, as in the smelting of metals or of glass.

Hessian Crucibles are made of fireclay (composed of about 71 per cent. silica, 25 alumina, and 4 iron oxide), mixed with one-third to half its weight of quartz sand. Though refractory, and capable of resisting temperature changes, their porosity and coarseness of grain renders them unsuitable for some chemical operations, being corroded by lead oxide, alkalies, etc.

Graphite (or **Plumbago**) **Crucibles** are made of graphite mixed with 20 or 25 per cent. of refractory clay (usually fireclay). They are highly refractory, and have high conductivity for heat.

English Crucibles are made from Stourbridge clay mixed with 50 per cent. of coke. Such crucibles reduce metallic oxides heated in contact with them.

Crucibles have also been made of lime, chalk, magnesia, bauxite, mixtures of bauxite or cryolite and magnesia, of zirconia, carborundum, etc.

FIRECLAY WARE.

Sanitary and other articles have been largely made of fireclays both in this country and abroad. They were formerly subjected to a biscuit firing, and afterwards covered with a lead glaze. In some cases salt-glazing was resorted to for such goods.

Such ware is now commonly subjected to only a single firing in large rectangular muffle kilns with arched roofs. The articles—baths, lavatories, sinks, etc.—are first made of a stiff, slightly moist mixture of clay and grog, the latter being either the same kind of clay calcined, or clean refractory fireclay bricks, etc., which are crushed and sieved to give various grades. In many cases, especially for the larger pieces, a proportion of saw-dust or similar carbonaceous material is added, which burns off in the firing and gives a more porous product.

Fireclay goods are often finished white (instead of buff), which is effected by covering the finished clay surface with a white clay "body" or "engobe," and covering that in turn with a transparent leadless porcelain glaze, or the engobe is sometimes dispensed with, and the clay covered with a similar glaze rendered opaque and white by addition of suitable material (as tin oxide), the composition being also modified in other respects if necessary or desirable. Both engobe and glaze are generally applied by preparing the sloppy material with water and gelatine (or similar substance) and brushing it on the ware, as many coats as may be considered necessary being applied, with drying between two consecutive coats. The smaller articles are commonly glazed by dipping. The firing is usually carried out at a comparatively high temperature, the whole period of firing being rarely less than 12 or 14 days, and sometimes longer.

SILICA BRICKS.

These, as the name implies, are made of silicious material occurring in the form of silica rock (quartzite, ganister, flint, etc.), or of loose natural material of similar character.

The chief points to be considered are mechanical strength, melting point, and behaviour on heating, especially under load. From experience it is found that for producing strong bricks the quartzite should be hard, and when crushed should not give rounded grains but angular fragments of different sizes and shapes. The rock should contain 96 to 98 per cent.

silica, with alumina and iron oxide together preferably not exceeding 2·5 per cent. (usually about 1·75 is present), and less than 0·5 per cent. of alkalies. It is remarkable that pure quartzite containing as much as 99 per cent. silica has not proved satisfactory for making silica bricks.

Quartzite suitable for refractory purposes does not crack when strongly heated, but shows considerable expansion after the first firing, and not much further change after subsequent firings. Unsuitable quartzites—especially coarsely crystalline varieties—crack badly when heated, and usually expand slightly when first fired, but considerably in subsequent firings.

Silica bricks are made from quartzite (or similar silicious material) with usually lime or clay as bond. Less than 1·5 per cent. lime gives weak bricks, and with more than 3 per cent. the refractoriness is decreased; about 1·75 to 2 per cent. gives the best results. When fired for the first time, the quartz of silica bricks is largely converted into cristobalite, the remainder being similarly transformed very slowly in subsequent firings. The cristobalite in its turn is inverted to tridymite, slowly at first, but afterwards more rapidly, the actual rate in all cases depending on the firing temperature and the time; variations in grain size have comparatively slight effect at very high temperatures (cone 13 and upwards). All the lime passes into the ground mass which cements the silica crystals, and accordingly it becomes more concentrated in coarsely-ground material (which has the smallest proportion of fine particles). An increase in the amount of lime should hasten the inversion of cristobalite to tridymite, the latter forming a strong framework of crystals. At 1250° C. the specific volumes of cristobalite and tridymite are about 14 to 15 per cent. greater than that of quartz. Tridymite expands much less than cristobalite on heating. The gradual inversion of cristobalite into tridymite probably takes place in furnace linings. The spalling or cracking of silica bricks under quick temperature changes is probably owing mainly to the rapid expansion (about 3 per cent.) which accompanies the inversion from

α to β cristobalite between 230° and 270° C. (The α–β quartz inversion at 575° C. gives a volume change of about 1·4 per cent.) This spalling tendency of silica bricks diminishes with repeated firings.

A large proportion of tridymite is apparently advantageous in silica bricks—at any rate if not heated continuously above 1470° C.—because tridymite shows less temporary expansion than either cristobalite or quartz, because it has a greater specific volume and shows no permanent expansion after repeated firings below its melting point, and because tridymite bricks would bear rapid temperature changes with slight risk of cracking.

At temperatures continuously above 1470°, a tridymite brick would be likely to revert slowly to cristobalite; tridymite is not known to be formed under any conditions above 1470° C. Long-continued firing would favour the formation of tridymite more than repeated firings. Hence in firing silica bricks, the highest temperature should be held for a considerable time; the rate of inversion is more rapid at cone 14 or 15 than at cone 13.

Bleininger and Ross, on heating the prepared mixture to 1300° C., observed no tridymite and not more than 5 per cent. cristobalite. At 1350° the cristobalite was 57·13 per cent., the rest being quartz and calcium silicate. At 1400° C. there was 72·17 per cent. cristobalite, at 1450° 81·26 per cent., and at 1500° C. 90 per cent., with a little tridymite in each case. The minimum firing temperature of silica bricks should apparently be cone 18. Seaver found at still higher temperatures (up to a maximum of 1630° C.) no clear indication of the formation of tridymite, but practically all cristobalite.

Rapid crystallization of silica from a melted glass always gives cristobalite in the first instance, and this crystallization serves to unite the undissolved silica grains. Only the very fine grains in silica bricks are dissolved, along with a little of the outside of the larger grains, the latter being eventually transformed into cristobalite with swelling of the grains. Formation of cristobalite by solution in the fluxes involves no swelling, the crystals being deposited in the spaces left free.

According to Le Chatelier, cristobalite is less stable than tridymite at high temperatures, and tends to become transformed into tridymite, and all the conditions which promote the change of quartz into cristobalite, afterwards (if prolonged sufficiently) promote change of cristobalite into tridymite. In steel furnaces, the transformation of silica bricks into tridymite becomes complete, at least where the temperature exceeds 1400° C. Le Chatelier found that in well-fired silica bricks there is a continuous network of tridymite, in the pores of which the melted mass lodges without reducing the mechanical resistance. The formation of this network results from solution of the quartz in the melted magma, and recrystallization of the silica first as cristobalite, and then as tridymite. Underfired bricks, in which no network is formed, consist of quartz grains floating in the melted material; these are at high temperatures plastic like fireclay or magnesia bricks. The most favourable conditions for the formation of the tridymite network seem to be several days firing at a temperature approaching 1450° C.—below that at which the quartz is directly and rapidly transformed into cristobalite—especially when the quartz is fine-grained, though a certain proportion of large grains is necessary to prevent the formation of cracks, which develop easily in uniformly fine-grained material. If a brick containing unchanged quartz grains is suddenly heated to a temperature at which quartz is rapidly transformed, the resulting expansion shatters the network and deprives the brick of its strength.

D. W. Ross found that on re-heating commercial (American) silica bricks to 1400°, 1450°, and 1500° C. respectively, there was usually increased porosity, the increase in pore space being roughly proportional to the increase in volume of the solid material.

Artificial tridymite and cristobalite have specific gravities of about 2·27 and 2·33 respectively, and to determine approximately the degree of firing it is only necessary to find the specific gravity of a piece of the brick from the relationship: sp. gr. = dry weight divided by volume of the solid material, *i.e.* by exterior volume (= wet weight less suspended weight) minus pore volume (= wet weight less dry weight). This method might readily be used for rapid inspection work, and is independent of any changes in porosity. The average specific gravity of bricks from ten different works was 2·3546 after firing once at 1400° C., and the average volume expansion was 1·45 per cent. The average volume expansion of two series of 14 each, fired once at 1450° C. and 1500° C. was 1·38 and 5·66 respectively. The quality of silica refractories can be tested by comparing the percentage volume increase of materials which have been reheated (once or oftener). The extreme porosities 22·64 and 31·96 per cent. (of original brick) show the range likely to be found in American industrial practice. A combination of the volume and specific gravity methods should determine accurately whether or not silica refractories have been properly fired.

For making silica bricks, the silica rock is crushed, then ground on pan-grinders to the necessary fineness, usually to pass a sieve of 16 meshes to the linear inch, the bond (mostly lime or fireclay) being added to the silica on the pan. Lime is added during the grinding, as milk of lime. Part of the silica is sometimes used in the form of grog, obtained from old or defective silica bricks, crushed or ground to suitable size. In some cases a small proportion of sand is added as well as grog. The lime helps to give the material a certain degree of plasticity. Le Chatelier, Philipon, and others in France, and Mottram in England, recommend the use of a proportion (up to 30 per cent.) of very finely ground silica. Mottram specifies grinding 15 to 30 per cent. of the raw silicious material along with the lime, clay, or other binder, to a fine slip, and then adding this to the rest of the graded silica material.

The shaping of the silica bricks may be done in open moulds (made of wood or iron); the finishing is effected either by using a hand-press or a power-driven press with a revolving table. For hand-making, an iron plate is placed under the mould and the mixture is worked and pressed into shape; the mould is then lifted off, and the brick or bricks with the supporting plate are set to dry. For hand-made bricks 9 to 11 per cent. water is best for avoiding moulding defects.

The dried bricks are set (as freely as possible) in the kiln, which is usually a circular down-draught or up-draught kiln. The bricks should be thoroughly dried, before heating up, if fire cracks are to be avoided. The firing may last 7 to 10 days, at a maximum temperature of 1400° to 1600° C., but sometimes only 4 days. In the United States they are fired 10 to 15 days, including 1 to 3 days at the maximum temperature (cone 16 or higher). They are allowed to cool slowly down to 700° or 800° C., Dinas or ganister bricks being very liable to crack if cooled suddenly or unevenly. In the United States, cooling usually takes about 5 days. For certain special purposes silica bricks may undergo several firings at higher temperatures.

The desirable qualities in silica bricks with lime bond are resistance to temperature changes and to the highest temperature in the furnace, resistance to combustion and reaction products in the atmosphere of the furnace, and regular but not excessive expansion. Texture is also very important.

In contrast with fireclay bricks, silica bricks and silicious bricks, though they may show some signs of a gradual deformation when heated under load, are characterized by a more or less sudden collapse. In a less degree the same is typical also of magnesia and chrome bricks.

In a seasoned silica brick, the darker and denser portion nearest the inside of the furnace is more refractory and resistant to temperature changes without fracture. According to C. John, a magnet applied to the finely crushed dark portion removes 15 per cent. magnetic oxide of iron, which is the stable oxide at high temperatures, and which neither combines with silica nor forms a solid solution at furnace temperatures. It is only with an oxidizing atmosphere that magnetic oxide of iron is advantageous in silica bricks.

The action of iron oxide on silica is very important. In France, Rengade, and also Le Chatelier and Bogitch, found in silica bricks removed from steel furnaces several distinct zones: (1) a more or less completely fused grey zone, in which the cristobalite has been partly and irregularly inverted to tridymite; (2) an apparently homogeneous blackish-brown zone, composed of large crystals of tridymite scattered regularly in a black ferruginous flux; (3) a zone strewed with white specks formed by the largest fragments of quartzose rock, which fragments retain their shape, though the quartz has been inverted to very fine tridymite; and (4) a zone consisting of cristobalite grains surrounded by very fine tridymite. From analyses it appeared that the grey zone—in contact with the flame, and exposed to the action of ferruginous dust—contains less of the bases (iron oxide and lime) than the upper layers, and the brown and clear yellow zones contained more lime. By experimental investigation, Le Chatelier and Bogitch found that the iron oxide penetrated inwards by capillary ascent, and the silicates of iron, thus rising, push before them the alumino-silicates of lime pre-existing in the brick. In case an accidental flash should melt the superficial layer, the next layer, suddenly brought into contact with the flame while still rich in bases, will also melt, and thus a brick can lose half its height in a few minutes; this is one reason why the management of a steel furnace is such a delicate operation.

Graham and Stead, in this country, separately made independent observations which essentially agree with the foregoing, as also did Bigot in France. An interesting result of these investigations, as pointed out by Bigot, is that parts of the silica bricks in use—viz., the grey parts—though containing only 85 per cent. silica, with 15 per cent. bases, proved to be as refractory as products containing 95 per cent. silica, and are much superior as regards crushing strength at all temperatures—though it is commonly assumed that silica should not be less than 94 per cent.

Also the same grey parts contain 10 to 14 per cent. lime and iron oxide together, though 3 to 4 per cent. is usually regarded as the permissible limit. Bigot also states that enamelled silica bricks from the frieze of archers at the palace of Darius, made 500 years before the Christian era, which are now in the Louvre Museum, contain about 11 per cent. of foreign matters (other than silica), and are equally refractory. Another significant statement by Bigot is that ferruginous sandstones, containing from 3 to 8 per cent. iron oxide are suitable for making silica products.

It is worthy of note that the Dinas firebricks, the first silica bricks ever made for use as refractories, were the invention of W. W. Young, a Glamorganshire land-surveyor, who in 1822 established a company to make the bricks. The material occurs in the Vale of Neath in the state of solid rock, and also disintegrated like sand. Its colour when dry is pale grey. The method of manufacture was essentially like the method of making silica bricks at the present time.

Some other refractory materials may be briefly noticed, though they are mostly non-silicious :—

Magnesite, or native magnesium carbonate, is converted into magnesia on calcining. The amorphous powder so obtained has a specific gravity of about 3·2 to 3·3, but it may be considerably higher if calcined at a high temperature for a prolonged period. If strongly calcined so as to become crystalline, the specific gravity is nearly 3·7. The specific gravity of the mineral periclase (crystalline magnesia) varies from 3·50 to 3·75. The change in specific gravity is accompanied by a corresponding change of volume, and such change is liable to cause spalling (cracking or flaking off) at high temperatures. The most extensive deposits of magnesite occur in Greece, Hungary, and Styria (Austria), but it is also found in Italy, India, the United States, and Canada. The magnesite from Greece is the purest, but the Austrian has been found best for making bricks, owing to its containing about 5 to 7 per cent. iron oxide.

The magnesite has to be calcined before making into bricks, etc. The magnesium carbonate is decomposed at

400° C., but a much higher temperature is necessary to ensure that all the CO_2 is removed.

The calcined magnesite (really magnesia) is crushed and ground (to about $\frac{1}{16}$ in. grains) much in the same way as silica. The unfired magnesia bricks (often called magnesite bricks) crumble easily, being almost devoid of tenacity. The dried bricks are set in chamber kilns or in up-draught beehive kilns. Strong and dense bricks are required for steel furnaces, and to obtain them a very high firing temperature is necessary. The temperature must be raised very gradually in the early stages, and a good soaking should be given at the maximum temperature. English bricks are hand-pressed, but hydraulic pressing would give better products.

Magnesia bricks do not soften gradually, like fireclay bricks, when heated under load. They are chiefly used for linings of basic steel furnaces (both converters and open-hearth furnaces) and electric furnaces. The calcined magnesite is also used for making repairs.

Dolomite has properties somewhat similar to those of magnesite; it is equally refractory, but the presence of a large percentage of lime makes it much inferior in other respects, mainly because it readily slakes in air. It cannot be kept long after calcination without being injuriously affected owing to slaking of the lime present, especially if the calcination has not taken place at a very high temperature. Dolomite is largely used for temporary repairs of hearths in basic furnaces, because it sets more quickly than calcined magnesite, besides being much cheaper, but it does not set as solidly as the magnesite.

Better service is given in the furnace by special dolomitic refractories, in which the dolomite is treated with pulverized basic slag, iron ore, etc.

Chrome or **Chromite Bricks** are used in parts of furnaces where a neutral refractory is required without the reducing action of carbon refractories. They are sometimes used as a buffer between the magnesia bricks at the bottom of a steel furnace, and sometimes as a neutral layer between the basic (magnesia) bricks below and the acid (silica) bricks above in basic furnaces. They are also used for certain special purposes.

Chrome bricks contain up to about 40 per cent. chromic oxide. The method of manufacture is generally similar to the method used for magnesia bricks, no bond being used as a rule.

Alumina is used chiefly as a product from bauxite. Sometimes raw bauxite is employed, generally mixed with fireclay for bonding purposes, but has the great disadvantage of excessive contraction. Fused bauxite has been brought into use in two forms: *alundum*, for which the bauxite has been fused in an electric furnace, and *corindite*, in the making of which the bauxite is heated with coke or other carbonaceous substance (according to N. Lecesne's patent), forming in the first instance aluminium carbide, the subsequent combustion of which melts the re-formed alumina and even volatilizes silica. Both alundum and corindite are high-grade refractories, but the use of the former is limited by reason of its high cost, and the latter has not yet been produced on any large scale.

Sillimanite ($Al_2SiO_5=Al_2O_3.SiO_2$) has valuable properties as a refractory, especially when fused. It does not occur naturally in quantity, but A. Malinovszky has recently prepared fused artificial sillimanite from a mixture of aluminous materials and coke by a method very similar to Lecesne's process for making fused bauxite (corindite) and this fused artificial sillimanite so obtained is said to have no expansion or contraction at any temperature.

Zirconia is another high-grade refractory which has sprung into a prominent position within the last few years. Formerly regarded as a comparatively rare material, it has been discovered in considerable quantity in Brazil, and is now an important export from that country.

Zirconia possesses a most exceptional combination of properties: it is highly refractory (the melting point for the ordinary raw material being little short of 2000° C.); it has very low conductivity for heat, and very low coefficient of thermal expansion (the latter being nearly the same as that of quartz glass), so that it can be plunged while red-hot into water without cracking or breaking; it is highly resistant to acid and basic slags. All these properties are possessed by native zirconia containing 80 per cent. or more ZrO_2. It also resists fused cyanides and alkalies, the only substances which attack it seriously being fused bisulphates and fluorides. Its low conductivity for electricity (except when strongly heated) makes it well adapted for insulating purposes, as in electrical heating apparatus. Other important applications are possible from the fact that though very hard it is very voluminous.

At high temperatures in contact with carbon, zirconia is very apt to form zirconium carbide, which, though very hard and refractory, has not the other valuable properties of zirconia. This will not happen in an ordinary furnace, where there is a sufficiently oxidizing atmosphere.

Zirconia has been used for coating (or replacing) the lime and magnesia pencils used in the Drummond (or lime) light, especially in spectroscopy and microphotography; in the Bleriot lamps forming headlights for automobiles, a rod of zirconia is heated in a blow-pipe flame fed with oil vapour and oxygen; zirconia is also used in the filaments of the Nernst, Sanders, and Zernig electric lamps, a preheating of the filament being necessary to enable it to conduct the current.

When more readily obtainable at moderate prices, native zirconia will be very useful as a lining for electric arc furnaces, though the tendency to form zirconium carbide should not be lost sight of.

According to Podzsus, zirconia which has been fused or heated to beyond 2000° C. is well suited for making refractory ware, having no tendency to crack like raw zirconia used without a bond. The fused zirconia is ground finely, part of it so very finely that it assumes a colloid form and gives sufficient plasticity to the whole.

About 1 per cent. of alumina, thoria, or yttria forms a serviceable addition to zirconia for some purposes.

Zirconia makes a non-poisonous, non-discolouring, permanent white paint of good covering power, not affected by sulphuretted hydrogen, acids, or alkalies. It has also been used in making X-ray pictures, and for other purposes.

Zircon is the native zirconium silicate ($ZrSiO_4$), which is of widespread occurrence, but not very often in large supplies. It is useful as a refractory, though not comparable with zirconia itself in that respect. It has been found suitable for spark plugs and high-tension insulators, and also for use in crucibles, saggars, etc.

BRITISH DEVELOPMENTS.

Immediately after the outbreak of war steps were taken to ensure a supply of Seger cones, previously obtained from Germany, and used in many works for the control of firing operations. Dr. J. W. Mellor undertook to supervise the manufacture of them at the Stoke-on-Trent Pottery School, and the cones have been supplied regularly since as required, without a break.

The same school has been for some years well equipped for carrying out, not only the work of teaching and training, but also original investigation, and its capacity in the latter direction has been greatly extended. In 1915, the Governors of the School, in co-operation with local manufacturers, asked the Department of Scientific and Industrial Research to assist them to investigate the methods of making hard porcelain similar to the continental domestic ware. It was eventually arranged that Dr. Mellor and Mr. Bernard Moore should undertake the inquiry, the department making a substantial contribution towards the cost. A small factory outfit was provided, with a suitable gas-fired kiln. Meanwhile, preliminary laboratory experiments had been made, and early in 1916 operations were commenced on a larger scale. It was intended from the first to use materials of British origin, and English methods of working (with minimum modification) and of firing were to be adhered to; other points borne in mind were the colours and methods of decoration, and the cost of manufacture (which should not exceed that of the ware with which it would have to compete. Within eighteen months of the beginning of experiments, marketable ware was produced. A number of firms are now preparing to produce the new ware commercially when the present great demand for ordinary classes of ware eases off somewhat.

Through the enterprise of several firms in different parts of England (Stoke-on-Trent, London, Worcester), the threatened stoppage of supplies of chemical laboratory ware was met by the production of new ware of the type required.

STATISTICS.

The following figures showing the weights and values of the total exports and imports, between this country on the one hand, and foreign countries and British possessions respectively on the other hand, are significant. They include china ware and parian, tiles (except for roofing and street paving), sanitary ware, other earthenware, electrical ware, door fittings, chemical ware, jet, rockingham, glazed terra-cotta ware, stoneware, red pottery, brown and yellow ware. Had there been space available for giving details, they would also prove interesting.

	Exports to Foreign Countries.		Exports to British Possessions.	
Year.	Cwts.	£	Cwts.	£
1913	2416636	1946355	1625451	1453101
1914	1883246	1418992	1282549	1177860
1915	1433874	1048071	1026936	1006369
1916	1138154	1303532	980520	1310764
1917	942767	1542687	781739	1164451
1918	770099	1807534	573677	1117332

	Imports from Foreign Countries.		Imports from British Possessions.	
Year.	Cwts.	£	Cwts.	£
1913	831133	1089329	1646	7518
1914	618428	748917	1195	6269
1915	150057	194353	786	2946
1916	87144	160300	552	2368
1917	15890	31867	11	37
1918	4820	21451	4	17

The exports of clay tobacco-pipes were as follows :—

	Exports to Foreign Countries.		Exports to British Possessions.	
Year.	Gross.	£	Gross	£
1913	52268	4400	80567	8869
1914	74264	5660	62776	6500
1915	38816	3158	73338	7534
1916	40231	4040	97471	13402
1917	42439	6715	98951	17445
1918	25719	5386	98781	20102

LITERATURE.

"English Earthenware and Stoneware," W. Burton. London, 1904.

"Porcelain," W. Burton. London, 1906.

"English Earthenware," A. H. Church. London, 1904.

"English Porcelain," A. H. Church. London, 1904.

"Gesammelte Schriften," H. A. Seger. Berlin, 1896.

"Collected Writings of H. A. Seger" (American Translation). Easton, Pa., 1902.

"Traité des Industries Céramiques," E. Bourry. Paris, 1897.

"Ceramic Industries" (English Translation), E. Bourry. London, 1901 and 1911.

"Notes on the Manufacture of Earthenware," E. A. Sandeman. London, 1901 and 1917.

"Chemistry of Pottery," K. Langenbeck. Easton, Pa., 1895.

"Chemistry of Pottery," S. Shaw. London, 1837 and 1900.

"A Text-book on Ceramic Calculations," W. Jackson. London, 1904.

"La Céramique Industrielle," A. Granger. Paris, 1905.

"Manuel de Céramique Industrielle," Arnaud et Franche. Paris, 1906.

"Ceramic Chemistry," H. H. Stephenson. London, 1912.

"Ceramic Technology." Edited by C. F. Binns. London.

"Manual of Practical Potting." Edited by C. F. Binns. London.

"Handbuch der Gesammten Zonwaren Industrie," B. Kerl. 1907.

"Traité des Arts Céramiques," A. Brongniart. Paris, 1844 and 1877.

"Report on the Pottery Industry." Washington, 1915. This embodies interesting and useful statistics relating to the States, the United Kingdom, and various continental countries, collected by the U.S. Dept. of Commerce.

Thorpe's "Dictionary of Applied Chemistry." Revised edition Especially article on "Pottery and Porcelain," by William Burton.

Encyclopædia Britannica, 11th edition. Articles on "Ceramics," etc., by William Burton and others.

Also various periodicals, etc., which will be more fully referred to at the end, but especially *Transactions of the Ceramic Society* and *Transactions and Journal of the American Ceramic Society.*

SECTION V.—GLASS AND ENAMELS

GLASS-MAKING AN ANCIENT INDUSTRY.

THAT glass was known in very early times is beyond doubt, but the precise period of its invention is very uncertain. According to a tradition mentioned by Pliny, it was accidentally discovered by Phœnicians; some mariners who cooked their food on the sands at the mouth of the river Belus (a small stream running from the foot of Mount Carmel in southern Phœnicia), where the herbaceous plant known as saltwort or glasswort (*Salsola Kali*) is common, noticed that when the sand was intimately mixed with the ashes of the plant, it melted to form a vitreous substance. Theophrastus, about 300 B.C., refers to the use of sand from the river Belus, and from that time glass was fairly well known in most countries. Alexandria (in Egypt) early attained lasting fame for the skill of its glass workers, who supplied glassware to the Romans among others. From remains of furnaces and workshops, it is known that glass rods and beads, and small vases, were made in Egypt as early as 1400 B.C. In Britain glass was obtained by trading with the Venetians, long before it was made in this country. The earliest authentic record of glass being made in England is in 1230 A.D., on the border of Sussex and Surrey, and the manufacture continued only there until the latter half of the sixteenth century. Glass windows were little used here before the eleventh century, and then only in the houses of the upper classes and in public buildings, whilst in ordinary private houses they were scarcely used until the thirteenth and fourteenth centuries; linen cloths or wooden lattices were the means previously resorted to for the admission of light.

COMPOSITION AND PROPERTIES OF GLASS.

The components of glass include acid oxides, basic oxides, and certain elements and compounds which occur in coloured glasses.

The acid oxides comprise silica, boric oxide, phosphoric anhydride, and arsenious anhydride (sometimes possibly with arsenic anhydride).

The basic oxides fall into three groups: those of the R_2O type, including Na_2O, K_2O, and occasionally Li_2O and Tl_2O; those of the RO type, including CaO, MgO, BaO, ZnO, MnO, FeO, PbO; those of the R_2O_3 group, including Al_2O_3 and Fe_2O_3.

The additional components which may be present in coloured glass include gold, silver, copper, carbon, sulphides of sodium and calcium, fluorides of calcium and aluminium, oxides of cobalt, nickel, chromium, copper, uranium, tin.

Silica has the power of existing in the vitreous state, that is, the amorphous solid condition, and the only other inorganic binary compounds possessing the same property are boric oxide and phosphoric anhydride. All substances can exist in the amorphous state, but then they are nearly always fluid (liquid or gaseous). The normal conditions of existence of the amorphous state always correspond to the highest temperature, and those of the crystallized state to the lowest, whilst the temperature of fusion or of crystallization is a transformation point, on either side of which only one of the two varieties is stable; even by such a device as very sudden cooling it is almost impossible to preserve a body in the unstable state on either side of the transformation point. Silica exhibits the peculiarity of being easily preserved in the amorphous state at all temperatures up to that at which it becomes completely solid. For most substances the point of crystallization corresponds to temperatures at which the amorphous state of the same substance still exhibits a very weak viscosity, the mobility of the particles then making crystallization so easy, that it cannot be prevented. With silica the point of crystallization corresponds to a temperature at which its amorphous condition is fairly viscous or even pasty, so crystallization is so slow that it can be quite prevented by cooling rather slowly. Boric oxide and phosphoric anhydride resemble silica in this respect, and the various metallic silicates, borates, and phosphates—unlike other metallic salts—also possess the property of keeping the vitreous state more or less easily. It is almost impossible to crystallize lead silicate (SiO_2, PbO), and crystallization of the corresponding calcium and magnesium silicates is hindered by sudden cooling. Many definite silicates, found well crystallized in rocks, give, when melted, glasses which cannot be crystallized again; orthoclase is a good example, and it is owing to this property that it can be used for making ornamental pearls.

These various definite compounds, silica and silicates, can be mixed in the amorphous state, and thus give solid solutions equally amorphous, which essentially constitute what are called glasses. These solutions have all the properties of ordinary liquid solutions, except that which depends on the coefficient of viscosity. All glasses are at ordinary temperatures out of equilibrium, the stable state corresponding to complete crystallization. Glasses can also dissolve and keep in the amorphous state substances which alone would not take that state, as sodium chloride and sulphate, magnesium or lithium silicate, etc., which by themselves would crystallize easily. The addition of bases to silica materially reduces the viscosity of vitreous silica. The silica crystallizes much more easily in alkali or lead glasses than in the free state.

Many glasses, when reheated until they begin to become pasty, are able to crystallize more or less rapidly, but generally only within a very limited range of temperature. This confused crystallization of glass—through formation of long very slender crystals in a pasty mass—is termed "devitrification."

The passage from the solid to the liquid state of an amorphous substance shows no sudden fusing point, but according to the composition of a glass the coefficient of viscosity may vary more or less rapidly, and this forms the basis of all glass manufacturing processes.

Grenet (quoted with approval by Le Chatelier, in whose laboratory Grenet worked) characterizes the range of fusibility of glass by means of three points: (1) The *squatting temperature* or *depression temperature*, at which a vertical glass rod, 1 cm. diameter and 3 cms. high, becomes depressed under its own weight to about half its height (the load supported by the base of the glass being about 10 g. per sq. cm.), corresponding to the normal temperature of glass-blowing, to the solidification temperature of ceramic glazes, and to what is called the fusion point of Seger cones; (2) the *annealing temperature*, at which irregular tensions (caused by too rapid cooling of glass) disappear, and which is notably lower than the squatting temperature industrially; it is the temperature at which glass is annealed after manufacture; (3) the *tempering temperature*, at which the glass begins to be very slightly deformable under the strongest force it can support without breaking; the stress in these cases may be estimated at 1000 kg. per sq. cm.

Grenet's experiments gave the following results for St. Gobain glass:—

Composition.	Squatting Temp.	Annealing Temp.	Tempering Temp.
$2{\cdot}6SiO_2$, $0{\cdot}37Na_2O$, $0{\cdot}63CaO$	800° C.	604° C.	524° C.
$2{\cdot}45SiO_2$, $0{\cdot}47Na_2O$, $0{\cdot}53CaO$	845° C.	641° C.	573° C.
$2{\cdot}45SiO_2$, $0{\cdot}47Na_2O$, $0{\cdot}53PbO$	720° C.	460° C.	390° C.

Replacing the lime in the second of these by equivalent quantities of other bases gave the following squatting points:—

CaO	BaO	ZnO	PbO	K_2O	Li_2O
845°	1010°	890°	720°	705°	690°

The lowest squatting point of a glass studied by Grenet was 475° C. for a lead borosilicate of the composition $0{\cdot}5SiO_2$, $0{\cdot}5B_2O_3$, PbO. For all industrial glasses the squatting points fall between 750° and 850°.

The range of fusibility for industrial glasses, defined by the characters indicated, is about 300° C., that is to say, their mechanical resistance has in that interval of temperature exceeded a rapid stress of 10 g. to 1000 kg. per sq. cm.

The range of fusibility and its average temperature are very important for the easy working of glass. The lower the average temperature the more slowly the glass cools during the working, and the greater the range the greater the number of degrees through which the glass cools without ceasing to be workable. The range of fusibility and its average temperature depend exclusively on the chemical composition of the glass. The range increases with the ratio of the number of molecules of silica to that of protoxides (R_2O and RO), and the average temperature becomes lowered as the basic oxides in the glass are more fusible and in greater proportion. The presence of lead in crystal, and of high potash in Bohemian glass, enabled 3 molecules of silica to be used for 1 molecule of bases, whereas in ordinary white glasses (rich in lime) the proportion cannot exceed 2·5 : 1 without the fusibility being so much reduced that the glass could not be worked.

According to S. English and W. E. S. Turner (*J. Soc. Glass Tech.*, *2*, 90, 1918), at least three things should be known in connection with the annealing of glass : (1) the temperature at which strain can be removed rapidly without causing the glass to undergo deformation ; (2) the lowest temperature at which for all practical purposes the strain can be removed ; (3) the quickest rate of cooling between these two temperatures at which the glass can safely be cooled without the recurrence of strain. In the case of three lead glasses containing 57 to 64 SiO_2, 17 to 30 PbO, and 11 to 15 per cent. K_2O and Na_2O, the annealing temperatures were found to be practically the same, that with 17 per cent. PbO annealing quickly at 460°, and the other two at 450° C. Three lime alkali glasses with about 73 per cent. SiO_2, 7 per cent. CaO, and 18 per cent. Na_2O and K_2O, have annealing temperatures very close to 550° C. Two boric oxide glasses of practically the same composition, 65 per cent. SiO_2, 23 per cent. B_2O_3, 2 per cent. Al_2O_3, and 10 per cent. (Na_2O, K_2O), had annealing temperatures 585° to 590° C. Chemical glassware containing 64 per cent. SiO_2, 10 Al_2O_3, 7 CaO, 7 B_2O_3, 11·5 (Na_2O, K_2O), annealed at 630°. Another chemical glass containing 70 per cent. SiO_2, 10 Al_2O_3, 2 ZnO, 7 B_2O_3, 8 to 9 (Na_2O, K_2O), annealed at 635°. A third chemical glass, with rather less alumina, only 2 B_2O_3, but 6 per cent. more alkalies, annealed readily at 570° C., and a soft soda glass (for lamp working) annealed quickly at 530° C. The same authors (*J. Soc. Glass Tech.*, *3*, 125, 1919), in reporting results of an investigation on the annealing temperatures of lime-soda glasses, point out that whilst lead glasses seem to be readily annealed, chemical glassware requires a high annealing temperature followed by slow cooling, in order to remove strain and prevent its recurrence. They found that glasses with high soda content can be annealed at a comparatively low temperature (though higher than for lead glasses), and that they soften with comparative readiness like lead glasses. As soda decreases and lime increases the annealing temperature rises. Thus the different soda-lime glasses cannot be treated alike in the lehr, and any change of batch composition involves a corresponding change in the heat applied in order to produce effective annealing, as a variation of 5° greatly influences the speed of annealing.

CLASSIFICATION.

Industrially only a small proportion of the different mixtures possible are used. They are chosen so as to combine the greatest number of desirable qualities, and particularly a reasonable price. The qualities to be considered include transparency and absence of colour, slight chemical changeability, mechanical resistance, certain optical properties, etc.

Nearly all industrial glasses belong to one of a small number of main types; Noel Heaton's classification, slightly modified, is as follows:—

A. Glass with only silica as the acid constituent, combined with an alkali and one or more other bases.

1. Soda-lime glass or white glass (often called "crown glass") is much used for window glass, chemical glassware, bottles, etc. Lime is sometimes partly replaced by barium oxide, and a little alumina is commonly present. The silica is usually about 69 to 72 per cent., the composition approximating to $2·5SiO_2$, $0·5CaO$, $0·5Na_2O$ (which corresponds to 71·5 per cent. SiO_2, 13 per cent. CaO, and 15 per cent. Na_2O). Soda-lime-alumina glass is a modification with a substantially increased alumina content, and is used chiefly for beer, wine, and spirit bottles, owing to its strength and insolubility. The silica is 58 to 69 per cent., with alumina about 12 to 3 per cent.

2. Potash-lime glass, generally known as Bohemian glass, and used for making hollow-ware, or crown optical glass, the latter having more lime and less silica. The silica is usually about 72 per cent. or higher, the composition sometimes approximating to $2·5SiO_2$, $0·5CaO$, $0·5K_2O$.

3. Potash-lead glass, generally called flint glass or crystal glass. This is much used for making hollow-ware, bottles, and for optical glass. The composition sometimes approximates to $3SiO_2$, $0·5PbO$, $0·5K_2O$ [or $0·5(K_2O, Na_2O)$]. The theoretical percentage composition of this normal glass is 53·2 of SiO_2, 32·9 of PbO, and 13·9 of K_2O. In some varieties the lead oxide is substantially increased at the expense of the silica and potash, giving a denser glass. In one variety of flint glass, barium oxide and zinc oxide are the chief bases, and there is a little boric oxide as well.

B. Glass containing silica and also other acid oxides:

4. Borosilicate "crown" glass. Like 1, but with B_2O_3 partly replacing silica. Used for optical glass, thermometer tubing, boiler gauges, and laboratory ware. May contain 72 per cent. of silica, 12 of B_2O_3, 5 of Al_2O_3, 11 of Na_2O.

5. Borosilicate flint glass. Like 3, but with B_2O_3 partly replacing silica. Used for optical glass, etc., like No. 4,

may contain 67·5 per cent. of SiO_2, 2 of B_2O_3, 2·5 of Al_2O_3, 14 of Na_2O, 7 of ZnO, 7 of CaO. A glass transparent to X-rays consists of 39·6 per cent. of SiO_2, 30 of B_2O_3, 20 of Al_2O_3, and 10 of Na_2O.

6. Phosphatic glass, with P_2O_5 partly replacing silica.

C. Glass containing no silica.

7. Borate and phosphate glasses are sometimes used in optical work. Phosphate crown glass contains 56·6 per cent. of P_2O_5, 5 of B_2O_3, 11·3 of Al_2O_3, 14·8 of K_2O, and 11·6 of MgO. Borate flint glass contains 66·3 per cent. of B_2O_3, 11 of Al_2O_3, 4·12 of Na_2O, 6·87 of PbO, and 12·6 of ZnO. A special glass (mentioned by Le Chatelier), which contains no alkali, is very slightly attacked by acids and only slightly sensitive to temperature changes, contains 68 per cent. of SiO_2, 13 of B_2O_3, 3·7 of Al_2O_3, 12 of BaO, and 3·7 of ZnO. It is useful for chemical purposes.

8. Soluble glass or water-glass is soluble in water. It may contain about 60 per cent. of silica and 40 per cent. of Na_2O, but the composition varies to some extent, and sometimes K_2O replaces Na_2O, partly or wholly. Water-glass has already been considered in Section II.

9. Quartz glass, consisting of pure silica in the amorphous state. Quartz glass was considered in Section I.

According to Tscheuschner, Weber, Benrath, and others, the composition of alkali-lime glass can be expressed by the formula $xR_2O+yRO+zSiO_2$. For the normal composition (the so-called Tscheuschner normal formula), $x=y=1$, and $z=6=3(x+y)$. Judging from Weber's analyses of 49 glasses (quoted by Tscheuschner) the relationship $z=3(x+y)$ is only correct when $x=y$, that is, with molecular equivalents of alkalies and RO oxides equal; otherwise the value is too high with low alkali and too low with high alkali, and in these cases better results are obtained by substituting $3\left(\frac{x^2}{y}+y\right)$ for $3(x+y)$, the composition of the glass being then expressed as $xR_2O+yRO+3\left(\frac{x^2}{y}+y\right)SiO_2$. On this basis, for $y=1$ in Weber's analyses, x can range from 0·6 to

1 for plate glass, from 1·5 to 2 for Bohemian glass, and from 0·8 to 1·5 in glass for hollow-ware.

C. J. Peddle (*J. Soc. Glass Technology*, 1920), after a prolonged investigation, has come to the conclusion that the best glasses of this type approximate to the formula R_2O, RO, $5SiO_2$, or $0{\cdot}5R_2O$, $0{\cdot}5RO$, $2{\cdot}5SiO_2$. This finds independent confirmation in the compositions of St. Gobain glasses quoted by Le Chatelier, viz. $0{\cdot}37Na_2O$, $0{\cdot}63CaO$, $2{\cdot}6SiO_2$; $0{\cdot}47Na_2O$, $0{\cdot}53CaO$, $2{\cdot}45\ SiO_2$; $0{\cdot}47Na_2O$, $0{\cdot}53PbO$, $2{\cdot}45SiO_2$, In the case of lead glasses (crystal) the silica may be increased to 3 (instead of 2·5), which answers to Benrath's formula for "normal" crystal glass, viz. $K_{10}Pb_7\ Si_{36}O_{84}$ (or $5K_2O$, $7PbO$, $36SiO_2$).

The most important properties of glass are its transparency and its rigidity at ordinary temperatures—passing into plasticity at high temperatures and fluidity at still higher temperatures. This combination of properties is common to only a few colloidal substances, and only vitreous materials are also hard and fairly resistant to chemical changes. Water and dilute acids have a slight action on most kinds of glass; even a moist atmosphere produces sooner or later slight surface decomposition, especially with lead glasses, or glasses containing too much soda, potash, or boric acid. Hydrofluoric acid readily attacks glass as well as other silicates, forming gaseous silicon fluoride, an action which is utilized in etching. In the hot plastic condition glass is ductile and malleable, and can be welded, cut, drawn, pressed, etc. Glass cracks under sudden changes of temperature, a character which sometimes finds practical application during manufacture.

Ordinary glass is to a great extent opaque to both ultraviolet and infra-red rays, but the absorption varies greatly according to composition, being least in pure quartz glass and greatest in dense glasses containing lead oxide (the latter being opaque to X-rays). The density of glass varies with the molecular weights of the constituents, ranging from 2·25 for the lightest borate glasses to 6·33 for the heaviest lead and barium glasses. The average density for alkali-lime glass is 2·5, and that for ordinary flint glass is 3·0. Hardness and resistance to abrasion is proportional to the content of silica, lime, and alumina, and inversely proportional to the content of lead and alkali. Soda glasses are generally harder than the corresponding potash glasses.

Glass is a poor conductor of heat, and a non-conductor of electricity (except when moist). It breaks with a conchoidal fracture.

RAW MATERIALS.

Silica is chiefly used in the form of sand. Long ago (in the seventeenth century) calcined and ground flints were used for making the best glass, and this gave rise to the name "flint glass." Though the name persists, the use of flints for this purpose was abandoned when comparatively cheap supplies of pure sands became available; those of Fontainebleau and Lippe (for instance) are almost entirely composed of silica. Sometimes crushed sandstone is used, and in exceptional cases ground quartz. Fine white sand from certain British localities, as Lynn, Alum Bay (Isle of Wight), and Aylesbury, have been much used in recent years. For the best glass, the sands used should contain, besides silica with a little alumina and iron oxide, preferably only traces of other substances. The iron oxide should always be under 0·1 per cent., and is often under 0·04 per cent. Alumina may for some glasses amount to 3 or 4, or even as much as 8 per cent. In the absence of alumina, the silica should be at least 98 per cent., and for the best glasses should be 99·5 per cent. or more. In this connection, however, a statement of R. L. Frink (*Trans. American Ceramic Soc.*, *11*, 296, 1909) may be mentioned, that a certain American factory produced glass of the highest quality from a low-grade sand containing 88·51 per cent. silica, with 7·26 alumina and 1·07 calcium carbonate, etc., and when under new management a pure sand with 98·89 per cent. silica was substituted, though the quality and quantity of the product remained substantially the same, the low-grade sand produced a glass far superior in physical properties to that made with the purest sand. As regards mechanical composition of sands (or crushed rock) for glass-making, it is desirable to have as large a proportion as possible of nearly the same size, preferably the medium grade (diameter between 0·5 and 0·25 mm.) or the next smaller grade (diameter between 0·25 and 0·1 mm.). Smaller particles (less than 0·1 mm. diameter) of silt and clayey material are injurious, owing to their "blowing out" in the batch, to producing "cordiness" by differential melting, to entangling air bubbles, and to being more difficult to melt. Particles larger than 0·5 mm. diameter should be sifted out if present. As to mineral composition, good glass-sands consist almost entirely of quartz grains; alumina may be present in the form of felspar or kaolin; heavy minerals like magnetite, hematite, limonite, ilmenite, sphene, rutile, zircon, should only occur in small quantities.

Prof. Boswell lays down the following for guidance in the use of sands for glass-making: For the commonest glass (bottle-ware, etc.) the sand must be well graded, and composed of grains of suitable size. The iron oxide may range up to 1 per cent., the presence of small amounts of titanium oxide, alumina, lime, and alkalies are of little importance, but the silica should be fairly high.

For medium-class glassware (flint-glass bottles, chemical ware, globes, chimneys, pressed table-ware, etc.) high silica and low iron content are required, with high alumina for much laboratory ware, etc. The size of grain should not be more than 0·5 mm. nor less than 0·1 mm. diameter.

For high-class ware (optical glass, table glass for "cutting," and other special glasses) high silica with little or no iron oxide are required, and sometimes high alumina. As the batch is sometimes powdered, and the mixture kept melted for a long time (usually with stirring), crushed rocks and quartz, and poorly graded sands, can be used.

Fine silicious material undoubtedly introduces numerous minute air bubbles, which are not entirely removed by stirring or during the final "fining." It is questionable whether stirring ever produces the homogeneity obtained by using well-graded and evenly-melting sands.

Boswell gives the limits of iron content for some glasses as follows: optical glasses containing barium and zinc, below 0·02 per cent.; "crown" optical glass, up to 0·04 per cent.; table glass ("cut" and "crystal" ware), 0·02 per cent.; laboratory and medical ware 0·04 or 0·05 per cent.; plate glass, 0·05 per cent.; window glass, 0·1 per cent. The possible presence of iron in the limestone, felspar, manganese, etc., should not be overlooked.

Many British sands contain 2 to 3 per cent. alumina. In a few cases as much as 10 to 18 per cent. alumina is present, as in the refractory sands of Derbyshire and Staffordshire. A small proportion of alumina tends to strengthen glass, making it tougher and more resistant to pressure. Sands with a high percentage of alumina are valuable for glasses used for making thermometers, gauge glasses, combustion tubing, and other resistant glasses.

As regards British glass-making sands, the sands of the shore and dunes are only useful for bottle glass, and Thanet sands are also used only for bottle glass; even sands made by pulverizing blast-furnace slag have been used for this purpose, and natural igneous rocks such as basalt have been similarly used. Aylesbury sand can be used for optical glass and many other varieties. Leighton and Lynn sands are used for all kinds of lighting glass (electric globes, chimneys, etc.), laboratory ware, pressed ware, flint-glass bottles, etc. Aylesford and Reigate sands are good enough for something better than bottle glass. Some of the Yorkshire sands (Huttons Ambo, etc.) when washed are suitable for nearly all the better kinds of glass. The best Irish silicious material is the crushed quartzite of Muckish Mountain (Donegal).

Glass containing about 0·02 per cent. iron oxide is almost colourless, a glass with 0·1 per cent. iron oxide is quite green, and with 1 per cent. it is dark green.

For the best glasses, British manufacturers used Fontainebleau sand (from near Paris), which is high-class, with generally less than 0·03 per cent. iron oxide, with even grain (favouring production of homogeneous glass), and angular grains (ensuring quick melting), uniform in quality and obtainable regularly.

C. J. Peddle (*J. Soc. Glass Technology*, *1*, 27, 1917) reports that with thorough washing several British sands, etc., can be used advantageously for glass-making; the crushed quartzite of Muckish Mountain will give a good glass even without washing. Aylesbury and Lynn sands, with those from Huttons Ambo and Burythorpe (both in Yorkshire), will all give colourless glasses when washed, and with manganese dioxide as decolorizer, should certainly be good enough for flint glass. He is satisfied that with reasonable treatment many British sands could successfully replace Fontainebleau sand for many kinds of good glass.

Alkali was in olden times used in the form of native sodium carbonate. Afterwards the ashes of plants were used, and later manufactured sodium carbonate (from salt). Sodium sulphate was used instead of the carbonate—first in France in 1825, and in England in 1831—and is now in extensive use. It is customary, but not necessary if the temperature be high enough, to add carbon (as anthracite coal or charcoal) to deprive the sulphate of oxygen and so facilitate its decomposition, but this can only be done with leadless glasses. It is advisable to reduce the sulphate to sulphite, not to sulphide (which would give the glass a yellow colour).

Though sodium sulphate is much cheaper than the carbonate, it should be remembered that 53 parts by weight of the latter are equal to 71 parts of the former, and the sulphate needs a much higher temperature than the carbonate to react with silica.

Potash is invariably used as carbonate, generally known as pearl-ash. In lead glass and certain coloured glasses, part of the potash is used as nitrate, mainly to obviate any tendency to reduction.

Lime is generally introduced as carbonate, or hydrated oxide, both being obtained from chalk, or limestone. Chalk is contaminated with flints, which are only objectionable when large, some of the silica then possibly remaining undissolved, causing opaque enclosures (called " stones ") in the finished glass. In limestone, magnesia is generally objectionable, as it tends to make the glass hard and viscous.

Barium Oxide is used as precipitated carbonate.

Alumina is mostly present as an impurity, being dissolved by the molten glass from the fireclay vessels. In the hard glasses, alumina is added in the hydrated condition. In opal glasses it is added in the form of cryolite, but this is used mainly on account of the fluorine.

Manganese is generally added as the dioxide. It is essentially a colouring oxide, but is much used to counteract the coloration caused by iron, thus making the glass white, or rather colourless.

Cullet (which is waste or broken glass) is invariably added as well as the other ingredients, partly to use up the bits left over, and partly to facilitate chemical reaction at lower temperatures, that is, it acts as a flux. The cullet melts, and dissolves both alkali and silica. The cullet used should closely correspond in composition to the kind of glass it is intended to make with it, and should be as far as practicable free from iron in any condition.

MIXING.

The mixing of the materials is very important, for unless it is done well, irregularities may easily arise in the resulting glass. Sometimes the mixing is done by hand, the powdered raw materials being turned over by a workman with a wooden shovel, and afterwards passed through a sieve until well mixed. More usually a mechanical mixer is employed. It is a curious result of experience that, when the batch is mixed mechanically, China clay may always be used as a source of alumina, but with hand-mixing a batch containing China clay will never produce a satisfactory glass. Dr. Travers believes materials like China clay can be advantageously ground with one of the other constituents of the batch. He also concludes that it is distinctly advantageous to grind the cullet and mix it with the batch, instead of following the usual practice of adding it separately at the outset.

Wet mixing of the batch has been recommended, on the ground of securing more intimate mixture, the material to be afterwards dried by some of the waste heat from the furnaces.

The proportions of the constituents must largely depend on the temperature of firing, the time of exposure of pots at different temperatures, and the composition and amount of cullet added to the batch. When sodium sulphate is used, a substantial amount is removed by skimming, for it does not all react with silica. Some alkali passes off as vapour, and so is lost to the glass.

DECOLORIZING.

This is the process of correcting the undesirable tints given by small amounts of iron occurring as impurity, by adding small amounts of other colouring substances such as manganese dioxide, nickel oxide, selenium, etc., to neutralize the colouring effect of the iron. Iron may be derived, not only from impurities in the raw materials, but also by solution of the fireclay from the vessels containing the molten glass (or "metal," as it is called), and tends to produce a greenish tint. It should be remembered that sodium silicate in glass tends to communicate a bluish-green tint, and lead silicate is distinctly yellowish. Dr. E. W. Washburn showed that even iron in the furnace atmosphere can colour glass. Manganese dioxide colours glass purple, and this being complementary to the green colour from iron, a suitably proportioned application of the former practically eliminates the colour due to iron. This effect of manganese dioxide is only produced under oxidizing conditions, and if a sufficiency of oxidizing agent (or agents) be not present in the glass batch the purple colour is unstable and its decolorizing effect is not to be relied on. In mixtures for crystal glass, strong oxidizing agents are therefore to be used, generally in the form of nitre (saltpetre) and red lead, both of which give off oxygen when heated. If the melted glass be kept very hot for a long time there is a possibility of all the liberated oxygen being driven off, after which further heating would tend to make the glass greenish again. If by addition of too much manganese dioxide the glass becomes distinctly purple, a little carbonaceous material (in the form of a bit of charred wood or potato) can be pushed to the bottom of the glass by a forked rod, and the resulting vapours soon discharge the purple colour. Pure manganese dioxide should be used, as the native pyrolusite (often used as a decolorizer) is apt to contain substantial proportions of iron oxide, which is of course highly objectionable.

Nickel oxide has also been used as a decolorizer, and selenium or alkaline selenites oı selenates. In some cases preparations containing cobalt have been used for the purpose of neutralizing colour in glass (particularly when it tends to be yellowish), but only a very small amount is needed.

According to W. Frommel (*Keramische Rundschau*, 1917), the green colouring effect of 1 kg. iron is compensated by 0·208 g. selenium (or 0·0208 per cent.), and as a glass batch rarely contains more than 0·2 per cent. iron oxide, the selenium necessary would not usually exceed 0·00416 per cent. of the batch, or rather more than double that amount of sodium selenite.

The yellow colour imparted to glass by ferric oxide is much less intense than the greenish tint imparted by ferrous oxide, and advantage is sometimes taken of this fact by adding instead of a colouring substance (such as manganese dioxide) an oxidizing substance to ensure that the iron shall be in the ferric condition. Oxide of arsenic is used in this way, and the liberated arsenic, being volatile, seems to escape into the flues, though in some cases indications of the higher oxide of arsenic have been found in the resulting glass. Nitre and similar oxidizing agents have a similar effect on iron in glass, though the main object of adding a little nitre is generally to destroy carbonaceous matter, and to assist in preventing premature volatilization of arsenic.

In connection with the use of a colouring substance as a decolorizer, it should not be forgotten that the result is only attained through the loss of a portion of the light which would be transmitted by really colourless glass. For this reason that device cannot be adopted for optical glass, in the manufacture of which the purest materials available should be used so as to avoid any such loss of light. If it should still show some colour, it is not advisable to attempt to neutralize it by the use of a decolorizer.

GLASS FURNACES.

Both furnaces and pots are made of refractory fireclays, which occur chiefly in the districts about Glasgow, Leeds, Stourbridge, and other Midland and North of England centres, as well as in foreign countries (Belgium, France, Germany, etc.). The dry weathered clay is ground, sifted, mixed with grog (consisting of ground burned fireclay or old pots), tempered with water, and the plastic mixture used for making into blocks or pots, etc. The grain size, especially of the grog, should be adapted for the purpose to be served. For resisting sudden temperature changes, coarse grains answer best, but to resist the chemical action of molten glass or slag, fine grained material is better. Often it will be advantageous to combine the two in various degrees. Furnace blocks, when shaped, are slowly dried, and finally fired in much the same way as other fireclay goods, preferably up to cone 14, but never below cone 12.

The essential constituents of the fireclays are silica and alumina, and the latter should not be less than 30 per cent., whilst the silica may range from about 45 to 65 per cent. The other constituents are more or less accidental impurities, which mostly act as fluxing agents. The percentage of ferric oxide should not exceed 1·5, lime 0·5, magnesia 0·2, and total alkalies (potash and soda) about 2.

The plasticity of the fireclay should be increased as much as practicable by weathering, after removal of all injurious foreign materials, such as pyrite, stones, vegetable matter, etc. It is afterwards treated as described above.

The glass furnace is a heated chamber, in which the glasshouse pots are set. In the old round furnace, commonly used in England until comparatively recent times, and still largely used, six or twelve pots are arranged in a circle on the "siege," a kind of hob forming the floor of the furnace. The fire is placed below, and the flames rise through the "eye" of the furnace—centrally situated as regards the chamber, and below the level of the siege—to heat the pots. The fire burns in a round box with a bottom formed of strong iron bars. Passing right across below the furnace is the "cave," an underground tunnel, through each end of which air is drawn by the action of the draught in the chimney cone above the furnace. Coal is supplied to the fire at intervals through a passage under the siege from the floor of the glasshouse sloping towards the firebox. Sometimes a mechanical feeder is used, fitted below the firebars. The crown of the furnace, supported by pillars of firebricks, covers the pots and the siege. From this crown the flames are reflected down upon the pots, and passing between the pots they escape by small openings connecting the siege with small flues or chimneys leading upwards to the outer chimney cone.

Modern glass-melting furnaces are generally gas-fired, usually with regeneration or recuperation of waste heat. They are smaller and more convenient than the old coal-fired furnace, and combine more complete combustion of the fuel with easier regulation and increased production, being thus more economical. They also give much higher temperatures.

The regenerative system was invented by Siemens, the air or gas being pre-heated in regenerators, that is, chambers occupied by a checker-work of firebricks. The gases from the furnaces pass through two regenerators and heat the bricks, while the gas and air going to the furnace pass separately through two other regenerators. At definite intervals the direction of the gas and air is reversed by the manipulation of two valves, so that the gas and air for the furnace becomes pre-heated in the regenerators through which the hot waste gases have passed. Owing to the periodical reversal, the system of heating is intermittent.

In the recuperative system the waste gases and the air pass continuously in one direction, one tube or passage usually surrounding the other, so as to allow the air to be very satisfactorily pre-heated. The gas producers are usually close to the furnaces, so that the gas is hot enough when it enters the latter.

A semi-gas-fired system, in which for the burning of the gases (produced by the burning coal), secondary air, pre-heated to some extent by traversing passages in the furnace walls, is delivered at suitable points of the furnace, is still in vogue in many glass-works, both abroad and in England. The Boetius furnace is of this type, which is an improvement on the old coal-fired furnace, but has the disadvantage that the contents of a broken pot will run into the fire.

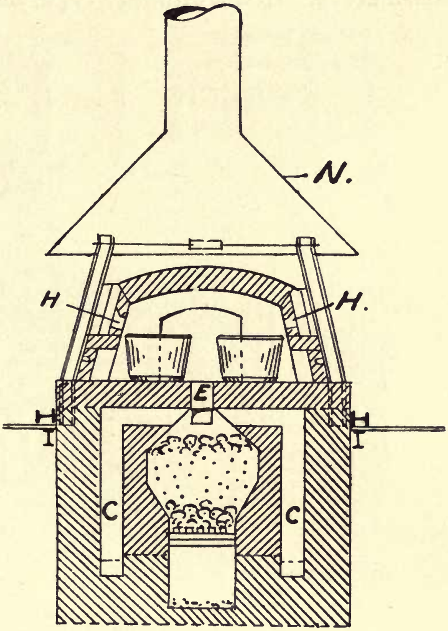

FIG. 22.—Boetius furnace (cross section).
(By courtesy of Mr. T. Teisen.)

C, Air channels.
E, Eyes of furnace.
H, Working hollows.
N, Chimney.

Several forms of regenerative glass-melting furnaces—modifications of the Siemens furnace—are in use, especially on the Continent, but, while economical as regards fuel, they suffer from the disadvantage that owing to the periodical reversals the temperature varies, first one end of the furnace and then the other end being the hotter.

Among the better known continuous furnaces are the Hermansen, the Nehse-Dralle, and the Stein, the Nehse-Dralle being mainly used in Germany. The **Hermansen Furnace,** of Danish origin, is used in Scandinavia, Germany, Russia, England, and other countries, and has proved very satisfactory. In the ordinary type, the burner is placed in the centre of the circular upper part of the furnace, and the pots are arranged in a ring within the circular wall, between the pillars which support the crown. The flues are in these pillars, near the fronts of the pots, the latter being oval in horizontal section. The recuperator—made of tubes of special shape and of special fireclay—is placed on each side of the producer in the lower part of the furnace, fully protected by cooling channels for the flow of glass. The burned

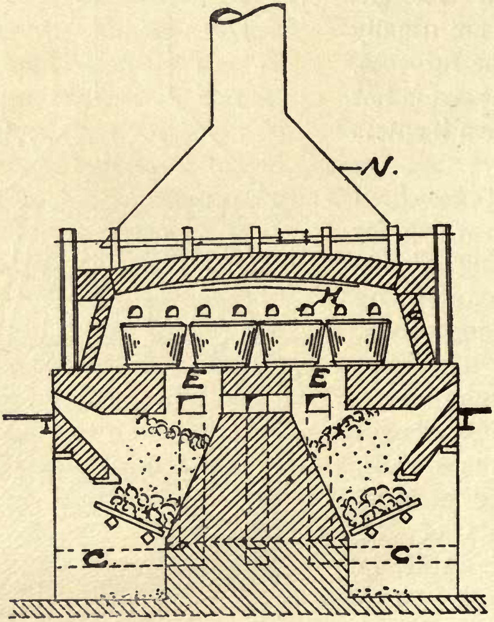

Fig. 23.—Boetius furnace (longitudinal section). (By courtesy of Mr. T. Teisen.)

gases pass through the larger channels of the recuperator, and the secondary air is pre-heated on passing through small cross channels formed by projections from adjacent tubes. Leakage between the products of combustion and the air is successfully avoided. Like other modern recuperative furnaces, the Hermansen melts the glass during the night, ready for working the next day, whereas the old direct coal-fired furnaces are usually worked only two or three times a week. The Hermansen type of furnace is much easier for the workman to tend than the more complicated regenerative furnaces. With greater units it may be fired from separate producers.

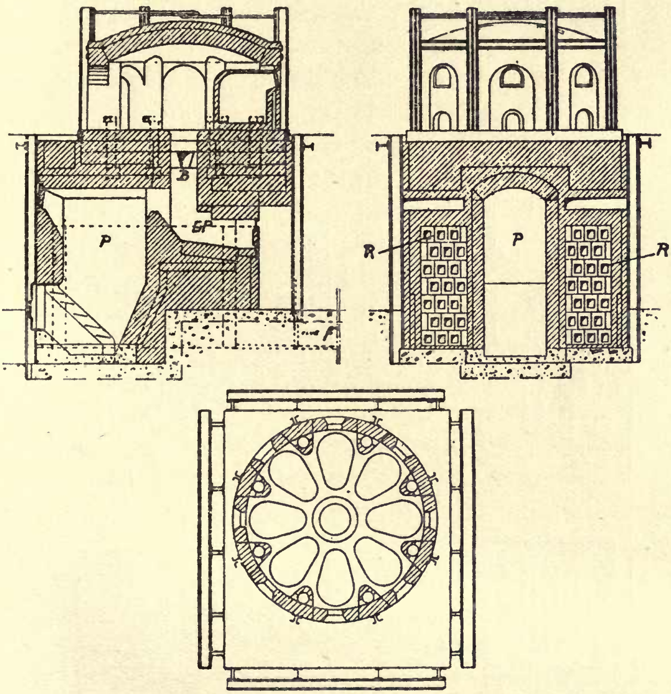

FIG. 24.—Hermansen recuperative furnace (for 8 covered pots).

F, Fire door.
P, Producer.
GP, Glass pocket.
B, Burner (eye, with 2 air inlets).
R, "Hermansen" recuperator.

The **Stein Recuperative Furnace** has recuperative chambers on each side of the furnace, so that the flow of glass from a cracked or broken pot does not reach them.

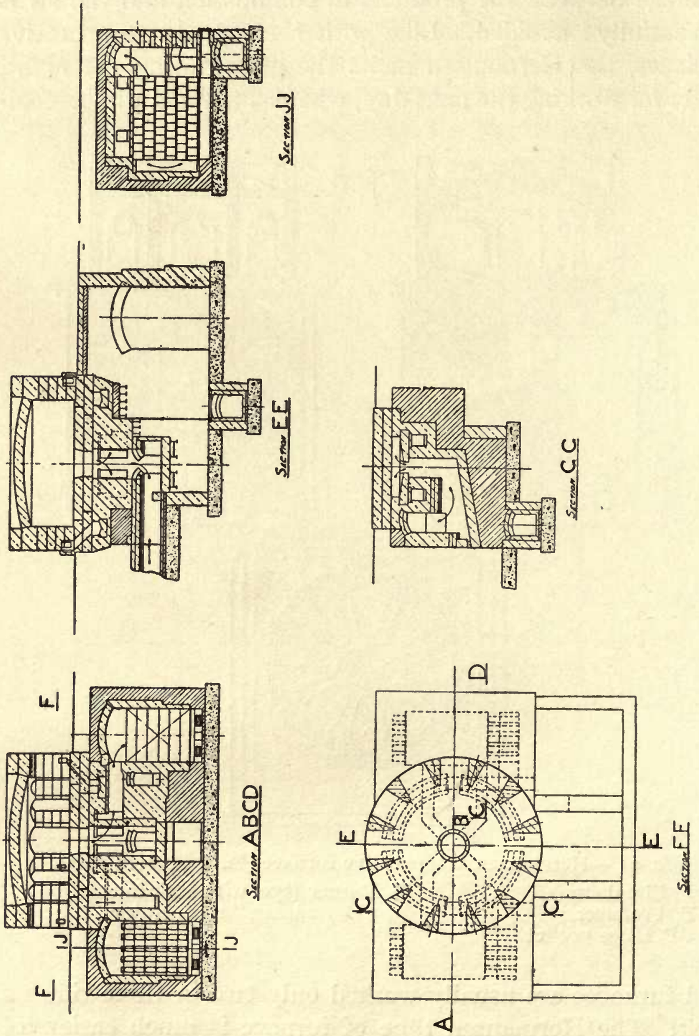

FIG. 25.—Stein recuperative pot furnace.

The air passages in the recuperators are vertical, and air is constantly rising in them, and expanding as it is heated, the space round the pots being quite filled with flame, thus ensuring uniform temperature. The producers can be independent, or built with the furnaces. Here also much greater economy of fuel is claimed than in modern regenerative furnaces.

Brief reference may also be made to a remarkably efficient type of gas-fired furnace—the **Dennis Simplex Furnace**—described by Dr. M. W. Travers in *J. Soc. Glass Technology*, *4*, 205, 1920. It was evolved in a somewhat haphazard fashion from a gas-fired furnace of a continental pattern, having two producers built into the centre of it, and flanked by recuperators. This furnace did not work satisfactorily, and when eventually it was put out of action, it was decided not to rebuild it but to reconstruct it, the producers being completely removed and replaced by a Frisbie under-feed grate. The new furnace thus obtained was found to work very efficiently, and to be exceptionally easy to manipulate.

The **lehr** (leer, or annealing furnace) is in most English glasshouses an arched chamber more than 40 ft. long, with a laterally-placed firebox at the hot end. The glass articles are placed in pans, which are heated directly by the fire. As the pans are drawn down the lehr, the contents gradually cool off. This method answers well for annealing lead glassware, but is unsatisfactory for resistance beakers and flasks, notwithstanding their lightness. Dr. M. W. Travers (*J. Soc. Chemical Industry*, *37*, 238T, 1918) attributes this to the presence of a kind of skin, which may account for the fact that unless the glass is thoroughly soaked at the annealing temperature it is not properly annealed. Scientific glassware has enormous bulk for very small weight, and as the goods must pass very slowly through the hot part of the lehr, it follows that this class of ware requires very large lehr accommodation. The use of producer gas has been found very effective with lehrs for resistance glass, as in the Teisen patent lehr illustrated, the gas entering a space below the bed of the lehr, which is formed of a brick arch, and then passing up ports at the side. Secondary air enters through slides at the front and meets the gas at the bottom of the ports;

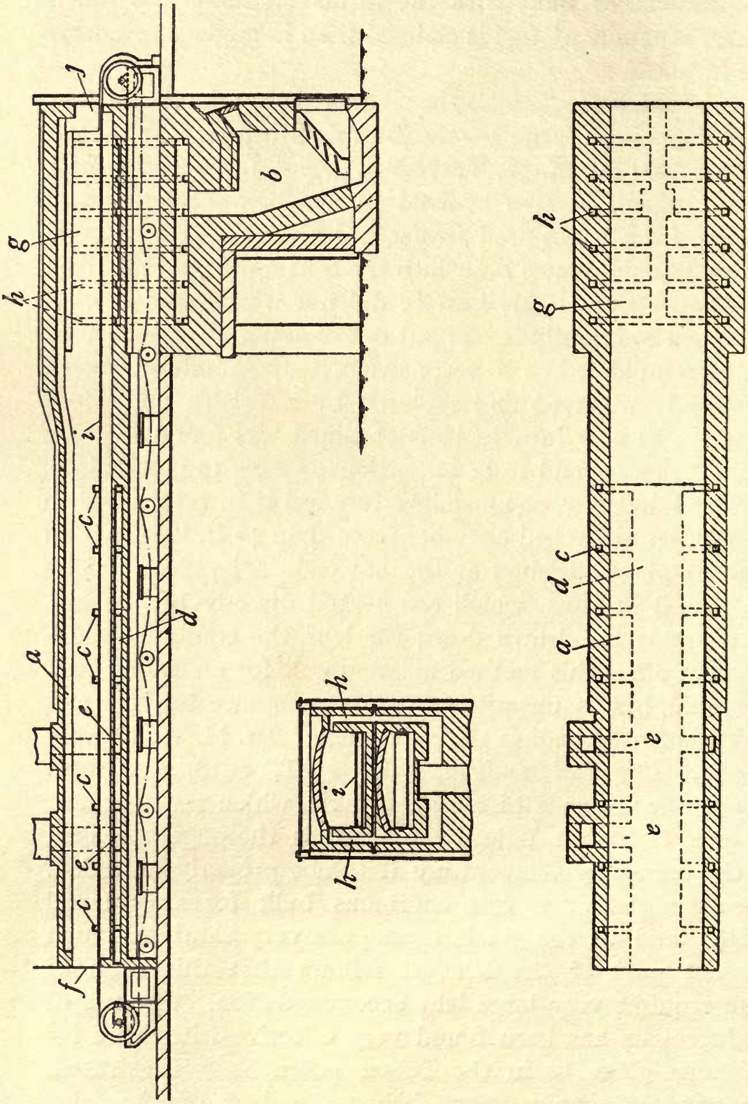

FIG. 26.—Teisen patent gas-fired Lehr with conveyor.

b, Producer; *i*, Endless belt conveyor; *j*, Entrance or charging opening; *f*, Discharging end; *h*, Heating channels; *c*, Draw-off holes; *d*, Hot bottom flues; *e*, Chimneys.

the length of the flame issuing from the ports—and therefore the temperature of the lehr—can be increased or decreased by closing or opening the air slides. The temperature of the hot part of the lehr can be thus regulated to within 10°, and as the hot gas from the producer heats the bed of the lehr from below, the temperature can be maintained fairly uniform. The fall of temperature along the lehr is regulated by taking away the hot gases into a flue, through openings controlled by dampers. Resistance glass may be removed from the lehr at 300° C. with safety. Optical glass needs very careful annealing.

Very thin glass does not require annealing, but thick glass may need a very long time. For most ordinary glassware about 3 to 6 or 8 hours are generally occupied in passing it through the lehr. Very bulky articles are usually put in annealing kilns, and often take about 3 days. The annealing of optical glass (especially the heavy lead and barium glasses) may take as much as 10 days. It may be noted that the peculiar behaviour of the well-known Rupert's drops (or Dutch tears) is due to internal strains.

GLASSHOUSE POTS.

The pots used for melting glass are made from mixtures of clay and grog prepared in the same way as for furnace blocks. For crystal or flint glass, which contains lead oxide, the melting batch has to be protected from reducing agencies, especially the flames, smoke, and ash of the old coal-fired furnace chambers, as otherwise metallic lead would be formed and the glass spoiled; hence, covered pots are used for melting these lead glasses, each pot having an opening in front, through which the materials are charged and the molten glass withdrawn. Covered pots are also used for optical glass. For most other kinds of glass, the pots used are open at the top. In the latter case the melting may be aided by directing the heat on to the surface of the materials within the pot. In the case of covered pots, the heat has to pass through the cover.

The pots are subject to the corrosive action of their contents, and have also to withstand the furnace heat and the pressure of the contained glass. The cracking of a pot has serious results, as the molten glass is not only lost, but it attacks the parts of the furnace that it comes into contact with, and on reaching the firebox it combines with the fuel ash and soon interferes with the draught.

The proportion of grog to clay in the mixture depends on the plasticity of the clay, but usually as much grog is incorporated as is practicable, and it may vary from about 6 volumes of grog to 5 of clay, to 1 volume of grog to 3 of clay. After mixing with water, and soaking for some time, the mixture is tempered by treading well with bare feet, which seems to consolidate the clay mass better than any mechanical treatment. It is then left to mature for a few weeks before being used, and it is ready after this for making into pots. Various shapes and sizes are used, but the commonest is a round pot 38 ins. in diameter and 42 ins. high. In making a pot, the workman arranges little rolls of clay on a round flat board of the same size as the bottom of a pot. These rolls are laid in circles, and pressed together so as to exclude air, until a circular slab about 4 ins. thick is formed, which is made smooth. The sides or walls of the pot are built upon the slab in the same way from little rolls, to a thickness of about 3 ins. The wall is built up about 6 ins. at a time, with intervals of a day or so to enable each section to stiffen a bit before the next section is added. When a height of about 30 ins. has been reached, a clay ring about 18 ins. in diameter is put in the pot. This clay ring afterwards floats on the melted glass, and keeps scum away from the middle portions. After this, the potmaker begins to draw the remaining portions of the sides inwards to form the cover of the pot, at the same time reducing the thickness of the walls. The working opening is made by cutting out the clay while it is soft. These openings are closed by stoppers while the glass is being melted. The pots are dried very gradually over a period of several months. Open pots are made in the same way, but are finished off at the proper height before putting to dry.

Mechanical contrivances of different kinds—a hydraulic press, etc.—have been tried for shaping pots with the aid of moulds, but with no great success. Better results have been obtained by casting, the whole pot or parts being made by pouring prepared slip into the mould. For this purpose the slip is made very heavy, though quite mobile, by adding to the prepared clay a little sodium carbonate and sodium silicate along with a limited amount of water. In the United States this has been combined with the use of a special grog, having a composition resembling that of hard porcelain, for pots intended for optical glass; this proved more resistant than ordinary grog to the molten glass. In this country, a modified casting process, patented by Allen and Ames, involving vacuum pressure in some cases, has been tried with considerable success, at the University of Sheffield and elsewhere.

Reference may also be made to articles relating to the casting of glasshouse pots in the *Journal of the American Ceramic Society*, *2*, 647, 659, 1919, the first by F. H. Riddle, and the second by J. W. Wright and D. H. Fuller; also to an article by A. V. Bleininger, *1*, 15, 1918.

When dried, the pots are set in a small auxiliary furnace termed a "pot arch," where they are annealed and then heated to whiteness, after which they are removed into the furnace for use in melting glass, to replace old pots which are first withdrawn. A pot is left in the furnace empty for a day or two to regain full heat before raw materials are charged into it. It is generally first glazed inside by means of melted glass from another pot. The cracking of pots while in the furnace is very troublesome. Most commonly the cracking takes place down the front of the pot, either through the lip or below it, and the mischief is probably due, as Travers points out, to insufficient firing in the pot arch and subsequent unequal heating in the glass furnace. The pots removed from the pot arch (where the temperature probably seldom reaches 1100° C.) are subjected in the furnace to a much higher temperature (usually 1300° to 1400° C.), which makes at least the surface portions semi-vitreous. But under ordinary circumstances the front of the pot does not reach the higher temperature, and the strains thus produced from unequal contraction give rise to a tendency to crack. The front is also more subject to corrosion. All this could be avoided by care in heating the pots in the pot arches, and by building a temporary wall in front of the pots when set in the furnace, and leaving the pots undisturbed several days. An instructive paper by Dr. M. W. Travers, on the firing of glasshouse pots, will be found in the *Journal of the Society of Glass Technology, 2,* 170, 1918.

G. W. Wilson (*J. Soc. Glass Technology, 2,* 177, 1918) points out that the white porcelain-like layer formed round the pots or blocks is often packed with sillimanite crystals. Sillimanite is only developed in vitrified pots, and it lengthens the life of the pot or block by reducing the liability to corrosion. In practice, highly aluminous clays should be used, but the vitrification temperature should be near the furnace temperature.

For very basic glasses, plumbago pots have been found very satisfactory. They are made of mixtures of raw fireclay and graphite (plumbago).

Lieut.-Col. C. W. Thomas (in *J. Soc. Glass Technology, 4,* 107, 1920) suggests making covered pots in two pieces, the upper part consisting of the hood and adjoining portions all round down to the level of the flat lower lip of the opening, with the idea of improving the inside of the pot by beating it, when hard and tough, with a beater. It is proposed to fit a jointing cushion of asbestos rope between the two parts, each of which is grooved to hold the packing in position. The asbestos rope is said to make an effective gas-tight and dust-tight joint. This device is not patented.

TANKS.

For the production of glass on a larger scale, the ordinary pots are replaced by tanks, more particularly for bottle glass and other common glasses, as the glass melted in tanks is much more liable to contamination than that melted in pots ;

recent improvements have been effected in this respect, and owing to their greater capacity tanks may be preferred in the future for other kinds of glass as well.

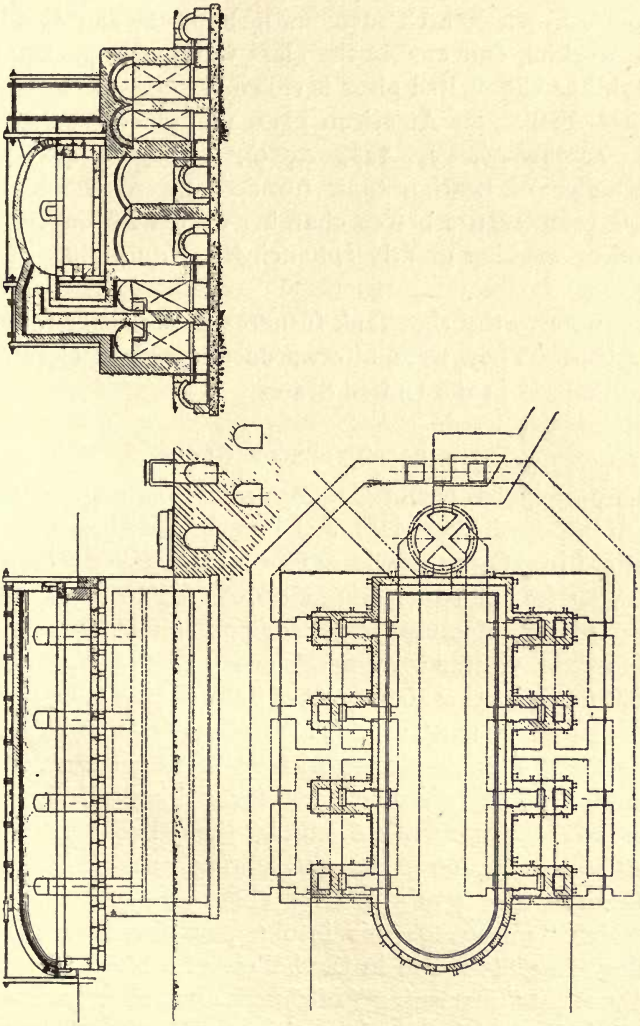

FIG. 27.—Stein and Atkinson's tank furnace.

Tank furnaces contain only one tank, of rectangular shape, commonly about 18 to 24 ins. deep, and 30 to 100 ft. long, and are economical in working. The bed and walls of the tank are made of fireclay blocks, specially selected for resistance to corrosion. These furnaces are gas-fired. The tank has a centrally placed shallow bridge, which prevents all unmelted material from passing to the working compartment. A crown or arch surmounts the tank, and openings at the working end enable the glass workers to gather the "metal," as the melted glass is called.

E. E. Fisher, an American glass manufacturer (*J. Soc. Glass Technology, 3,* 147, 1919), strongly advocates the practice of heating tank furnaces up to the highest possible temperature before charging even with cullet, this method of working greatly enhancing the durability of the tanks.

It is noteworthy that tank furnaces were first introduced in England. They were afterwards adopted in Germany, and much later in the United States.

PRINCIPAL TYPES OF GLASS.

The principal types of glass are soda-lime glass, potash-lime glass, potash-lead glass, and borosilicate glasses.

Soda-Lime Glass, or white glass, is often called "crown" glass, though that name originally referred to a particular method of manufacture. The composition (as previously mentioned) sometimes corresponds nearly to $2·5SiO_2$, $0·5CaO$, $0·5Na_2O$ (representing about 72% of SiO_2, 13% of CaO, 15% of Na_2O). Davidson and Turner (*J. Soc. Glass Technology, 3,* 222, 1920) state that such glasses with 13 to 17 per cent. Na_2O are durable. They are much used for making window-glass by the crown or disc method, and by the cylinder method.

In the crown process the workman collects on his blow-iron (an iron tube 4 to 5 ft. long) about 10 to 14 lb. of hot glass, and "marvers" this into a pear-shaped lump by spinning the glass round in the hollow of a block of wood; sometimes the "marvering" of glass is done on a "marver" consisting of a thick flat plate of iron. He then blows the glass out, and by rapid spinning it is made to flatten out so that its diameter becomes many times greater than the distance from front to back. Another workman then fixes by means of a little molten glass a pontil (or pointel, that is, a solid iron rod of about the same length as the blow-iron) on the middle of the outer curved surface, and the blow-iron is disconnected by wetting the glass close to the blow-pipe, the glass breaking off and leaving an aperture. The glass on the pontil is next taken to a "flashing" furnace, which has a large round opening in front; the glass soon becomes softened, and, as the pontil is rotated rapidly, the opening in the glass gradually enlarges until suddenly the glass spreads out into a large flat round sheet or disc. This circular crown table, while still rotating, is brought away from the furnace, and allowed to set, and is then conveyed to the annealing oven, the pontil being removed, leaving its position marked by the "bull's eye" or bullion.

In the cylinder method for making what is called **Sheet Glass** (formerly known as broad glass) the workman gathers glass into a large ball, which is then blown out and widened by rapidly spinning the blow-iron as in the previous method. But in this case, by repeatedly blowing and swinging in turn, the shape becomes elongated until it is cylindrical. The free end of the cylinder is reheated, and opened out with the help of a special tool until the diameter at the open end is the same as that of the cylinder in general. The end attached to the blow-iron is next cracked off, which may be done by letting the glass cool, then wrapping a thread of hot glass round it, removing the thread, and quickly applying a cold hook at the end of an iron rod. The glass cylinder is taken to a flattening kiln, being first cut or cracked lengthways on the inside, then placed further in the kiln, where the heat makes it uncurl and flatten out gradually. As the sheet becomes flattened, it is levelled out with a flat block of charred wood called a "polisher." Each sheet when levelled is taken away to the annealing oven. This method gives larger sheets than the crown glass method, but cylinder glass always shows some surface waviness and is less brilliant than crown glass. The superior surface of crown glass is doubtless due to the "fire-polishing" it gets during its expansion. Glass shades are also blown by sheet blowers.

In the United States the production of sheet glass by the cylinder method was successfully accomplished by the application of mechanical means, the cylinders being opened and flattened out as before. Another method—the Colburn process—which has recently been practised with some success in America, is the direct drawing out of the molten glass into sheets without any blowing or other intermediate operation.

E. H. Bostock has suggested (in the *Journal of the American Ceramic Society*, *3*, 36, 1920) that possibly an extrusion method might be devised to furnish a superior product.

Plate Glass is another variety of soda-lime glass used for glazing shop windows and show cases, and for mirrors. More care is taken in the selection of materials and in the manipulation than for crown or sheet glass. The melted glass when plain and free from seeds is either ladled out into smaller pots for casting, or (more usually) the whole pot is removed from the furnace, and after skimming the glass it is taken to the casting table. The casting table consists of an iron bench with level top and a raised flange running along each side to determine the thickness of the glass plate. The hot glass is poured on the table, and a heavy metal roller is passed along to roll out the hot glass to the regulated thickness. The cast plate is then trimmed at the ends, and when set is pushed into an annealing oven. After annealing, the glass plate has rather wavy, rough, and uneven surfaces, and has to be ground and polished on both sides by means of a grinding machine. It is then ready for being made into mirrors if desired.

Sometimes the molten glass is passed between two or more parallel rollers to make plate glass.

Wired glass, or strengthened plate, is produced by causing a network of specially suitable wire to be embedded in the soft glass during the rolling. Plate glass may also be strengthened by connecting two plates with an intervening celluloid film.

Mirrors are made by laying tinfoil over a smooth horizontal table, pouring mercury (quicksilver) on the tinfoil and distributing it evenly, then carefully sliding a glass plate over the mercury without touching the tinfoil with it, applying weights on the plate so that the latter is brought into contact with the tinfoil and the excess of mercury is squeezed out gradually. Another method of silvering glass plates is by the reduction of silver nitrate solution to which has been added excess of ammonia and also some reducing agent such as grape sugar, oil of cloves, etc. The glass plate is well cleaned, placed horizontally, and the silvering solution is poured over the surface, the temperature conditions being kept favourable. When a sufficient covering of silver has been formed, the liquid is poured off, the plate is dried, and the silver film is protected by a coating of hard varnish.

Pressed Glass is practically a crown glass in which part of the lime is replaced by barium oxide (baryta), the latter helping to give the pressed ware a good surface. Seam marks are left on the pressed glass articles. Pressed glassware is made by dropping hot glass into a two-piece iron mould fixed in a lever press, so that by bringing down a lever arm the plunger presses the hot glass into shape. The plunger is then released, and the pressed article turned out of the mould, the article being removed for finishing operations before being annealed.

Bohemian Glass has potash instead of soda, along with lime and silica, and a little alumina. It forms a hard, brilliant glass, much used for tableware, mirror glass, and chemical glassware, and is specially suitable for enamelled glassware.

Bottle Glass is a variety of lime-soda glass containing a distinctly larger percentage of alumina at the expense of the silica. Some of the soda may be replaced by other bases, such as magnesia. It is more complex in composition than other ordinary glasses. It is very hard, and more resistant to chemical action, as well as more difficult to melt, than ordinary crown glass. It is melted in tank furnaces. Common bottle glass is coloured, usually greenish, according to the amount of iron and other colouring substances present in it. Common sand (which would not be pure enough for other varieties) is used in its manufacture, as well as other materials of common quality. Even basalt, granite, phonolite, and other igneous rocks have been used in its preparation, and also artificial materials such as blast-furnace slag.

Mixtures containing equal parts of decomposed basaltic earth and sand, as well as other mixtures including basalt, were found to give a dark-coloured, hard, tough glass highly resistant to corrosive liquids. Difficulty arose in getting materials sufficiently uniform. Basaltic earth alone was also used.

Nearly fifty years ago in this country a process was evolved and patented for preparing glass from a mixture of 100 parts of Welsh or South Staffordshire iron slag, 65 of common ferruginous sand (yellow or red), and 10 of common sodium sulphate (salt cake). The appliances for the manufacture of glass from slag, involving the utilization also of the heat of the slag, were described at a meeting of the Iron and Steel Institute at Leeds in 1876 (see the Institute's *Journal* for 1876, p. 453), and many specimens were then exhibited, the colour of which was stated to be little if any darker than much of the rough glass plate at that time used for skylights. See also Bashley Britten's patent No. 3750, November 19, 1873. There may have been good reasons for hesitating about adopting such a process at that period, but in the light of recent experience, and especially with modern bottle-making machinery available, the idea seems now to merit the serious consideration of practical glass workers.

It may be of interest to give the following quotation from the fourth volume (Supplement), p. 817, of Ure's "Dictionary of Arts, Manufactures, and Mines, 1878," which was edited by the late Robert Hunt: "We learn from Mr. Britten that the extensive experiments which have been carried on during the years 1876–7 have proved perfectly successful, and that under the title of 'Britten's Patent Glass Company,' for which Mr. Herbert Canning is the Secretary, large works are being built at Finedon, in Northamptonshire, where in a few months they will be ready to manufacture large quantities of glass bottles." I am not able to supply any later reference to this venture.

The shaping of bottles is at present done mostly by means of automatic or semi-automatic machinery, which originated chiefly in the United States. Common bottles are extensively made in this way, but sometimes a hand tool finishes the neck after the mould has formed the body. Modern bottle-making machines have been brought to such a degree of perfection that they gather the metal, effect the shaping, and complete the bottle, so that hand labour is practically superseded in the actual making of the bottles; travelling arms are made to cool the mould forms by dipping them into water, the moulds then open to receive the hot metal and afterwards close, air pressure is applied within the mould, and the bottle is then delivered on to a travelling belt which takes it away to be annealed. The output of some of these bottle-making machines is enormous.

It may be mentioned that in this country the Hartford-Fairmont patents have been introduced into a number of works by the British Hartford-Fairmont Syndicate, Ltd., London; these include the Hartford-Fairmont Feeder and the O'Neill bottle-making machines. The Millar, Lynch, and Owens are other well-known machines. The Owens machine is capable of producing 700 bottles in an hour.

For working with automatic or semi-automatic machines, it is found advantageous to have the glass less viscous than for ordinary blowing, and this is ensured by a slight increase in the percentage of soda in soda-lime glasses, the best proportions of soda being 15 to 17 per cent., according to Davidson and Turner's researches.

FLINT GLASS OR CRYSTAL.

Flint glass or crystal is essentially a silicate of potash and lead oxide, the density increasing with the proportion of lead, which latter is increased at the expense of the silica and potash jointly. It is the greater fusibility due to the lead which enables extra silica to be taken up, so that in some cases the composition of flint glass approximates to $3{\cdot}0SiO_2$, $0{\cdot}5PbO$, $0{\cdot}5K_2O$. Good ordinary flint glass is colourless, but excess of lead imparts a yellowish tinge. All or part of the potash may be replaced by soda, but the resulting glass has not the same brilliance. According to Hodkin and West (*J. Soc. Glass Technology*, *4*, 124, 1920), 2 parts borax per 100 parts sand in the batch increases the durability of lead glasses, as does also equivalent proportions of soda and potash instead of either alone. Most English cut glass is made from the best crystal. Bismuth oxide might be substituted for lead oxide in the manufacture of glass, giving a very similar product, but it is much too expensive for general use.

The proportions of the ingredients actually used for making flint glass vary considerably. Nitre (saltpetre), manganese dioxide, and white arsenic (arsenic trioxide) are added in small quantities. The materials intimately mixed together are charged into the covered pots, previously heated to a white heat, so as to fill them. When all is melted the bulk is much less, and a further charge is added, this being repeated until the vessels become full of melted glass. Even when melted the glass only loses its opacity gradually, and it only becomes transparent after the removal of a white porous scum which rises through the glass, and is known as glass-gall or sandiver. This scum apparently consists of certain salts present in alkalies; these have a lower specific gravity than the glass and have only slight affinity for silica. Another substance called sandiver is sometimes found at the bottoms of pots, and is shifted when the glass is worked off; this is quite different from the scum previously referred to, and is a vitrified mass of earthy and other impurities. Glass-gall is very volatile at high temperatures, and the resulting dense vapour acts corrosively on the pots. When vitrification becomes complete, the glass is in too fluid a condition for shaping, so its temperature is lowered by stopping the draught in the part of the furnace where the pot is, when the glass loses its perfect fluidity and becomes soft and tenacious. Below redness glass becomes rigid, brittle, and transparent. Glass may remain a long time in the melted state without changing its qualities, that is, the working temperature has a considerable range. The blow-iron and pontil are used, in the manner already referred to, for collecting glass and blowing it into various shapes.

Lead Silicates are more fusible as the proportion of lead oxide increases. The metasilicate ($SiO_2.PbO$ or $PbSiO_3$) melts at a bright-red heat, and is itself yellowish.

Rocaille Flux, strass metal, or diamond paste, is made by fusing together 100 parts sand and 66 parts red lead. It is used chiefly for making soft enamels (by addition of borax) and imitation gems. The original Rocaille flux was a silicate of lead containing lead oxide (or red lead) in the proportion of 3 parts to 1 part of sand; this has a yellow colour.

DEVITRIFICATION.

When glass is kept for a time at the freezing point (or solidification point) of any of its constituent compounds, such compound or compounds will tend to crystallize out from solution, and glass which thus becomes cryptocrystalline is said to be devitrified. Réaumur in 1727 noticed that glass heated for a long time at its softening temperature, but without melting, became dull, opaque, and milky white, and such devitrified glass was called Réaumur's porcelain.

Glasses rich in lime and alumina readily devitrify, whilst glasses rich in lead or alkali can be maintained at the critical temperature for a long time before devitrification takes place. Smaller proportions of alumina, as well as boric oxide and oxides of titanium, zirconium, tin, thorium, arsenic, and antimony tend to prevent devitrification. Devitrification is sometimes intentionally promoted for decorative purposes, as in "ambitty sheet."

In the widest sense of the term, devitrification means the separation from glass of any constituent in either crystalline or amorphous condition. Some writers regard it as crystallization, whether evidently so or (as is more usually the case) in an incipient stage. Others consider as devitrification only visible aggregates, whether crystalline or amorphous, as distinguished from opalization, which results from separation of very finely divided particles, either crystalline or amorphous.

Separations from glass fall into four classes :

(1) Separation of easily visible crystalline particles, with no milkiness or cloudiness in the glass.

(2) Separation of easily visible non-crystalline particles.

(3) Separation of minute crystalline particles giving the glass a milky or opal effect.

(4) Separation of minute non-crystalline particles with accompanying opal effect.

C. J. Peddle (*J. Soc. Glass Technology*, *4*, 3, 1920) suggests for these four varieties the names crystalline devitrification, amorphous devitrification, crystalline opalization, and amorphous opalization respectively. It is implied that in each case there was at one time total solution, followed by separation. Some " opal " glasses instead of being clear, are suspensions (not solutions), when gathered at founding temperatures.

A disadvantage of Peddle's proposal as it stands is that it provides no satisfactory term to cover the four varieties, and, as all the varieties represent important departures from the normal structure of glass, devitrification seems a very appropriate comprehensive term to use in the widest sense as defined above. The first and second classes of separations might, for want of better terms, be referred to as crystalline and amorphous segregations respectively, when it is desired to emphasize the distinction from opalization.

The commonest crystalline deposit in glass seems to be silica, which may separate from various types of glass, including lime-soda glasses ; it is mostly in the form of cristobalite, but with some tridymite. Calcium metasilicate ($CaSiO_3$) may separate from ordinary lime-soda glasses. From glasses very rich in lead may be deposited lead metasilicate ($PbSiO_3$). All these may develop as spherulites—more or less globular masses consisting of radiating microscopic crystals with interstitial glassy material. In some special glasses crystals of barium disilicate ($BaSi_2O_5$) may separate.

Closely resembling devitrification "stones" in general appearance are *pot stones, batch stones*, and *crown drops*. Pot stones are derived from pots, and consist entirely of crystals of sillimanite with a little interstitial glass. Batch stones consist entirely of silica, often a quartz core surrounded by cristobalite (or cristobalite and tridymite), or occasionally entirely cristobalite; they represent undissolved silica of the batch, but considerably altered. Crown drops are due to the corrosive action of vapours on bricks of the crown, and consist of crystals of tridymite coarser than the fine-grained cristobalite of batch stones.

Reference may be made to two papers in the *Journal of the American Ceramic Society* by N. L. Bowen, on "Identification of Stones in Glass" (*1*, 594, 1918), and "Devitrification of Glass" (*2*, 261, 1919).

SOME SPECIAL KINDS OF GLASS.

Aventurine (or avanturine) is a golden yellow glass with minute yellowish spangles, the reflections from which give the characteristic appearance. It is produced by using excess of copper along with strong reducing agents in the glass; partial reduction of the copper taking place within the glass. Chromium aventurine is a somewhat similar product, obtained by the use of excess of chromium compounds in the presence of reducing agents, and consisting of a translucent green glass filled with minute spangles. In both cases slow cooling of the melted glass is necessary to aid crystallization. A remarkable effect is also obtained by rolling or marvering some dark-coloured glass upon a thin layer of flaked mica, then making another gathering or coating of clear crystal glass, and finally blowing the whole so as to form an ornament or vase, when the mica flakes give a silvery reflection against the dark background.

Gold Ruby Glass.—Gold forms very unstable colourless compounds with glass, and the gold can only be kept in solution by cooling suddenly. When cooled slowly, or when the quickly-cooled colourless glass is reheated so as to soften it, metallic gold is precipitated as minute particles dispersed all through the glass, and the glass acquires a fine ruby red colour, due to the reflection by these minute particles of light of shorter wave length than red. A very small quantity of gold is required, the solubility of gold in glass not exceeding 0·01 per cent.

Red Glass may also be obtained by the use of copper along with a reducing agent; the copper can be thus precipitated as minute metallic particles, giving a ruby red colour in the same way as with the gold particles referred to above. When completely oxidized copper forms soluble silicates, which give a strong green or blue colour, depending on the composition of the glass.

Silver acts in the same way as gold, but the particles transmit yellow light in this case. The silver is readily absorbed by the glass, and sheet glass is coloured yellow by penetration in this way. On painting glass with any silver salt, and heating to about 400° C., the glass absorbs some silver, and on raising the temperature to about 800° C. the silver is precipitated, producing what is technically termed silver stain. Potash-lime glass with low silica gives the richest effect, but the silver is not easily absorbed by hard glasses.

Carbon colours glass yellow to brown, but in lead glasses the lead would be reduced as metal.

Sulphur produces a greenish yellow coloration (except in lead glasses) due to formation of coloured sulphides of alkali and calcium. Addition of 7 to 10 per cent. of sulphur gives a black glass.

Selenium produces a pale rose coloration, especially when calcium is replaced by barium. The finest rose colour is got with potash glasses. According to O. N. Witt, alkali-lime glasses take up at most 0·06 per cent. selenium, the excess being volatilized, and it is better to introduce the selenium as a selenite or a selenate.

Kirkpatrick and Roberts (*J. American Ceramic Soc.*, *2*, 895, 1919) state that selenium gives a very pure red colour to some glasses, but the red colours from other colouring agents transmit light from other parts of the spectrum. After the selenium becomes incorporated in the glass (probably in colloidal suspension) it is retained permanently if the temperature does not exceed 1400° C. Good red colours were produced in a zinc-alkali glass with 0·8 per cent. each of borax, cadmium sulphide, and selenium, and in a plate glass by using 0·65 per cent. selenium and 0·85 per cent. cadmium sulphide. The two most essential steps are: (1) to prevent escape of selenium vapour, and (2) to allow the glass to cool long enough immediately after gathering (usually 30 to 60 seconds).

Uranium Oxide gives a peculiar fluorescent yellow colour. The fluorescence is stronger in potash-lime glasses than in soda-lime glasses, and is not noticeable in lead glasses. Glass coloured by uranium oxide or sulphur is often used when it is desired to exclude the chemically active (actinic) light rays.

Antimony Oxide, combined with lead oxide to form lead antimoniate, gives an opaque yellow colour with only lead glasses.

Manganese Oxide gives a reddish violet colour to lead glass or soda-lime glass, but an amethyst tint to potash-lime glass. The tint is modified or even discharged altogether when reducing agents are present. Glass containing manganese can be coloured purple even by exposure to actinic light, and the colour of such purple glass on heating it to the softening point can be made to disappear.

Cobalt Oxide strongly colours all glasses blue, with 0·1 per cent. Even 0·01 per cent. produces a pale blue.

Nickel Oxide also strongly colours glass reddish to purple, but its action is somewhat uncertain, so it is not much used for colouring purposes, though it is sometimes employed instead of manganese dioxide as a decolorizer.

Chromium Oxide produces green tints, but it is only slightly soluble in glass, and any excess over 4 to 5 per cent. separates out on cooling, producing an opaque green glass.

By various combinations of these colouring agents a very wide range of tints can be obtained. The tint of glass may vary if the thickness of the glass is not uniform, as is the case with coloured solutions. Black glass is obtained by the use of mixtures of cobalt oxide, iron oxide, and some other oxide (as manganese oxide or nickel oxide); a very fine black is produced by iridium oxide.

A practically opaque glass is the subject of a patent by the Corning Glass Works, etc. (pat. 127,586, May 28, 1919); it is very transparent for ultra-violet rays. The preferred composition is given as 50 per cent. of SiO_2, 16 of K_2O, 25 of BaO, and 9 of NiO.

White or opal glasses are produced by including in the batch materials either tin oxide, calcium phosphate, calcium fluoride, cryolite, alumina, zinc oxide, talc, arsenious oxide (white arsenic), or more than one of these. Tin oxide is now much too expensive for general use.

Sprechsaal (52, 30, 265, 1919) gives two typical batches for opal glass without cryolite, with the use of bone-ash in one case, and a mixture of felspar and fluorspar in the other, as opacifying agents:

	Sand.	Potash.	Soda-ash.	Limespar.	Bone-ash.	Borax.	Saltpetre.	Fluorspar.	Felspar.
I.	100·0	10·0	24·5	18·0	22·0	2·0	2·0	—	—
II.	100·0	2·5	27·5	—	1·5	—	—	11·0	27·5

Alabaster glass is semi-opaque, and does not materially alter the colour of the light it transmits, whereas in the case of opal glass, which is also semi-opaque, the transmitted light acquires an opal or fiery colour. The most desirable alabaster glasses are produced by aluminous substances with fluorides and chlorides or sulphates. Other substances used for the same purpose are calcium phosphate, magnesium silicate, tin oxide, arsenious oxide, zirconia (Ger. pat. 189,134), and titanium oxide (Ger. pat. 18,708). Alabaster effects may also be obtained in high silica glasses through devitrification.

The earlier white glasses were chiefly alabaster glasses, due to the effect of impurities in the form of chlorides and sulphates present in the potash used, which caused the precipitation of the colloids in the glass. Reference may be made to a comprehensive paper by A. Silverman on "Alabaster Glass" in the *Journal of the American Ceramic Society, 1*, 247, 1918, which includes a copious bibliography, etc.

Sometimes coloured glass has not the colour distributed throughout. Such glass is made by the blower dipping the end of his pipe first in coloured glass, then in colourless glass, or vice versa ; or he may take up first colourless glass, then coloured glass, and then colourless glass again ; in any case he proceeds to blow the glass into a cylinder, which can then be cut and flattened out like sheet glass.

As glazes are merely glasses spread in thin layers, there seems no valid reason why the suggestions thrown out in connection with crystalline ceramic glazes (in Section IV.) should not (with the aid of proper appliances) be more or less applicable to glass also. In that case, it should be a comparatively easy matter to colour the surface of glass red with copper or gold, yellow with silver, etc. (See p. 225.)

GLASS PAINTING OR STAINING.

Glass painting or staining implies the art of painting on glass (either colourless or already coloured) with vitrified or vitrifiable colours, which are afterwards fixed to the surface of the glass by firing in a muffle. In some cases a flux or glassy composition has to be mixed with the colouring base to enable it to be fixed to the glass. This flux is sometimes simply mixed with the colouring substance before firing it on the glass, but in other cases it is vitrified by previous melting with the colouring substance, and then ground before putting it on the glass. The effect is practically the same as laying finely powdered coloured glasses on the surface of the glass to be painted, and then firing. The various substances should of course be insoluble in water, and they should have (after firing) approximately the same coefficient of expansion as the glass to which they are to be fixed ; the fusibility should be greater than that of the glass, which is generally ensured by the addition of the colouring substance.

The flux may be simply a combination of silica (1 part) and lead oxide (3 parts), a combination long known as Rocaille flux; more generally the flux contains also some borax, and sometimes nitre as well, the ingredients being present in various proportions. Flint glass, mixed with potash (pearl-ash) and a little borax, is sometimes used. For some colours lead oxide is undesirable, and borax may then be used.

OPTICAL GLASS.

Optical glass is not circumscribed by any narrow limits as regards chemical composition, but may belong to any of the main groups of glasses, such as the normal or modified crown or flint glasses, borosilicate glasses, etc. In view of the special importance of optical glass, it may be well to briefly review the characteristics of greatest value in glasses intended for optical purposes. In general, optical glasses may be said to be superior to ordinary glass as regards such properties as transparency and colour, hardness, and durability. The optical properties, which determine the refraction and dispersion of the rays of light, vary widely according to the composition of the glass and the treatment it receives in the course of manufacture.

For many lenses of a cheap type, and usually small in size, the stipulation as to superior quality applies only in a relative sense. Ordinary plate glass, for instance, is largely used for making cheap lenses, when it is of reasonably good quality.

Transparency and colour are closely connected, for the degree of transparency may (and often does) vary for different coloured rays. At a casual glance, common window glass seems colourless, but if viewed through a considerable thickness (several inches), as by looking through a piece edgeways, it appears of a sea-green tint. Even the very best optical glass made from exceptionally pure materials seems distinctly coloured when light passes through a considerable thickness of it; this of course is due to absorption of certain light rays as they pass through the glass. Common glasses owe their greenish colour to the presence of impurity, mainly ferrous oxide, and this is also true (in a lesser degree) of the better glasses. It is noteworthy in this connection that the same impurity present in the same proportion may produce a much more pronounced effect in one kind of glass than in another. Thus, the effect of the impurity which would produce a distinct greenish tint in a dense barium glass would scarcely be noticeable in a hard crown glass. To avoid the greenish coloration which is popularly associated with glass of poor quality, glass makers use "decolorizers," that is, substances which alone would produce a reddish tinge, the effect being to neutralize the greenish colour. But this remedy is very inappropriate in the case of optical glass, because it involves further absorption of light rays, with consequent loss of light. As it is usually necessary for optical purposes to have as much light as possible transmitted, it is important to avoid colour as far as practicable by excluding colouring impurities. Apart from all this, the colour of a glass may be intimately associated with important optical properties, arising from unequal dispersion in different parts of the spectrum.

Transparency of glass is diminished by the presence of foreign bodies, and these should be cut out during the selection of the glass, and their presence obviated, when practicable, during the process of manufacture. More trouble is caused by foreign bodies which arise in the glass itself, as bubbles or "seed," and as devitrification products. Bubbles or "seed" are liable to appear in all glass, and may be derived in the first place from air in the powdered batch, and afterwards from gases—chiefly carbon dioxide and nitrogen oxides—liberated by decomposition of carbonates and nitrates among the raw materials. By adjustments to suit the furnace and the particular method of working, a manufacturer can generally arrange to use a mixture which gives mostly large bubbles, by which the smaller ones are swept out of the melted glass. But in the manufacture of optical glass the manufacturer has much less latitude, since it is necessary, in order that the glass shall have the stipulated optical properties, to produce a glass of definite chemical composition. In some cases the glass cannot be produced quite free from small bubbles, but as these do not involve the loss in transmission of more than 0·02 per cent. of the light, it is no serious disadvantage to the lens. Devitrification has already been considered. Generally it is possible to avoid this difficulty by cooling the glass quickly through the dangerous zone of temperature, which for most glasses is in the neighbourhood of a dull-red heat.

The most serious interference with transparency comes from the "striæ," or veins, which occur in all ordinary glass, and which have to be removed for the best optical glass. They arise from irregularities in the mixing of portions of melted material of different densities and different refractive indices, and are variously disposed in streaks, streams, layers, etc. Careful stirring might naturally be expected to result in uniform mixing, but the matter is greatly complicated by the corrosive action of the molten glass on the material (usually fireclay) of the pot; the product of this action is very viscous and mixes with the other glass slowly, and while it is being incorporated by stirring, fresh striæ would be forming. Hence the stirrer has to be kept away from the walls of the pot, and only a portion of the contents can be freed from striæ. In plate glass and sheet glass (window glass) striæ are numerous and are arranged in fairly even layers parallel to the surface; they appear clearly when the glass is viewed through a polished edge. In optical glass the striæ are often of microscopic size, but can be detected by placing the glass across the path of a beam of parallel rays, and viewing it through a lens (or combination of lenses such as an eye-piece), when any striæ present appear as either shadows or brighter lines. In the absence of sunlight, a small light a few yards away will answer the purpose.

Glass is often subjected to internal strain, due to tension or compression, or both. In the case of ordinary glass, this is of little or no consequence unless the strain leads to rupture, but in optical glass strain appreciably changes the optical properties, and as the strains are seldom distributed symmetrically in a lens, the resulting image is distorted. It fortunately happens that this defect (unlike striæ, colour, etc.), can be eliminated by very careful annealing of the finished glass, without re-melting it.

Hardness in optical glasses is necessary to enable it to resist abrasion while it is being made into lenses, and to enable the lenses to resist accidental abrasion or scratching. Durability implies the power to resist the chemical action of air, water, or other things which may touch it; glasses show wide differences with respect to this property. For want of sufficient durability, certain glasses which would otherwise prove very valuable for optical purposes, are quite useless—as borate flint glasses and phosphate crown glasses. On the other hand, the best glasses—as certain hard crown glasses and borosilicate crown glasses—are not appreciably affected by atmospheric moisture and carbon dioxide, or by the organic matter of dust which might be left on glass surfaces touched by the fingers. Other glasses (chiefly very dense flint glasses high in lead), though resistant to moisture and carbon dioxide, are liable to become spotted by the action of the organic matter of dust. The presence of much alkali, and of barium oxide and boric oxide, tends to make glass susceptible to chemical action of the air. Modern chemical glassware, such as the well-known Duroglass, for example, is very resistant even to the prolonged action of hot water, of alkalies, and of acids.

Milkiness is occasionally found in optical glass, and has been traced by Professor Turner and his colleagues at Sheffield, and by Fenner and Ferguson in the United States (*J. American Ceramic Soc.*, *1*, 468, 1918) to the action of very small amounts of sulphates and chlorides—chiefly the former—the direct cause of the milkiness being attributed to separation of clouds of minute crystals of cristobalite.

With reference to refraction, the refractive property of a glass is usually expressed by the refractive index, as measured for sodium light (yellow) represented by the D line of the spectrum. For this refractive index the symbol n_D is used.

The refractive indices for other lines are similarly represented by n_A, n_C, n_F, etc.

The dispersive power (or dispersion) is the power of a glass to spread or disperse white light into a spectrum of different colours. The mean dispersion is defined as the width of the spectrum between the lines C and F, and is measured by the difference between the refractive indices for C and F—that is, mean dispersion $(\triangle) = n_F - n_C$. Another important quantity, known as ν (it has not received any special name), is obtained by dividing (the refractive index less one) by the mean dispersion, that is, $\nu = (n_D - 1)/(n_F - n_C)$.

The optical defects of simple lenses give rise to chromatic aberration and other irregularities, but these can be remedied by suitable conbinations of lenses made of different kinds of glass.

In an article on the "Manufacture of Optical Glass" (*J. American Ceramic Soc.*, *2*, 422, 1919), W. S. Williams and C. C. Rand state that with a glass consisting of 44·4 per cent. of SiO_2, 46·0 of PbO, 4·1 of K_2O, 3·5 of Na_2O, 2·0 of CaO, and 0·4 of As_2O_3, the refractive index and ν varied as follows in different melts :—

Refractive index	1·6282	1·6283	1·6268	1·6278	1·6288	1·6248	1·6242	1·6221	1·6285	1.6265
ν	36·7	36·7	36·7	36·8	36·5	36·6	37·2	37·4	36·6	36·7

The effects of changes in composition on the average values of the index and of ν are shown in the following :—

Glass.	No. of melts.	SiO_2.	K_2O.	Na_2O.	CaO.	ZnO.	B_2O_3.	PbO.	BaO.	As_2O_3.	Refractive average index.	ν.
Medium flint	10	44·4	5·0	3·5	3·0	—	—	44·0	—	0·2	1·62446	37·2
,,	10	45·6	4·1	3·5	3·0	—	—	44·0	—	0·2	1·62741	36·9
,,	10	44·4	4·1	3·5	2·0	—	—	46·0	—	0·4	1·62658	36·8
Light barium crown ..	7	48·1	7·5	1·0	—	10·1	4·5	—	28·3	0·4	1·56907	57·3
,, ,,	7	48·0	6·1	2·0	—	10·0	4·0	—	29·5	1·4	1·57343	56·7
,, ,,	7	47·6	6·0	2·0	—	9·8	4·0	—	30·5	1·5	1·57700	56·5
,, ,,	5	46·0	6·1	2·0	—	10·5	5·5	—	29·5	1·5	1·57990	56·7

The effects are due partly to differences in raw materials, and partly to volatilization of materials in melting the glass.

Attention may be directed to Dr. W. Rosenhain's "Cantor Lectures on Optical Glass" (London, 1916), and to several other interesting papers on optical glass in the *Journal of the American Ceramic Society* by C. N. Fenner, G. W. Morey, H. S. Roberts, and R. J. Montgomery (*2*, 102, 146, 543, 1919, and *3*, 404, 1920, respectively). By plotting out the known optical glasses according to their refractive indices and dispersion constants, Montgomery finds there are twenty-three ordinary types of optical glass, each type comprising a number of glasses quite similar in optical properties, composition, and method of manufacture. They range from borosilicate crown glasses through various ordinary crowns and barium crowns, barium flints, and borosilicate flints, and through ordinary flints, to the densest silica flint glasses.

In the same journal (*1*, 730, 1918) T. D. Yensen, in a paper on "Magnesia Ware," incidentally points out that large crystals separate from electrically-fused magnesia, and that these crystals are cubic and isotropic, and combine very high refractive index with low dispersion—a valuable combination of properties in material for lenses.

A special variety of optical glass is made into spectacles for use by glass-furnace operators to avoid injury to their eyes. This glass contains cerium, derived from waste material left after extraction of the relatively small proportion of thorium oxide from monazite. (See report on monazite in "The Mineral Industry of the British Empire and Foreign Countries," 1920.)

STRASS AND IMITATION GEMS.

The glass or "paste" used for making imitation jewels is made from the purest obtainable materials, including the colouring oxides. The base of all these products is the paste or strass, generally made of white sand or quartz, red or white lead, and potassium carbonate, with boric acid or borax. After thoroughly melting the product is quenched in water, the melting and quenching being repeated several times. For the finest strass, the potash is used in the form of purified caustic potash. The paste is thus a heavy lead glass or crystal, which is strongly refractive and very brilliant. The powdered strass is mixed with the appropriate colouring materials, subjected to prolonged fusion, and cooled so slowly as to be annealed in the melting pot. It is finally broken up, and the pieces of glass are used for making imitation gems.

Varying proportions of the materials are given, but in all cases lead oxide forms approximately half the whole weight, and silica about one-third the whole weight. The boric acid, or borax, is usually about 2 per cent. of the total quantity.

The colouring material added to 1000 parts by weight of strass or paste is:

For imitation topaz, 40 parts glass of antimony, 1 part purple of Cassius; alternatively 10 parts iron oxide may be used.

For imitation ruby, glass of antimony as for topaz, but with a little more purple of Cassius, and with longer heating.

For imitation sapphire, 15 parts cobalt oxide.

For imitation emerald, 8 parts copper oxide, and 0·2 part chromium oxide.

According to W. Stein ("Die Glasfabrikation," 1862), for coloured imitation gems may be used not only every lead crystal or flint glass, but also mixtures containing little lead and even leadless mixtures.

ENAMELS.

Enamels are vitreous or glassy materials which, when melted, can adhere firmly to the surface of metal or of pottery. Those on pottery, as mentioned in the preceding section, are merely glazes of a particular type. These latter have not as a rule been vitrified before being applied on the ware, but enamels for metals are commonly, though not invariably, melted before they are applied to the metal; in most enamelled iron advertisement tablets, the enamel is applied in the raw state, as on pottery.

Enamelling on metal was practised in early times, the enamel being for a very long period sunk into cells (or cloisons). The base of the enamel is generally a colourless flux or glass—consisting of silica, red lead, and potash—in which are suspended particles of opaque material, generally tin oxide. Above 900° C. tin oxide may have undergone combination or solution, resulting in diminished opacity. Tin oxide has been substituted by titanium oxide or antimony compounds, and opacity may also be obtained by using arsenious oxide, calcium phosphate, cryolite (natural or artificial), or fluorspar. Coloured enamels are best prepared by adding the colouring material to a flux previously prepared by the usual method of fusing the components together. Enamels are hard or soft according as they require a very high or a lower temperature to melt them; the harder enamels contain relatively more silica.

The softer enamels are more readily affected by weather influences. Great fusibility may be secured, if necessary, by mixing borates with the silicates. Pure metals and hard enamels make the best combination for durability. Enamels containing much soda or potash are more liable to crack and to separate from the metal than enamels with more red lead in them. All transparent enamels can be made opaque by adding a calx consisting of lead oxide (litharge), and tin oxide, made by calcining a mixture of lead and tin. The enamel is very finely powdered and well washed with water, and the metal on which it is to be applied is carefully cleaned by immersion in dilute acid—nitric acid for copper, sulphuric acid for silver, and hydrochloric acid for gold; the acid is thoroughly cleaned off, and finally the powdered enamel is applied evenly, and after drying, the metal object is transferred to the muffle, where it is heated to bright pale redness. In contrast with pottery or glass, the firing of enamel only takes a few minutes, and annealing is hardly ever required.

J. Minneman (*Trans. American Ceramic Soc.*, *13*, 514, 1911) gives as the best soft enamel flux found in the course of his investigation a high lead flint glass of the formula $0{\cdot}5$ PbO, $0{\cdot}5$ K_2O, $1{\cdot}5$ SiO_2, made from 12·9 parts white lead, 10 parts nitre, and 9 parts silica. This flux compared favourably in every way with a German commercial soft flux. For a hard enamel he found the following very suitable: 0·5 PbO, 0·5 K_2O, 2·0 SiO_2, made from 12·9 parts white lead, 10 parts nitre, and 12 parts silica.

Champlevé Enamelling has the design outlined by cutting hollows in the plate with the graver, leaving raised lines and bands of metal between; the hollows are filled with powdered enamel, which is melted, and the whole is then ground smooth.

Cloisonné Enamelling is another mode of inlaid enamelling, in which thin metal strips, fixed to the metal plate by solder or by the enamel itself, form a raised outline, and the cells enclosed are filled with enamel and treated as in champlevé.

The **basse-taille** process is also a combination of metalwork in the form of engraving, carving, and enamelling. A design was first engraved, followed by carving into a bas-relief (low relief, below the general surface of the metal), so that, when the enamel was melted on, the design showed through the translucent enamel, the varying thickness of which produced differences of tint.

Plique-à-jour is a kind of cloisonné work in which, by removing the ground upon which they are fired, the pattern is left outlined by strips of metal, the spaces enclosed by the metal strips being filled with translucent enamel.

Painted enamels are usually done on copper, but sometimes on silver or gold, the plate of metal being slightly convex. The metal was cleaned with dilute sulphuric acid, then coated evenly over front and back surfaces with white enamel powder, and afterwards fired. As a result the metal ground was concealed. The design is next laid on in a "flux," or more fusible and more transparent enamel, which may be either white or some colour which can take other colours later. Painted enamels were introduced in the fifteenth century in Limoges.

In **Grisaille Painted Enamels** the white enamel is painted thickly in the lighter parts and thinly in the grey parts, giving great light and shade with a slight sense of relief.

In **Coloured Painted Enamels** the painting was executed on the smooth fluxed surface in transparent enamel colours, or powdered glasses mixed with a suitable vehicle, each colour being vitrified, by a separate firing in a muffle. Touches of gold in lines, etc., are sometimes added to improve the effect, and foil is occasionally used under the transparent enamel.

Two new enamelling processes were brought out by A. Fisher not many years ago. The first is an inlay of transparent enamel resembling *plique-à-jour* without separation of the colours by cloisons, for if (as in painted enamels and *basse-taille* enamels) the melted enamels do not run together, there should be no need for the separation in this process, the result being a clear transparent subject in colour. The second new process consists of a coloured enamel relief, the colour of the enamel permeating the whole depth of the relief; it resembles the relief on della Robbia ware, but the colour is only on the surface of the latter, and another difference is that one has a fresco surface whilst the surface of the other is highly glazed. The shapes of the various parts of the relief are selected for the different enamels, and these enamels are melted together, in the mould of the relief, which is finished with lapidary's tools.

Miniature Enamel Painting is not true enamelling; the white enamel is fired upon the plate as in other cases, but the colours used are not vitreous compounds—that is, not true enamels—but are raw oxides, etc., with a little flux added (not combined). These colours, after being painted on the white enamel, are made to adhere to the surface by partially fusing the enamel.

Enamelled Sheet Iron has been largely used for street names, advertisements such as railway notices, etc. Soft sheet steel is much used for domestic hollow-ware Cast iron is also enamelled, but is used mainly for sanitary goods, such as sinks, lavatories, tubs, etc.

The metal, after being thoroughly cleaned by pickling in an acid bath, is covered with a thin coating of ground enamel, which need not be opaque, and generally contains a little cobalt or nickel oxide. When this coating is dry, the article is fired at a temperature a little under 1000° C. in a muffle furnace. The ware is next scrubbed to remove scale, and a thicker coating of opaque white cover enamel is applied over the ground enamel; the articles are again fired, but at a somewhat lower temperature. Sometimes a third coat is applied, and sometimes a single white coating is put directly on the metal, the coating of ground enamel being omitted. The surface may finally be decorated by painting or transfer printing in enamel colours, or by photographs.

The enamels used for **cast-iron** goods are soft borosilicate frits, made opaque by tin oxide. If the enamel is for a ground or slush coat, it is made more infusible by adding clay, felspar, flint, etc., to the fritted material sent to the mill to be ground dry. If it is a cover enamel it may have additions, usually supplementary opacifying agents; the finely ground material is ready for enamelling. Ground material for a slush coat is mixed with water to the thickness of paint. The slush coat serves to protect the casting from oxidation during the first heating, and to form a close union with the iron (which the cover enamel could not do). The cover enamel should fit the iron exactly, both as regards melting point and coefficient of expansion. A slight difference in the coefficient will cause the enamel to craze (if too soft), or to peel or chip off (if too hard). Most of the good ground coats for cast-iron enamels contain borax, red lead, and sodium nitrate (J. H. Coe, *Trans. American Ceramic Soc.*, *13*, 531, 1911); this author states that the use of cobalt oxide in these is of doubtful value. Other writers take the view that the cobalt oxide improves the enamel. F. H. Riddle (*Trans. American Ceramic Soc.*, *9*, 646, 1907) gives the range of favourable composition of cover enamels for cast iron as: alkalies, 0·2 to 0·6 equivalent, preferably near the lower limit (on account of solubility), and mostly as felspar, but some as nitrate, with B_2O_3 as borax; fluoride, not less than 0·083, but satisfactory at 0·125 (perhaps up to 0·25 or 0·3 if introduced in the form of barium fluoride or cryolite); barium, 0·0 to 0·45 equivalent; the ratio of BaO+PbO to the remaining RO bases should be about 10 : 5 to 7; boric acid, 0·05 to 0·3 equivalent, preferably as borax when permissible; lead oxide, 0·1 to 0·4 equivalent (in high proportions it produces transparency and yellow colour); zinc oxide, 0·0 to 0·1 equivalent, aids in opacifying, and tends to overcome the yellow cast from lead, but is rather infusible; alumina, 0·1 to 0·25 equivalent (the higher the alumina the less tin is required); silica, 0·75 to 1·25 equivalent, should be kept as high as possible, as these glasses are generally basic; tin oxide, 0·2 to 0·25 equivalent is mostly used, but 0·15 equivalent (about 7·5 per cent.) works very well; the most likely formula would be about as follows: 0·40 PbO+BaO, 0·15 K_2O, 0·15 CaO, 0·05 ZnO, 0·25 Na_2O, 0·15 Al_2O_3, 1·0 SiO_2, 0·2 B_2O_3, 0·2 SnO_2—the lower the lead and the higher the barium the better.

H. Vogel (*Keramische Rundschau, 23*, 109, 1915) states that enamel adheres on hard white cast iron better than on the softer grey, so that it is advantageous to obtain a thin layer of white iron on the inner surface of a casting to lay the enamel on. This is attained by keeping the moulding sand for the inside (that is, for the core) as cool as possible, and wetter than the sand for the outside. Also, by melting iron containing sulphur, a hard iron resembling the white is produced; this is effected by dusting the surface of the core with sulphur powder. Dusting of the mould with graphite is to be avoided, as some graphite would adhere to the iron even after careful cleaning.

H. F. Staley (*J. American Ceramic Soc., 1*, 98, 1918) states that, in ground coat enamels for cast iron, the potash felspar, flint, and clay, could be substituted for one another without changing the fusibility of the enamel, the ratios being 100 felspar : 66⅔ flint : 40 clay, and that the "flint equivalent" (obtained by thus substituting all the clay and felspar of a ground coat formula by flint, and expressing the total flint calculated as the number of pounds to 1000 pounds of melted batch) gives a fair indication of the refractoriness.

With regard to **Sheet-iron Enamels,** R. R. Danielson (*Trans. American Ceramic Soc.*, *18*, 343, 1916) points out that in order to make a good enamel, as the ground coat must soften sufficiently for the more fusible cover enamel to fuse into the ground, part of the flint might simply be added to the frit for the ground coat, thus producing a tougher ground coat. All combinations of cobalt and nickel oxides were found to give good tough enamels; probably 0·4 per cent. cobalt oxide with 0·75 per cent. nickel oxide would give the best results for a ground coat of high quality. White grounds are not certain enough for commercial practice, and the use of cobalt and nickel oxides is strongly recommended for the production of good coats. J. B. Shaw (*Trans. American Ceramic Soc.*, *11*, 103, 1909) gives the following limits of variation in enamels for sheet steel: ground coat formula, 0·15 to 0·75 K_2O, 0 to 0·6 Na_2O, 0·14 to 0·64 CaO, 0 to 0·06 CoO, . . . MnO_2, 0·1 to 0·5 Al_2O_3, 1·1 to 1·7 SiO_2, 0·2 to 0·5 B_2O_3; cover enamel formula, 0 to 0·60 K_2O, 0 to 0·65 Na_2O, 0·2 to 0·60 CaO, 0 to 0·5 Al_2O_3, 1·0 to 1·8 SiO_2, 0·2 to more than 0·42 B_2O_3. He states that for producing opacity, SnO_2 may be either partly or entirely replaced by $ZnO+Sb_2O_3$, with equally good results, 0·13 equivalent of $ZnO+Sb_2O_3$, or of SnO_2, being sufficient to produce a good white opacity by using two coats of white.

H. F. Staley (*Trans. American Ceramic Soc.*, *13*, 502, 1911) in a paper on the "Control of Fusibility in Enamels," states that the following oxides have, pound for pound, the same fluxing power: K_2O from soluble salts, Na_2O from soluble salts, BaO from $BaCO_3$, ZnO, PbO. Calling the fluxing power of any one of these oxides unity, 0·8 lb. of either B_2O_3 or BaF_2 gives 1 unit of fluxing power, the fluxing power factor of these substances being $1\frac{1}{4}$. One unit of fluxing power is given by 0·6 lb. of CaF_2, which thus has a fluxing power factor of $1\frac{2}{3}$. Calling the refractoriness of an addition of 1 lb. dry flint 1, it takes $1\frac{1}{2}$ lb. of a particular felspar, or of bone-ash, to give 1 unit of refractoriness, so that this felspar and bone-ash have a refractoriness factor of $\frac{2}{3}$. The full statement of the fusibility of an enamel is embodied in the following :—

FLUXES (A).

$$\left.\begin{array}{l}K_2O\text{ from soluble salts}\\ Na_2O\text{ from soluble salts}\\ BaO\text{ from }BaCO_3\\ CaO\text{ from }CaCO_3\\ ZnO\\ PbO\end{array}\right\}\times 1=$$

$$\left.\begin{array}{l}B_2O_3\\ BaF_2\end{array}\right\}\times 1\tfrac{1}{4}=$$

$$\left.\begin{array}{l}CaF_2\\ Na_3AlF_6\end{array}\right\}\times 1\tfrac{2}{3}=$$

REFRACTORIES (B).

$$\begin{array}{ll}\text{Flint} & \times 1=\\ \text{Felspar} & \times y=\\ \text{Bone-ash} & \times \tfrac{2}{3}=\\ \text{Sand} & \times z=\end{array}$$

(y and z must be determined experimentally for each felspar and each sand.

CaO from $CaCO_3$ has the fluxing value here assigned for small amounts only.)

The quotient obtained by dividing the sum of the fluxing units (A) by the sum of the refractory units (B) represents the fluidity ratio (A/B). The ratios have been checked repeatedly in large batches used in regular factory practice. But though all the enamels given in the paper have the same fusibility, they differ in other properties, such as opacity, lustre, heat range, liability to craze, etc.

Reference may be made to numerous other papers relating to enamels, in the *Transactions and Journal of the American Ceramic Society*, by H. F. Staley, R. D. Landrum, J. B. Shaw, E. B. Poste, L. J. Frost, and R. E. Brown, more especially *8*, 172, 1906 ; *13*, 489, 1911 ; *14*, 489, 516, 740, 756, 1912 ; *15*, 620, 1913 ; *16*, 577, 1914 ; *17*, 137, 173, 1915 ; *18*, 570, 762, 1916 ; *19*, 146, 339, 1917 ; *J.*, *1*, 422, 502, 534, 640, 703, 1918 ; *J.*, *2*, 32, 944, 1919. Also to articles by R. Vondracek in *Sprechsaal*, *41*, 475, 493, 507, 1908, and *42*, 201, 220, 1909.

J. Schaefer (*Keramische Rundschau*, *25*, 75, 1917) states that 5 per cent. of zinc sulphide in enamels containing about 5 per cent. cryolite gave good covering power at 800° C., and was not decomposed into zinc oxide, the latter having little or no covering power. The covering power of the sulphide was as great as that of tin oxide, but the white colour and lustre were not so good. At 1000° C. the covering power of the zinc sulphide enamel nearly disappeared, and the enamel became yellowish, both effects arising from double decomposition between zinc sulphide and oxides of the ground enamel. Zinc sulphide is not decomposed in glazes not readily fusible, but the lustre is slight. The trials were all made on sheet iron, but zinc sulphide has also proved very suitable for cast-iron enamels. Special zinc sulphide is now produced which gives bright enamels. It cannot be used for coloured enamels, owing to decomposition and resulting discoloration, so the only other heavy metals which can be present are lead, antimony, and arsenic.

F. Kraze in 1914 published a paper on "Enamel Powder Technology," of which an abstract appears in *Trans. Ceramic Soc.*, *17*, Abs. 150, 1918. The finely ground dry enamel is applied to the red-hot iron vessel either by dipping the latter into the powder and turning it round or by dusting the powder on to it. In the case of lead enamels, subsequent heating in the muffle is unnecessary, but leadless powders require this subsequent heating. For lead enamel the dipping process is preferable to dusting, from sanitary considerations, as well as to avoid loss of enamel. The wet coating was rendered possible by the introduction of clay, which is added in the mill to the granulated enamel frit; it makes the enamel more refractory, but also more resistant to chemical action.

The constitution of these enamels is illustrated by the following molecular formulæ :—

I. $0{\cdot}20$ PbO, $0{\cdot}12$ BaO, $0{\cdot}20$ Na_2O, $0{\cdot}29$ ZnO, $0{\cdot}07$ CaO, $0{\cdot}12$ K_2O, $0{\cdot}12$ Al_2O_3, $0{\cdot}80$ SiO_2, $0{\cdot}16$ B_2O_3.

II. $0{\cdot}20$–0 ZnO, $0{\cdot}74$–$0{\cdot}70$ Na_2O, $0{\cdot}06$–$0{\cdot}11$ K_2O, 0–$0{\cdot}19$ CaO, $0{\cdot}12$–$0{\cdot}15$ Al_2O_3, 0–$0{\cdot}13$ Sb_2O_3, $0{\cdot}77$–$0{\cdot}64$ SiO_2, $1{\cdot}14$–$0{\cdot}68$ B_2O_3, $0{\cdot}043$–0 P_2O_5, $0{\cdot}34$–0 SnO_2, $0{\cdot}60$–$0{\cdot}86$ F.

I. is an actual lead enamel powder for dipping.

II. gives the limiting values of a series of practical leadless powder enamels for dusting. These powders are suitable for cast iron, and are not satisfactory without a ground. The ground also was formerly powdered, but is now laid on moist. The molecular proportions of formula II. to the left furnish a very easily fusible powder, and to the right a powder which will run on steep surfaces, but whose viscosity on hot walls inclined less than 45° is yet satisfactory.

For powder enamels the raw materials should be finely ground and well mixed before fritting. For enamels laid on moist, the opacifying oxides are not put in the frit, but added at the mill, which is not permissible for powder enamels, because of the bad effects resulting from differences in specific gravity. Zirconia is troublesome in this way, but a very fine leather-brown cloudy effect has thus been obtained. This enamel with earthy zirconia proved extraordinarily resistant to very sudden temperature changes and to percussion. Zirconia enamel has good covering power, and is fairly acid-proof, and resistant to reducing influences. Powder enamels containing zirconia can be applied direct on iron without using a ground enamel. In powders rich in lead, zirconia seems to have a stronger clouding tendency even than in leadless ones.

Tin oxide up to 10 per cent., fritted into the powder enamel, produced in lime-soda borosilicates no satisfactory clouding, and none at all with up to 3 per cent. Fluorine in addition to tin oxide greatly strengthens the cloudiness, though alone it has only slight effect. This clouding effect was still further strengthened by applying the powder on iron at a bright-red heat and then heating to smoothness in the enamel muffle. Similarly, fluorine causes cloudiness of otherwise clear-dissolving antimony oxide, calcium phosphate, barium phosphate, zirconium phosphate, and zirconia. Kraze has introduced barium and zirconium phosphates into enamels by using barium carbonate and zirconia respectively with sodium phosphate. Such barium powder enamels have brighter lustre than corresponding powders with calcium phosphate. The clouding effect of zirconia is strengthened by using it as zirconium phosphate, besides the combination with fluorine. In enamels containing lime, cloudiness is produced by tungstic acid. Clouded enamels can also be produced by merely adding enough cryolite, fluorspar, or sodium silicofluoride. The cloudiness of fluoride powder enamels is ascribed mainly to the presence of free silicon fluoride besides aluminium fluoride, but the enamel can be acid-proof and also clouded after complete removal of silicon fluoride, even if the enamel contains no other clouding agents, or is clear when it contains no fluorine. The feebly opaque enamel freed from silicon fluoride can be made to give a good white covering even over a not too dark ground enamel. The ground enamel for cast iron needs neither cobalt nor nickel. It is impossible to get acid-proof fluoride enamels by a single melting in a crucible. The melting should be repeated until satisfactory trials are obtained, the crucible being left open for the escape of gases (silicon fluoride, etc.).

BRITISH DEVELOPMENTS.

The colossal dislocation of trade and industry caused by the great world catastrophe revealed many weaknesses, and prominent among them were the practical absence of home facilities for the production of certain varieties of glass, notably resistance glass for scientific purposes, and (though not to the same extent) optical glass. In pre-war times only one British firm (Messrs. Chance, of Smethwick) was engaged in making optical glass, and although this firm had been long established, the output represented only a fraction of the nation's requirements even under normal conditions, and with the utmost extensions of the works was woefully inadequate to meet the sudden emergency. In order to meet the urgent demands which were soon foreshadowed, energetic efforts were made by a number of scientific men to provide a satisfactory basis on which the manufacture of optical and resistance glasses could be undertaken in existing glassworks and in others to be erected. Among those intimately concerned in this important work were Sir Herbert Jackson and Dr. T. R. Merton at King's College (London), Dr. W. Rosenhain and his colleagues at the National Physical Laboratory, F. W. Branson at Leeds, and Dr. M. W. Travers at Walthamstow, soon reinforced by Professor W. E. S. Turner and his band of research workers at the newly established Glass Department at the University of Sheffield. The results of their combined labours is sufficiently well known, and some interesting particulars may be found in the Society of Chemical Industry's Annual Reports on the progress of Applied Chemistry (which reports began for 1916 and part of 1915), and in the *Journal of the Society of Glass Technology* (which society was founded in November, 1916). The investigations of Professor Turner and his co-workers showed that some glasses of English manufacture were superior to the famous Jena glass as regards chemical resistance, a striking testimony to quality.

The increasing use of automatic and semi-automatic machinery for bottles and all kinds of small glassware has the effect of augmenting the output while decreasing the cost of production. Another important indication of progress is the substitution of gas-fired furnaces for the wasteful coal-fired furnaces. Recuperative furnaces, especially of the Hermansen and the Stein types, seem to be attracting considerable attention, no doubt in large measure owing to the lower cost of labour attending their use. The question of annealing has also received much attention.

On the whole it may fairly be claimed that remarkable progress has been made in the British glass industry. Further evidence of this is afforded by the number of different kinds of glass now being produced, one firm alone being engaged in the production of more than seventy new kinds of glass. It is particularly noteworthy in this case that, instead of being developed on the basis of analyses of foreign glasses—as was attempted in the first instance without much satisfaction—these are the results of a successful study (extending over a period of three years) of the influence of the several component oxides on one another. For further details reference may be made to C. J. Peddle's series of papers on "The Development of Various Types of Glass" in volume 4 of the *Journal of the Society of Glass Technology*.

The figures for exports and imports of glass for the years 1913 to 1918 are suggestive, but the variations in price should not be overlooked.

TRADE STATISTICS.

The following figures show the values (in £) of the total exports and imports between this country and foreign countries and British possessions respectively. The exports include plate glass, flint glassware, glass bottles, and miscellaneous goods. The imports include window and sheet glass, plate glass, flint glassware, glass bottles, with trifling amounts for miscellaneous goods. Prices should be borne in mind.

I. Exports to Foreign Countries.
II. Exports to British Possessions.
III. Imports from Foreign Countries.
IV. Imports from British Possessions.

	1913.	1914.	1915.	1916.	1917.	1918.
I.	712,149	586,065	437,975	454,078	506,511	442,924
II.	1,101,616	964,723	805,823	849,572	679,468	609,371
III.	3,448,983	2,238,330	1,973,007	2,856,894	620,292	290,372
IV.	437	1,091	5,834	33,453	3,244	48

LITERATURE.

Bastow, H., "American Glass Practice." Pittsburgh, 1920.

Benrath, H. E., "Die Glasfabrikation." Brunswick, 1875.

Bontemps, G., "Guide du Verrier." Paris, 1868.

Bull, P., "Die Emaille-Fabrikation." Hamburg—Bergedorf, 1895.

Cunynghame, Sir H. H., "Art Enamelling upon Metals." 2nd edition. London, 1901.

Dralle, R., "Die Glasfabrikation." Munich, 1911.

Eyer, P., "Die Eisenemaillierung." Leipzig, 1907.

Fisher, A., "Art of Enamelling upon Metal." London, 1906.

Flamm, P., "Le Verrier du XIX^{e} Siècle." Paris, 1863.

Grünwald, J., "Theory and Practice of Enamelling on Iron and Steel." Translated by Hodgson. London, 1909. "Raw Materials for the Enamel Industry." Translated by Hodgson. London, 1914.

Gessner, F. M., " Glass-makers' Handbook." Pittsburgh, 1891.

Heaton, N., " Glass " in Thorpe's " Dictionary of Applied Chemistry." London.

Henrivaux, " La Verrerie au XX^{e} Siècle." Paris, 1903.

Hovestadt, D. H., " Jena Glass." Translated by Everett. London, 1907.

Le Chatelier, H., " La Silice et les Silicates." Paris, 1914.

Millenet, L. E., " L'Émaillage sur Métaux." Paris, 1917.

Peligot, E., " La Verre." Paris, 1877.

Powell, Chance, and Harris, " Principles of Glass-making." London, 1883.

Randau, P., " Enamels and Enamelling." Translated by Salter. 2nd edition. London, 1912.

Rosenhain, W., " Optical Glass (Cantor Lectures)." London, 1916.

Schnurpfeil, H., " Schmelzung der Glaser." Vienna, 1906; " Two Hundred Recipes for Glasses of all kinds." Zurich, 1918.

Stein, W., " Die Glasfabrikation." Brunswick, 1862.

Tscheuschner, E., " Handbuch der Glasfabrikation." 5th edition. Weimar, 1885.

Zschimmer, E., " Die Glasindustrie in Jena." 1909.

Journal of the Society of Glass Technology. Sheffield, 1917 on.

Transactions of the American Ceramic Society. Easton, Pa., 1899 to 1917.

Journal of the American Ceramic Society. Easton, Pa., 1918 on.

Transactions of the Optical Society. London.

Transactions of the Physical Society. London.

SECTION VI.—MISCELLANEOUS APPLICATIONS OF SILICATES

IN this section are brought together for consideration a few silicious materials, and products obtained from silicious materials, which do not fall under any of the previous headings. They comprise certain special products derived from clay, shales, and slates, and from felspar and slag; also some earthy and other silicate pigments (ochres, siennas, umbers, etc.).

ALUM.

The name "alum" is applied to each member of a group of double sulphates which in the crystalline state are represented by the general formula R_2SO_4, $R_2O_3(SO_3)_3$, $24H_2O$, where R_2SO_4 represents potassium, sodium, or ammonium sulphate (or sometimes other similar sulphates), and R_2O_3 represents a sesquioxide such as alumina, ferric oxide, chromic oxide, or the corresponding oxide of manganese, etc. They all dissolve in water, and crystallize from aqueous solution, usually in the form of octahedra or cubes; octahedra when perfect are bounded by eight equilateral triangles arranged in two pyramidal groups of four each with the bases in both groups forming a square in common, and each group of four meeting in a common apex. The only alums with which we are concerned here are those containing aluminium along with potassium, sodium, or ammonium, known respectively as potassium alum, sodium alum, and ammonium alum.

Potassium Alum, Potash Alum, or **Common Alum,** K_2SO_4, $Al_2O_3(SO_3)_3$, $24H_2O$, is the substance to which the name "alum" was first given, and it is still often termed simply "alum." It occurs naturally as the mineral **kalinite,** forming fibrous crystals (occasionally octahedra), or as an efflorescence on aluminous minerals; it is found in some quantity in certain volcanic districts, produced by the action of volcanic gases upon felspathic rocks and minerals. A more abundant mineral is **alunite,** or **alumstone,** in which the aluminium sulphate is basic, and which has the composition indicated by the formula K_2SO_4, $Al_2O_3(SO_3)_3$, $2Al_2(OH)_6$. Alunite occurs in France, Italy, Hungary, Greece, Asia Minor, China, and Australia. In China a mountain nearly 1900 feet in height is officially reported to consist of alunite.

In the production of alum from alunite, the old process is still used in Italy, at La Tolfa (near Civita Vecchia), the broken mineral being first carefully calcined at a low red heat, in kilns or simply in heaps. About a third of the weight is lost (chiefly water), and alum and insoluble alumina remain. The roasted material is left exposed to the air for several months, being moistened occasionally, and the sludge thus obtained is treated with water at 70° C., and the clear liquid decanted off and concentrated. Alum crystals are deposited on cooling; they are tinged reddish by ferric oxide, which may be got rid of by recrystallization. The product is known as Roman alum, and is distinguished for its purity.

In the modern process, which is used in other parts of Europe, the calcination is carried out at a higher temperature, and sulphuric acid is added to the product, aluminium sulphate being formed along with the less soluble alum. The alum is crystallized out, and the aluminium sulphate is then obtained by evaporating the mother liquor, or alternatively sufficient potassium sulphate is added to form alum with all the aluminium sulphate.

Most of the alum manufactured in England was formerly made from alum shale, alum schist, and the like, which occur abundantly at Whitby, and at Hurlet and Campsie (near Paisley), as well as in numerous localities on the Continent.

These minerals consist of aluminium silicate, finely divided iron pyrites, and bituminous substance. The coarsely broken alum shale, with alternating coal layers, is built up into heaps, which are set on fire. As the roasting proceeds, fresh quantities of shale are added, the temperature being carefully regulated—by sprinkling water over the surface from time to time—so as to avoid loss of sulphur dioxide, and formation of slag. Aluminium sulphate is produced, and by long exposure to the air more oxygen is absorbed, ferrous sulphate and ferric oxide being formed. The roasted material is treated with the mother liquor from the alum, and afterwards with water—in each case leaving it in contact overnight—the liquors being run into settling tanks, and allowed to deposit calcium sulphate, ferric oxide, and other suspended impurities, and then taken away to be concentrated. When the shale contains little or no magnesia (as at Hurlet and Campsie) surface evaporation in a reverberatory furnace is resorted to, followed by further concentration in leaden pans, and the liquid is afterwards mixed with the proper amount of dry potassium chloride, which soon dissolves on agitation. The liquid portion is run off about five days later, and the large crystals left are washed and finally recrystallized. When (as at Whitby) the shales contain magnesia in fair quantity, surface evaporation would soon form a crust of magnesium sulphate, which would greatly hinder further evaporation. The evaporation therefore takes place in leaden vessels straight away, and when, after several stages, the specific gravity of the solution reaches 1·4 to 1·5, it is run into a tank and mixed with the calculated amount of potassium chloride or sulphate, agitation being kept up to cause a deposition of small crystals termed "alum meal." When there is enough iron sulphate present to convert potassium chloride into sulphate, the more soluble chloride is generally used instead of the sulphate, as the resulting iron chlorides (both ferric and ferrous) are very soluble, and the formation of iron alum is prevented. Excess of chloride would result in the formation of the very soluble aluminium chloride, which would be lost.

The brownish **alum meal** is drained and washed twice with cold water, which removes the ferruginous mother liquor, leaving the crystals nearly pure. The meal so purified is dissolved in as little water as possible, and left for about eight days before draining off the mother liquor, which is used to dissolve more meal. The mother liquor gives more alum when partly evaporated, and afterwards gives ferrous sulphate.

In 1845 Spence first used ammonium sulphate instead of potassium sulphate, thus producing ammonium alum. About the same time he produced alum from the bituminous shales below the South Lancashire coal seams. The shale was slowly roasted in heaps, using a little fuel only to start combustion, and the soft, porous, light-red product was digested at 110° C. for about 48 hours in lead-lined pans with sulphuric acid of specific gravity 1·35. The subsequent addition of ammonia (or ammonium sulphate) results in the formation of ammonium alum. The solution is kept agitated, and the small crystals thus produced are drained, washed with mother liquor from "block alum," and dissolved in a minimum amount of steam under pressure. A little size is added to the solution to promote precipitation of insoluble matter, and the clear liquid is run off to form "block alum" after standing; this is drained, the mother liquor forming about one-fourth of the total weight. A ton of ammonium alum is produced by this method from about 15 cwt. of shale. Spence's process enabled the alum to be ready for sale in a month, whereas by the old process it took a year to convert the crude shale into alum for the market.

Alum is produced by adding potassium sulphate to aluminium sulphate prepared in any convenient way. Very pure alum is obtained from the aluminium sulphate produced from cryolite, the yield of alum being three times the weight of the cryolite.

The preparation of alum from ordinary felspar (which contains potassium and aluminium in the proper proportions, but in the form of silicates) has often been proposed, but commercially it is difficult owing to the high temperature necessary to decompose the silicates.

At present, most of the alum of English manufacture is made either from shale or from the aluminium sulphate produced from China clay or bauxite.

Potassium alum usually crystallizes in colourless octahedra, but the crystals formed at ordinary temperatures in the presence of basic alum are cubes often with dull surfaces due to the basic salt; Roman alum generally forms cubes for the same reason. At 40° C., even when basic salts are present, octahedra are produced. The solubility of alum (potassium or ammonium) increases greatly as the temperature rises.

Potassium alum is strongly acid in reaction, and has a rather sweet astringent taste. The aqueous solution when heated is decomposed, depositing a basic alum, especially from a dilute solution. Advantage is often taken of this to add a little alum (not enough to give the characteristic taste) to impure water, when the gelatinous precipitate takes with it most of the organic impurities, including any colouring matter which may be present.

Alum is nearly insoluble in a saturated solution of aluminium sulphate. Exposure to air causes alum crystals to assume a white appearance on the surface, due to absorption of ammonia from the air, a basic salt being formed. The crystals lose no water below 30° C., but lose all of it at 100° C., though slowly.

Alum melts in its water of crystallization at 92·5° C., and when heated to redness it is converted into "burnt alum," a porous, friable material, which dissolves in water slowly. When heated to whiteness, alum leaves only alumina and potassium sulphate.

"Burnt alum," heated to redness with one-third of its weight of carbon, gives Homberg's phosphorus, which is spontaneously inflammable owing to the presence of finely-divided potassium sulphide.

Neutral Alum, along with sodium sulphate, is formed by adding caustic soda or sodium carbonate to alum solution until the precipitate first produced is only just redissolved on shaking (two-thirds of the acid being then neutralized). This solution of a neutral basic alum is used as a mordant by dyers, because it easily gives up the excess of alumina to the fabric. Alum is much used as a mordant in the dyeing industries, and for the production of other aluminium mordants, such as the acetate, etc., used in dyeing and printing, and also for shower-proofing fabrics. Alum is used for sizing paper, and for making fire-proofing materials. Alum used for the more delicate dyes, as alizarin red, must be extremely pure, as very slight amounts of iron cause dull tints to be produced.

Aluminium sulphate now economically replaces alum in most of its uses.

Sodium Alum or **Soda Alum,** Na_2SO_4, $Al_2SO_3(SO_3)_3$, $24H_2O$, occurs in South America and Japan as mendozite. It was first prepared by Zellner in 1816, from a solution containing the two sulphates. Ostwald questioned its existence, which has since been established by Wadmore, who obtained octahedral crystals of the composition indicated. The crystals do not appreciably effloresce in the air, though the contrary statement has often been made.

Sodium alum may be prepared in quantity by heating and keeping at 50° to 60° C. a solution containing 667 grams of crystallized aluminium sulphate per litre, and adding a solution containing 142 grams of anhydrous sodium sulphate per litre, until the specific gravity of the liquid becomes 1·35. On cooling—preferably at a temperature of 10° to 25° C.—sodium alum crystallizes out; at 28° C. crystallization is very slow, and below 10° C. sodium sulphate is deposited.

In the process patented by F. M. Spence and D. D. Spence (Eng. pat. 5644, March 26, 1900), a saturated solution of sodium sulphate along with crystals of the same substances are run together into a solution of aluminium sulphate in which solid aluminium sulphate is suspended. A mass of well-defined sodium alum crystals is obtained. Alternatively, solid aluminium sulphate may be added to the mixed solution and crystals of sodium sulphate, or to a similar mixture of sodium chloride solution and crystals.

Sodium alum crystallizes in regular octahedra. At ordinary temperatures it is much more soluble (in water) than potassium or ammonium alum, and accordingly it is more difficult to purify from iron. If it were possible to purify it easily by crystallization, it would be largely used instead of other alums, owing to the comparative cheapness of sodium compounds.

Ammonium Alum, $(NH_4)_2SO_4$, $Al_2O_3(SO_3)$, $24H_2O$, occurs in Bohemia, and in the crater of Mount Etna, as the mineral tschermigite. Its preparation is similar to that of potassium alum, a solution of aluminium sulphate, prepared in any convenient way, being mixed with the proper amount of ammonium sulphate, and the resulting alum separated and purified by crystallization.

Like potassium alum and sodium alum, ammonium alum crystallizes in regular octahedra, with 24 molecules of water. At ordinary temperatures it is somewhat less soluble in water than potassium alum. When heated the crystals lose water and sulphuric acid, swelling up and forming a porous mass; at a sufficiently high temperature only alumina remains, and this is a useful method for preparing very pure alumina.

The general properties and uses of ammonium alum are practically the same as those of potassium alum, except as regards the action of strong heat.

Aluminium Sulphate, $Al_2O_3(SO_3)_3$, $18H_2O$, or $Al_2(SO_4)_3$, $18H_2O$. This forms the chief constituent of the mineral known as *alunogen, feather alum, hair salt,* or *halotrichite,* which occurs in volcanic districts, and also in pyritous shales. It is abundant in the coal measure shales of Hurlet and Campsie, near Paisley. It is found in various continental localities and also in the United States and South America. It often contains considerable proportions of ferrous oxide, with small amounts of magnesia, potash, etc. *Aluminite* or *websterite* is a hydrated basic aluminium sulphate, the composition of which is represented by the formula Al_2O_3,

SO_3, $9H_2O$. It is found at Newhaven and other places on the Sussex coast. On the Continent it occurs in several localities in France and Germany. *Alunite, alumstone,* or *alum rock* consists of the basic sulphate just referred to—but with less water—associated with potassium sulphate, of the composition K_2SO_4, $3Al_2(SO_3)$, $6H_2O$. The mineral occurs in abundance at La Tolfa near Civita Vecchia (Italy), and is also found in Greece, Hungary, France, etc. It is the product of the action of sulphur gases upon trachytic rocks containing much felspar.

Aluminium sulphate is produced by the action of sulphuric acid on either hydrated aluminium oxide or aluminium silicate. The most important raw materials now available for the manufacture are China clay and bauxite. China clay (kaolin), as stated in Section II., is a very pure clay, represented approximately by the formula $Al_2O_3, 2SiO_2, 2H_2O$. In this country it is only found in workable quantities in Devonshire and Cornwall, but it also occurs in France and other continental countries, as well as in North America. Bauxite is an impure aluminium hydroxide with varying amounts of ferric oxide and silica. It is found in the north-east of Ireland, in the south of France, and in other countries.

Aluminium Sulphate from China Clay.—This method of manufacture is now practised extensively, the process being based on that described in Pochin's patents (No. 231, January 30, 1855, and No. 562, March 6, 1856). Cornish China clay is mostly used, as free as possible from iron oxide and grit. The clay, ground very finely in a mill, is sieved, dried, and then calcined at a dull-red heat, the temperature being raised gradually. The clay loses 20 to 25 per cent. of its weight, owing to expulsion of the moisture (10 to 15 per cent.), and most of the water of hydration (previously combined with the alumina and silica). The calcined clay still has about 3 per cent. of water, and is introduced into a lead-lined wooden vat charged with the proper amount of sulphuric acid at 85°, the specific gravity at this temperature being 96° Tw. The materials at once react strongly, and after 15 minutes with constant stirring, the contents of the vat are run into lead-lined wooden wagons in which the reaction keeps on for some time and the pasty material gradually becomes solid. The solid block is finally by mechanical means cut and crushed to produce a coarse powder. The product, sold under the name of "alum cake," contains all the silica, iron, and other impurities. About 60 per cent. of the alumina of the China clay is converted into aluminium sulphate.

The commercial product termed "white sulphate of alumina" is obtained from alum cake by lixiviating the coarse powder with water (or with weak liquors from earlier extractions) in steam-heated vats lined with lead; the clear liquid (after settling) is decanted, by means of a hinged pipe, into lead-lined evaporators, heated by steam coils, and is concentrated to 112° Tw. at the boiling point of the liquid (about 115° C.). The syrupy liquid is next run into shallow tiled troughs, and solidifies there on cooling, but by inserting in the troughs, before solidification, leaden partitions, the product is obtained as uniform, rectangular blocks. The "white sulphate of alumina" thus prepared usually contains about 14 per cent. alumina, and 0·25 per cent. ferric oxide, with practically no insoluble matter; a special grade of the material contains 17·5 per cent. alumina.

Aluminium Sulphate from Bauxite.—As compared with China clay, bauxite is more readily soluble in acid, and needs no preliminary calcination, but it contains a rather large amount of iron oxide. The use of bauxite instead of China clay was proposed by Le Chatelier in 1858.

According to P. and F. M. Spence's patent of 1875 (No. 1704, May 7), the bauxite is first digested with dilute sulphuric acid, aided by steam, until the acid is neutralized, and after letting the insoluble matter settle, the solution is evaporated to 100° Tw., and run off into lead coolers with shallow partitions. The yellowish-green solidified product forms blocks 18 or 20 ins. square, each weighing about 1 cwt. It contains a little iron and free acid, and is used in making brown and other papers (but not the finest), for precipitating sewage and refuse liquids, and for clarifying and decolorizing water on a large scale. Its general composition is about 14 per cent. alumina (or 47 per cent. aluminium sulphate), 0·28 per cent. Fe_2O_3, 0·32 per cent. FeO, about 35 per cent. combined SO_3, and 0·45 per cent. free SO_3, with 0·06 per cent. insoluble matter, the remainder being water. Instead of producing a solid, the mixed sulphates may be used in a liquid state.

The commercial aluminium sulphate which is sold as "concentrated alum" and "alferite" is a modern product of similar composition made by charging coarsely-powdered bauxite (usually a mixture of Irish and French bauxites) into a lead-lined vat containing boiling dilute sulphuric acid (at about 112° C.) of 96° Tw. After 6 hours' boiling, weak liquors are added to reduce the specific gravity to 70° Tw. (measured at the boiling point). After settling, the clear liquor is decanted, and evaporated in lead-lined vessels until the specific gravity reaches 112° Tw. (boiling). It is then run into partitioned coolers, to solidify into blocks or slabs, averaging 13·8 per cent. alumina, 0·7 ferric oxide, and 0·1 per cent. insoluble matter. French bauxite alone would give great difficulties in the clarification, but with mixed Irish and French bauxites a clear liquid is easily obtained. The solution should retain a little free acid, as the fully neutralized liquid is very slow in settling.

Aluminium sulphate, as prepared by any ordinary method, always contains appreciable quantities of iron, and it is doubtful whether any of the numerous purification processes is really satisfactory on a commercial scale.

"Pure aluminium sulphate" is prepared from pure alumina, which is obtained from bauxite by the "alkali fusion" process. The finely-powdered bauxite is mixed with soda-ash to give the proportion 1·0 Al_2O_3 : 1·0 to 1·2 Na_2CO_3, and the mixture is strongly heated in a reverberatory furnace for 5 hours, with frequent stirring. Carbon dioxide is driven off, and the sodium oxide (soda) combines with alumina and ferric oxide to form sodium aluminate and sodium ferrite. The material is lixiviated by treatment with weak liquor from previous batches, and finally with pure water; the sodium aluminate dissolves unchanged, but the sodium ferrite is decomposed to form caustic soda, which dissolves, and ferric oxide, which remains undissolved. The clear liquid is run into a boiler, and saturated with carbon dioxide (produced by burning coke or by decomposing limestone), the liquid being heated to 70°, and well agitated all the time. When all the alumina has been precipitated, it is allowed to settle, the clear liquid being decanted off and concentrated to facilitate the recovery of the sodium carbonate; the alumina meanwhile is drained in a hydro-extractor.

Bayer devised a cheaper method, for obtaining alumina from sodium aluminate. It depends on the fact that the addition of aluminium hydroxide with prolonged agitation effects the decomposition of the aluminate, and precipitates about 70 per cent. of the alumina (as hydroxide), the liquid now containing alumina and soda in the proportion $1Al_2O_3 : 6Na_2O$. The precipitated aluminium hydroxide (or hydrate) is allowed to settle, and the liquid is run off into weak-liquor tanks. The precipitate is filter-pressed, enough being left in the vat to precipitate the next charge, and the weak liquor may be concentrated for use in reacting upon a fresh charge of bauxite. The aluminium hydroxide (or hydrate of alumina) so obtained should contain less than 1 per cent. of mineral impurity, the more objectionable elements being sodium and silicon.

Alumina prepared by either process, when treated with sulphuric acid, gives very pure aluminium sulphate. Two grades of this sulphate are commonly produced for the English market, one in slabs or blocks (containing 14·0 per cent. alumina and 0·0025 per cent. ferric oxide), the other as powder (containing 18·0 per cent. alumina and 0·0040 per cent. ferric oxide).

Aluminium sulphate crystallizes with difficulty in thin six-sided plates. The solubility in water of both the crystals and the anhydrous sulphate (but especially the former) increases with rise of temperature.

When heated, aluminium sulphate melts in its water of crystallization, gradually forming a white porous mass of anhydrous sulphate, and at a red heat pure alumina remains.

The general industrial uses of aluminium sulphate are the same as those of ordinary alum. It is largely used in paper-making, and in the preparation of red liquor as a mordant. The coarser preparations are used for the precipitation of sewage, etc., as previously mentioned.

SLAG FERTILIZERS.

Basic Slag was first produced by the process patented by S. G. Thomas (1877 to 1879, beginning with No. 4422, November 23, 1877). Melted pig iron, mixed with lime in a lime-lined Bessemer converter, loses the bulk of its impurities through oxidation when the blast is applied. The phosphorus pentoxide produced combines with lime to form calcium phosphate. The resulting basic slag contains 40 to 50 per cent. lime, varying amounts of magnesia, alumina, iron oxide, manganese oxide, silica, and phosphorus corresponding with 20 to 50 per cent. tricalcium phosphate. Hundreds of thousands of tons of such slags have been produced annually for years past. It was at first thought that the slag was of no value, but it is now known that the phosphorus in the slag is nearly all combined with calcium (as phosphate), and that the calcium phosphate is readily disintegrated and rendered soluble in the soil, and that the ferrous oxide in the slag causes no injurious effects. A small proportion of the phosphorus (about 1·5 per cent. of the whole amount) occurs in the slag as iron phosphide, which in the soil becomes converted into phosphate. The phosphate in slag is not soluble in water. Attempts were made to dissolve the phosphates in slags, and then to precipitate them again for use in manuring, but after some time this was found to be unnecessary.

The Germans first realized the importance of slag fertilizers, and actually purchased much of the English output before English agriculturists began to appreciate its value. To be effective in soil, the slag must be very finely ground.

Basic slag is particularly valuable on moorland soils containing much organic matter, and on clay soils with insufficient lime on which it is undesirable to use superphosphate continuously. It has proved very valuable on pasture land.

The silica present in combination in the slags, though silica is a normal constituent of certain plants, is not to be regarded as among the essential plant foods.

Various mineral phosphates, known as coprolites, phosphorites, etc., are also used as fertilizers. They usually contain more or less silicious matter, but the latter ranks as an accidental impurity, and probably has little influence.

SOILS.

The natural soil consists of the superficial disintegrated portions of the solid earth, mixed with more or less material derived from animal and vegetable sources. The composition and properties of a particular soil will therefore depend mainly on the characters of the rocks and minerals which constitute the ground in the locality.

British soils may be broadly distinguished as *sedentary soils*, which have been gradually accumulated on the spot through the weathering of rock similar to that underlying the soil, and *drift soils* (soils of transport or alluvial soils), which have been conveyed to their present positions by the agency of running water or ice. On steep slopes are mixed soils which have largely been washed down or rolled down from a higher level, and contain angular fragments of different materials; such mixed soils are sometimes called colluvial soils.

Farmers and others generally classify soils according to the ease or difficulty of working them, as sand, loam, clay, chalk, sandy loam, etc. Unfortunately, these terms have very different meanings with different amounts of rainfall, and definite values can only be given through correlation with the mechanical analysis of the soil.

The texture of soil, and its behaviour under cultivation, are determined by the relative proportions of sand, clay, calcium carbonate, and humus (organic matter) in the soil. Sand includes the coarser particles,—say between 0·4 mm. and 1 mm. in diameter,—which mostly consist of silica. Such coarse material takes up very little water, and the dry grains have no cohesive power. Clay includes the finest particles in the soil; it will take a large amount of water, it is plastic and impermeable to water when wet, it shrinks and cracks on drying, and swells again on wetting. When distributed through water, clay particles can be flocculated or coagulated by small quantities of certain soluble salts. Particles not larger than 0·002 mm. in diameter are regarded as clay, and particles intermediate in size between sand and clay are classed as silt. Clay consists mainly of hydrated compounds of silica and alumina (kaolinite), but also contains zeolites (double silicates of alumina with soda, potash, lime, and magnesia), and also ferric hydroxides and very finely-divided silica.

All fertile soils contain some calcium carbonate finely disseminated, ranging from 60 per cent. or more down to mere traces. When the soil consists chiefly of calcium carbonate and clay it is called a marl, but this term unfortunately is in some districts applied to local carboniferous fireclays.

The organic matter of soils consists for the most part of vegetable remains, and is a variable mixture of complex substances, some of which contain nitrogen. The organic matter of fertile soils largely consists of calcium humate, a term which it is sometimes convenient to use, though the so-called "humic acid" (from which it is derived) has not a definite composition. Peaty or boggy soils, in which the organic matter predominates, are always very dark coloured; they hold water strongly, and are very friable when dry.

In the mechanical analysis of soils, the particles are graded according to the velocity of a current of water that can carry them, or according to the time required for their deposition from suspension in water (the column of water being of specified height). The grades recognized in the United Kingdom are as under:

Stones and gravel	3·0 mm.	and larger.
Fine gravel	3·0 ,,	to 1·0 mm.
Coarse sand	1·0 ,,	to 0·2 ,,
Fine sand	0·2 ,,	to 0·04 ,,
Silt	0·04 ,,	to 0·01 ,,
Fine silt	0·01 ,,	to 0·002 ,,
Clay	0·002 ,,	and smaller.

These differences in the sizes of particles have an important bearing on the value of soils for agriculture. The action of silica and silicates of the soil is very small from a chemical standpoint, with possible exceptions in the case of the zeolites and some of the very finely-divided silica. The grain size necessarily affects the distribution of air and water in the soil, and therefore has an important influence on the life and growth of plants. The various bacteria associated with soils are also powerful factors in connection with the fertility.

This very brief sketch may serve to indicate some of the very interesting problems arising in the cultivation of the soil. It would lead too far to attempt to pursue any of the lines of inquiry which readily suggest themselves.

EARTHY AND OTHER SILICATE PIGMENTS.

Pigments are insoluble finely-divided powders—white, coloured, or black—which yield paints when intimately mixed with suitable media (oils, water, etc.). Dyes or stains, which are soluble in the vehicles used, do not fall within this definition. Besides being insoluble in the media, pigments should be chemically indifferent to them. They should also be inert, *i.e.* have no action upon one another when mixed together. Other qualities usually desirable in pigments are durability or permanency; body or opacity, *i.e.* the property of completely covering and concealing the underlying surface; covering power or spreading power, the extent to which the pigment can be spread over a large surface; tint and shade, and ease of manipulation with vehicles on the palette are also important in connection with the use of pigments. In oil paints, some pigments have the useful property of promoting the drying of the oil, white lead being a good example of a pigment with drying quality; this drying quality depends on the power of the pigment to oxidize or promote the oxidation of the oily medium. As to durability or permanency, an ideal pigment should be "fast" to light, unaffected by air, moisture, acids, alkalies, or sulphur compounds, but comparatively few pigments fulfil all these requirements.

OCHRES, SIENNAS, UMBERS, ETC.

Yellow Ochre, Roman Ochre, Roman Yellow, Mineral Yellow, Stone Yellow, Oxford Ochre, Brown Ochre, Golden Ochre, Chinese Yellow, etc., are argillaceous and silicious earths, often containing compounds of calcium, barium, etc., owing their yellow or brown colour to the presence of hydrated ferric oxide, in varying amounts and different degrees of hydration. Apart from the differences just mentioned, the tints of yellow ochres depend chiefly upon the amount of light-coloured material (silica or white clay, etc.) and the presence of ferric oxide (which gives a ruddier tint). When burnt (calcined) all of them lose their essential water, and become converted into red ochre, light red, etc. Ochres containing large amounts of silica and clay (which often form two-thirds of the weight) yield the less translucent and paler burnt-red ochres. Some English ochres (from Oxfordshire, Derbyshire, etc.) are of fine quality.

Yellow ochres are generally prepared as pigments by careful selection, followed by elutriation or washing over, soluble substances and coarse material being thus removed. Before grinding in oil, it should be dried at a little below 100° C. These pigments are very durable, are inert with other pigments, are not materially affected by light or by impure air or other gases, and they can be used with any medium. Yellow ochre is rarely adulterated, because of its cheapness, but the richer-coloured varieties have sometimes had their colour heightened by turmeric or other organic yellow colour.

Mars yellow, Mars orange, Mars red, Mars brown, Mars violet, are artificial ferruginous pigments or artificial ochres, made by precipitating salts of iron (with or without alum added) by means of milk of lime, caustic soda, or caustic potash, drying the precipitate, and (except for yellow) calcining at a temperature depending on the colour required.

Brown Ochre is hydrated ferric oxide (limonite) with little impurity. An artificial brown ochre is prepared by heating yellow ochre to a low red heat with 4 per cent. of common salt.

Raw Sienna or **Italian Earth** is very similar to the last named, being a browner coloured yellow ochre containing a little manganese oxide. It is found near Rome and in Cyprus, etc., and is prepared in the same way as yellow ochre. It is inert with other pigments. Raw sienna is suitable for oil, water-colour, tempera, and fresco painting.

Burnt Sienna is an orange-brown or reddish-brown pigment, made by carefully calcining raw sienna. It is durable, and suitable for every kind of artistic work.

Light Red or **Burnt Ochre** is (or ought to be) yellow ochre which has been calcined or roasted on a red-hot iron plate for about 10 hours, or otherwise deprived of its combined water. The exact tint of the rather pale-brownish or orange-red depends on the variety of yellow ochre used, but it may be regarded as a scarlet modified by a little yellow and grey. It is opaque and durable, and inert with other pigments.

Red Ochre, Scarlet Ochre, Red Chalk, Ruddle, Bole, Sinopis, etc., are varieties of red hæmatite (ferric oxide), with clay, chalk, silica, etc., as impurities, and all are durable pigments. They are cherry-red when finely ground.

Indian Red, Persian Red, or **Indian Red Ochre,** is a variety of red ochre or red hæmatite, containing about

95 per cent. ferric oxide, and has a slightly purplish tint. Some Indian red is a calcined product from ferrous sulphate or from yellow ochre. Some so-called Indian red is a hæmatite from the Forest of Dean (Gloucestershire). Genuine Indian red is durable in all media, and is inert with other pigments.

Venetian Red, Rouge, Crocus, Colcothar, is a variety of red hæmatite less purplish than Indian red, but the name is now applied to a particular quality of ferric oxide produced by calcining green vitriol (ferrous sulphate), or by calcining ochres at a low red heat for 8 hours. Venetian red is less brownish than light red. Both the natural and artificial varieties of Venetian red are durable, and inert with other pigments. The pigment must, however, be quite free from soluble salts, and especially from sulphates.

Terre Verte, Green Earth, Veronese Earth, etc., are names given to an earthy material of very variable composition, consisting of silicates of iron, potassium, magnesium, etc. The colour ranges from olive-green to apple-green. It is prepared for use as a pigment by grinding selected material to a fine powder, washing it with rain water, and then drying it. Sometimes the selected material is heated, and then quenched in very dilute hydrochloric acid to remove ochre and other impurities, the undissolved portion being then ground, washed, and dried. Terre verte is generally quite durable both in water-colour and oil painting. It is inert with other pigments, but has not much body, and the colour has low intensity. The best terre verte comes from Italy and Cyprus.

Raw Umber, Levant Umber, Turkey Umber, etc., is a brown ferruginous and silicious earth found in many places, but especially good in Cyprus. It differs from yellow and brown ochres in containing a large percentage of manganese oxide and a small percentage of water. English specimens are poor in iron. For use as a pigment, the brown mineral is finely ground, washed with water, and dried. Raw umber is durable with any of the painting media, and is inert with other stable pigments. A ferruginous brown coal has occasionally been substituted for raw umber.

Burnt Umber, Velvet Brown, Chestnut Brown, etc., result from calcination of raw umber, and are equally durable and equally inert with other stable pigments. The colour is richer and redder than that of raw umber, owing to the conversion of ferric hydroxide into ferric oxide, and of some black oxide of manganese into red oxide.

Caledonian Brown is a natural earth which looks very like burnt sienna. It contains a little combined water, but consists mainly of the brown hydroxides and oxides of iron and manganese. When calcined it becomes brownish black. Either raw or burnt Caledonian brown is durable, inert with other pigments, and well adapted for oil and tempera painting.

Cappagh Brown, Mineral Brown, Euchrome, is a highly ferruginous and manganiferous earth, found at Cappagh Mine, in County Cork. It is redder than raw umber, but similar in composition and general characters, containing ferric hydroxide and oxide with oxide or hydroxide of manganese (probably a part as red oxide), and a little silica, alumina, lime, etc. When heated to 100° C., Cappagh brown gives off much water, and assumes a rich reddish-brown colour resembling that of burnt sienna and very like that of Caledonian brown. It is suitable for oil paint or water-colour. It should be dried (at 60° to 80° C.) previous to grinding in oil. It is durable, and inert with other pigments.

Vandyke Brown is the name given to three different commercial brown pigments. One is made by calcining certain very ferruginous earths (brown ochres); another is merely a dark-brown variety of colcothar; the third is a brown ferruginous earth rich in bituminous matter. This last is the kind generally met with in our country, and though it has a rich colour it is by no means durable. The other two varieties are much more durable, and are inert with other pigments, but their colours are not nearly so rich.

Imitation Vandyke browns are made from mixtures of ochre, colcothar, and lampblack.

Cologne Earth (or **Cullen Earth**), **Cassel Brown (Cassel Earth), Rubens Brown, Coal Brown,** etc., are mostly soft, impure varieties of brown coal (lignite). When slightly calcined, some of the organic matter is carbonized, and the material becomes darker and less changeable on exposure. Some so-called Cologne earth is merely bituminous Vandyke brown which has been gently roasted.

Mineral Black, Slate Black, Oil Black, or Black Chalk, is a carbonaceous shale of brownish-black to blue-black colour, which, after crushing and levigation or wet grinding, is suitable for a pigment. It is durable. *Coal blacks* are similar.

Monox, a very light powder of chestnut-brown colour, may be mentioned here. Its value as a pigment has already been alluded to on pp. 4, 5.

Kaolin or **China Clay,** which has already been considered in Section II., is a durable pigment, and practically unchangeable. In oils it has not good covering power, but in water and tempera painting it is a very useful white pigment, and may serve as a filler; a "Chinese white" for water-colour painting may contain as much as 3 parts China clay to 1 part zinc oxide. China clay for pigments is prepared by levigation and drying of the natural clay, by which means it is separated from the chief impurities (mica and quartz). Besides its use for white pigments, China clay serves as a cheap carrier for lake pigments.

Steatite or **Soapstone,** a hydrated silicate of magnesia, also referred to in Section II., is used to give a glazing effect to some special paints.

Silica in the form of an impalpable powder is too transparent to be used alone as a pigment, though it is very inert, and exceptionally stable. It is, however, very useful for mixing with all pigments except silicious ochres, as a reinforcing agent (or filler).

Zirconia also makes a good white paint. (See p. 269.)

Ultramarine, both natural and artificial, have been dealt with at some length in Section II. They form fine blue pigments. Ultramarine ash (bluish grey) and mineral grey are two inferior products obtained in the preparation of the blue pigment from the natural lapis lazuli. The blue colour of ultramarine is nearer to the pure normal blue of the solar spectrum than the blue of any other pigment, and contains very little violet; most samples of artificial ultramarine differ in this respect. Natural ultramarine is inert to other pigments, but all common acids (except carbonic acid), whether inorganic or organic, discharge the colour, as also does a hot solution of alum immediately; even cold concentrated solution of alum eventually bleaches it, and quickly bleaches all but the most stable varieties of artificial ultramarine. The texture of ultramarine is rather harsh and granular, but less so when a little Chinese white is mixed with it.

Other names used for artificial ultramarine are new blue, French blue, permanent blue, Gmelin's blue, Guimet's blue.

Green ultramarine, an intermediate product in the manufacture of artificial ultramarine, is the colouring matter of green water-paints. The more violet varieties of artificial ultramarine—but not the blue and greenish-blue pigments—have their colour considerably weakened when mixed with zinc white, a result not produced by other white substances. Ultramarine rich in silica—sometimes sold as "Oriental blue"—resist the action of alum best. Properly prepared artificial ultramarine is permanent both in oils and water. If a thin wash on paper seems to weaken as it dries, or soon afterwards, the change results from the action of alum (or other aluminium compound) in the size of the paper.

Smalt, Zaffre, Royal Blue, Saxon Blue, or Dumont's Blue, is a very deep blue glass (almost black) containing generally 65 to 71 per cent. silica, 16 to 21 potash, 6 to 7 cobalt oxide, and a little alumina, with oxides of iron and nickel in inferior varieties. It thus consists essentially of cobalt and potassium silicates. Smalt is durable, and inert with other pigments, but has not good colouring or covering power.

Manganese Blue is a pigment said to be obtained by calcining at a red heat a mixture of China clay or silica, with manganese oxide and barium nitrate. A similar product is obtained by calcining a mixture of soda ash, silica, calcium carbonate, and manganese oxide.

Copper Silicate has been tried as a blue pigment, but with little success.

Egyptian Blue.—This was a splendid blue colouring material, used by the Romans for several centuries from the commencement of the Christian era. It occurs in several beautiful frescoes in the Vatican, and has been found also at Pompeii. Fouqué found it to be a double silicate of calcium and copper, represented by the formula $CaO, CuO, 4SiO_2$, without even traces of alkali. It resists the action of nearly all chemical reagents, which accounts for its perfect preservation in paintings 1900 years old. The old method of preparation was to mix well fine sand and soda with copper filings, moisten, make into cakes, dry, and then fuse in an earthen pot until the blue colour is produced—but the temperature should not be above a bright-red heat. Fouqué found potassium sulphate preferable to soda as a flux, and he used excess of bases (the Romans used excess of silica), finally purifying the product by treatment with HCl. L. Bock recommends fusion of a mixture of 50 parts quartz, 21 chalk, 24·4 copper oxide, and 4·6 sodium carbonate, all very finely powdered and free from iron. The product, after washing with hydrochloric acid and hot water, had the composition given above, and agreed closely in all its properties with the ancient colouring matter. Laurie, McLintock, and Miles made a similar material. The exceptional qualities and fine colour of Egyptian blue should make it well worth manufacturing again. (References: *Compt. Rend.*, 108, 325; *J. Soc. Chem. Ind.*, *8*, 291; *J. Chem. Soc.*, 110, ii., 434, and 106, ii., 128.)

LITERATURE.

"Manufacture of Mineral and Lake Pigments," J. Bersch. Translated by Wright. 1901.

"Chemistry of Paints and Painting," A. H. Church. 1901.

"Manufacture of Paint," J. C. Smith. 1901.

"Chemistry of Pigments," E. J. Parry and J. H. Coste. 1902.

"Chemistry of Paint and Paint Vehicles," C. H. Hall. 1906.

"Painters' Colours, Oils, and Varnishes," G. H. Hurst. 1906.

"Chemistry and Technology of Mixed Paints," M. Toch. 1907.

"Colour Manufacture," G. Kerr and R. Rubencamp. Translated by C. Mayer. 1908.

"Chemistry of Paints," J. N. Friend. 1910.

"Materials of the Painters' Craft," A. P. Laurie. 1910.

"Pigments," "Paints," E. G. Clayton in Thorpe's "Dictionary of Applied Chemistry."

"Rubber, Resins, Paints and Varnishes," Morrell and de Waele. This series. 1920.

ADDITIONAL LITERATURE.

"Chemistry as Applied to the Arts and Manufactures," S. Muspratt. London, 1860.

"Die Feuerfesten Thone," C. Bischof. Leipzig, 1876.

"Portland Cement," H. Reid. London, 1877.

Ure's "Dictionary of Arts, Manufactures, and Mines." 7th edition. London, 1878.

"Fabricant de Couleurs." Paris, 1884.

"Bricks, Tiles, Terra Cotta, etc.," C. F. Davis. Philadelphia, 1884.

"La Porcelaine," Dubreuil. Paris, 1885.

"La Porcelaine," G. Vogt. Paris.

"Art of the Old English Potter," L. M. Solon. London.

"Constitution of the Silicates," F. W. Clarke. Washington, 1896 and 1914.

"Chemical Technology," R. Wagner. Translated by Crookes. London, 1897.

"Researches on Leadless Glazes," W. J. Furnival. Stone, 1898.

"Architectural Pottery," L. Lefêvre. English Translation. London, 1900.

"Notes on Pottery Clays," J. Fairie. London, 1901.

"Leadless Decorative Tiles, Faience, and Mosaic," W. J. Furnival. Stone, 1904.

"Clays: Their Occurrence, Properties, and Uses," H. Ries. New York, 1906.

"Clayworkers' Handbook," A. B. Searle. London, 1906.

"Modern Manufacture of Portland Cement," P. C. H. West. London, 1910.

"Matériaux et Produits Refractaires," A. Granger. Paris, 1910.

"Modern Brick-making," A. B. Searle. London, 1911.

"British Clays, Shales, and Sands," A. B. Searle. London, 1912.

"Mica," H. S. de Schmid. Ottawa, 1912.

"Handbuch der Mineralchemie," C. Doelter (Glas. E. Zschimmer). Dresden and Leipzig, 1912.

"Silicates in Chemistry and Commerce," W. and D. Asch. Translated by Searle. London, 1913.

"Clay and Pottery Industries." Collected Papers by J. W. Mellor and others. London, 1914.

"Sands Suitable for Glass-making," P. G. H. Boswell. London, 1916.

"Ceramic Receipts," John Bourne. Hanley, 1884.

"Book of Modern Recipes," W. R. Creyke. Hanley, 1887.

"Chemical Recipes" [W. R. Creyke and others]. Sunderland, 1896.

"Rezeptbuch" [Ceramic Bodies, Glazes, Colours], "Die Glasshütte." Dresden, 1907.

"Recipes for Flint Glass-making," by a British Glass Master and Mixer. 2nd edition. London.

For further references the following may be consulted:—

"Bibliographie Céramique Champfleury." Paris, 1881.

"Bibliography of Clays and the Ceramic Arts," J. C. Branner. U.S.A., 1896 and 1906.

"Ceramic Literature," M. L. Solon. London, 1910.

Also Supplementary List of Books in *Trans. Ceramic Soc.*, *11*, 65, 1912.

"Bibliography of Glass," Solon. *Trans. Ceramic Soc.*, *12*, 65, 285, 1913.

To the above may be added the British, American, and Foreign Technical Journals, especially those concerned with pottery, glass, etc. Among the more important foreign journals may be mentioned *Sprechsaal* (Coburg), *Keramische Rundschau* (Berlin), *Tonindustrie Zeitung* (Berlin), *La Céramique* (Paris).

Many valuable papers will be found in the *Transactions of the Ceramic Society*, the *Transactions* (*Journal* from 1918 on) *of the American Ceramic Society*, and the *Journal of the Society of Glass Technology*, as well as the *Journal of the Society of Chemical Industry*.

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