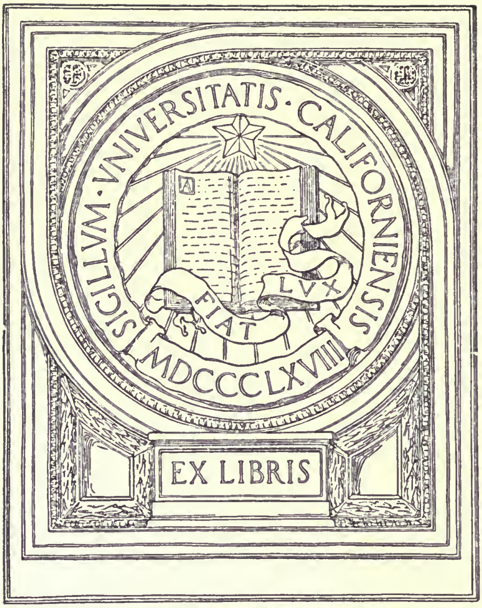

CERAMIC CHEMISTRY

By

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PREFACE.

Modern Ceramics may be said to date from Brogniart (1770-1847). The predominance of the French chemists in the science of pottery during the early and middle parts of last century caused the word *Ceramic* to be transplanted into English and German. Seger and his colleagues then caused potters to turn their eyes to Berlin for a generation; but there are not wanting signs that many of Seger's conclusions are being seriously questioned by the present school of ceramists. New vitality has sprung from the foundation of the American and English Ceramic Societies and from the adoption of the science as a subject for degrees in many American Universities.

That Ceramics is suitable for University study—both theoretical and practical—there can be no doubt. It is the natural means of transition from Geology to Chemistry, Mathematics, Physics, and Engineering. No other subject unites those five sciences so intimately. If this book should promote the secondary and higher study of the subject in England, the writer's aim will be accomplished. He wishes to express his indebtedness to the Transactions of the English and American Ceramic Societies.

H. H. S.

CONTENTS.

INTRODUCTION.

Ceramic chemistry is concerned chiefly with the reactions of silicates. It is complicated by the difference in conduct between body and glaze. In the latter, if properly matured, the chemical reaction between the constituents has proceeded to a finish, and the melt consists of a homogeneous mixture or solid solution of silicates and, it may be, borates and phosphates, and any eutectics that may be formed. With the body, on the other hand, it is different. The firing is only conducted to incipient vitrification, if as high as that. The chemical reactions are not allowed to proceed to a finish. The chemistry of pottery is therefore, as far as the body is concerned, one of incomplete reactions. Consequently, the nature and condition of the raw materials are of importance in the body, while in the glaze they are irrelevant as long as the same ultimate composition is preserved.

CHAPTER I.

GEOLOGICAL ORIGINS.

The composition of the earth's crust has been estimated by several observers, the latest being F. W. Clarke (1901), who based his calculations on 830 analyses of typical samples of the primary rocks, and found an average of :—

Silica	59.71	per cent.
Alumina	15.41	,,
Ferric oxide	2.63	,,
Ferrous oxide	3.52	,,
Lime	4.90	,,
Magnesia	4.36	,,
Potassium oxide	2.80	,,
Sodium oxide	3.55	,,
Water of combination	1.52	,,
Titania	0.60	,,
Phosphoric anhydride	0.22	,,
	99.22	per cent.

Which leaves less than 1 per cent. for all other combinations of elements.

Clarke's figures have the molecular formula:—

Na_2O	0.173	Al_2O_3	0.45	SiO_2	3.0
K_2O	0.090	Fe_2O_3	0.049	TiO_2	0.022
CaO	0.264			P_2O_5	0.005
MgO	0.327				
FeO	0.146				

The melting point of such a mixture would be about 1,200° C. As the temperature of the earth, according to the figure adopted by the British Association, increases 1° C. for every 117ft. in depth, it follows that we have at least 25 miles of solid earth beneath us. Owing, however, to the pressure of the superincumbent strata, the melting point of the rocks is probably raised appreciably, but the depth given indicates a minimum limit.

The specific gravity of the primary rocks of the earth's crust is 2.6, while that of the whole earth is 5.5, the difference being due either to pressure or to the sinking of the heavier elements towards the centre. The primary, or igneous, rocks are classified according to their silica content, the following table giving the most important, with the essential minerals of which they are composed.

PRIMARY ROCKS.

Group	Silica	Vitreous	Hemi-crystalline	Holo-crystalline	Essential Minerals
Acid	80-65%	Pumice, obsidian, pitchstone	Rhyolite, quartz, felsite	Granite	Quartz, felspar & mica
Intermediate	65–60%	Trachytic-pitchstone	Trachyte	Syenite	Felspar & hornblende
	60–65%	Andesitic-glass	Andesite	Diorite	Felspar & hornblende
Basic	55–45%	Tachylyte	Basalt, diorite	Gabbro	Felspar & augite
Ultra-basic	Below 45%	—	—	Picrite, peridotite	Olivine, etc.

Clarke found that felspars constitute 60 per cent. of the igneous rocks, pyroxenes and amphiboles 18 per cent., quartz 12 per cent., and micas 4 per cent.

Having thus briefly outlined the general composition of the earth's crust, we must now concentrate our attention on those rocks which yield the raw materials of the pottery industry.

The igneous rocks most suitable to the formation of clay are the felspathic granites. Granite, as will be seen from the foregoing table, consists of felspar, mica, and quartz, the crystals of these minerals being easily detected through a lens. During the cooling of the fused granite, the quartz was probably the last to crystallise, as the crystals of quartz, though much harder than those of felspar, often bear the imprint of the latter. The oblique rhombic felspar crystals, however, are not always well developed in granite, and they frequently present a more or less turbid appearance, which increases in proportion to the decomposition of the rock, until ultimately they become completely kaolinised and opaque. Before describing the process of decomposition of granite, it would be well to study the composition and properties of its essential minerals.

FELSPAR is the name attached to an important class of minerals, including a small number of closely allied species, which may occur not merely in the same mass, but even, through simultaneous crystallisation, in the same crystal. Tschermak supposes these species to form a continuous series based on the pure spars of lime, soda, and potash. The potash spar is orthoclase, $K_2O.\ Al_2O_3.\ 6SiO_2$; the soda spar, albite, $Na_2O,\ Al_2O_3,\ 6SiO_2$; and the lime spar, anorthite, $CaO.\ Al_2O_3.\ 2SiO_2$. According to Tschermak's view, the other spars are built up from these. Thus, 3 molecules of albite + 1 molecule of anorthite constitute oligoclase, $CaO.\ 3Na_2O.\ 4Al_2O_3.\ 20SiO_2$. Again, 1 molecule of albite + 1 molecule of anorthite make andesine, while labradorite is built up from 1 molecule of albite + 3 molecules of anorthite.

The theoretical percentage composition of the principal felspars is given in the following table :—

	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	Specific Gravity
Orthoclase	64.63	18.49	16.88			2.57
Albite	68.6	19.6		11.8		2.62
Anorthite	43.1	36.9			20.0	2.75
Oligoclase	62.1	23.7		14.2		2.64
Labradorite	52.9	30.3		4.5	12.3	2.69
Andesine	59.7	25.6		7.7	7.0	2.65

Hyalophane, a felspar containing baryta, is a mineral of some rarity. Its formula is $BaO.\ K_2O.\ 2Al_2O_3.\ 8SiO_2$, which contains equal molecules of orthoclase and a barytic anorthite.

Crystallographically, the felspars occur in two systems: the potash and potash-baryta spars crystallising in the monoclinic, and the others in the triclinic. But a true soda-potash spar is recognised in anorthoclase. The felspars can, to some extent, be quickly distinguished from each other by their flame tests and by their specific gravities, which have been given in the foregoing table.

MICA.—The minerals included under the general name of mica vary considerably in composition, but are marked by an extremely perfect cleavage parallel to the basal plane, the thin laminæ produced by cleavage being not merely flexible but quite elastic. They crystallise in either the hexagonal or rhombic system. The micas cannot be reduced to any single formula, and many classifications have been accordingly suggested for them. Tschermak, following his procedure in the case of the felspars, suggests that they are isomorphous mixtures of any of the following molecular groups:—

(1) $RO.\ Al_2O_3.\ 2\ SiO_2$, where R may be, singly or in mixtures, $K_2.\ Na_2.\ Li_2$, Fe'', or H_2. Hydrous micas, however, have usually undergone alteration. It will be seen from this formula how similar many hydrous micas are in composition to clay-substance, and Hutchings thinks that many fireclays are really hydrated altered micas formed subsequently to sedimentation.

(2) $2MgO.\ SiO_2$, or the equivalent ferrous or manganous compounds.

(3) $4H_2O.\ 5SiO_2$, or the equivalent fluorine compound, $4H_2O.\ 2SiO_2.\ 3SiF_4$.

The first group is common to all species. The first two together form the magnesian micas without fluorine; the first and third yield the muscovite and lepidolite series containing fluorine; while the combination of all three groups gives the magnesia-fluorine and iron-lithia micas. Clarke (1889) regards all micas as substitution products of a normal orthosilicate, $Al_4\ (SiO_4)_3$, in which one, two, or three atoms of aluminium may be replaced by their equivalents. In micas containing fluorine the groups MgF and AlF_2 act as univalent. Where there is a defect of silica, the univalent AlO and MgOH are supposed to enter. If there be excess of silica, H_4SiO_4 is partially replaced by $H_4Si_3O_8$. Hence micas are isomorphous mixtures of salts varying in composition from $Al_3R''_3\ (SiO_4)_3$ to $AlR'_9\ (SiO_4)_3$, and from $Al_3R'_3\ (Si_3O_8)_3$ to $Al_3R''_9\ (Si_3O_8)_3$.

Whatever be the real chemical classification of the micas, they are usually divided into two groups, the white micas, which are silicates of aluminium with alkalies and iron; and the black micas, in which magnesia and iron are more conspicuous. The first group includes muscovite, lepidolite, and paragonite; the second, biotite, phlogopite, and zinnwaldite. In granite, the most important mica is muscovite, the potash mica, which has the percentage composition:—

K_2O 3.1-12.4, Na_2O 0.0-4.1, FeO 0.0-1.2, Fe_2O_3 0.5-8.8, MgO 0.4-3.1
Al_2O_3 28.0-38.4, SiO_2 43.5-51.7, H_2O 1.0-6.2.

It will be seen from the indefiniteness of this analysis how variable in composition are the micas, but the formula of muscovite may roughly be given as:—

$$K_2O.\ 3Al_2O_3.\ 6\text{-}16\ SiO_2.\ 2\text{-}6\ H_2O.$$

QUARTZ may be dismissed with less detail. It is silica crystallising in the hexagonal system. Quartz often contains enclosures of other substances, sometimes as crystals which may be rutile, chlorite, or kyanite; sometimes as lacunæ containing gas or water, carbonic acid, or sodium chloride in solution, or liquid carbon dioxide.

Such are the essential minerals of granite. We are now in a position to understand the formation of clay by the weathering of granite. The important constituent in the making of clay is the felspar, and the best beds of china-clay found in Europe are due to the decomposition of pegmatite, a granite exceptionally rich in felspar. By the action, lasting through countless ages, of water, ice, and carbon dioxide, aided by the fluorides which are always present in small quantities in the rock, and by humic acids and bases from swamps, the spar is gradually deprived of its alkalies and some of its silica, losing in the process, if it be the potash spar, 55 per cent. of its weight and 33 per cent. by volume, although the kaolin often retains the shape of its mother-spar. Lime, when present in the spar, is the first to be removed as soluble bicarbonate; then the potash and soda are carried off as carbonates or soluble silicates. Should the waters contain magnesian salts, lime or soda in the spar may be replaced by the isomorphous magnesia so long as the alumina of the spar is not involved in the change, thereby giving rise to steatite and other pseudomorphs, a class so numerous that they cannot be touched on here. The process of weathering very seldom, perhaps never, reaches its last stage—that of the formation of pure clay substance, Al_2O_3, $2SiO_2$, $2H_2O$,—but remains in some intermediate position. Thus, besides clay in all its varieties, are formed gravel, detritus, sand, loam, lias. The process may even, through the solvent action of water increased by carbon dioxide, organic substances, salts, and a higher temperature, be changed into its opposite, and the original rocks may appear again as conglomerates, brecchias, sandstones, and shales, and perhaps as crystalline rocks.

Clays when indurated become mudstones, and when cleaved, slates. Shales exhibit a fissile character in the direction of lamination, while slates are fissile in parallel planes other than those of bedding.

It is unknown what period of time is required for the weathering of granite, which may extend to a depth of a hundred feet in the rock, as all attempts at the artificial decomposition of felspar have met with but moderate success. But glass and pottery ware a few centuries old show distinct signs of weathering, as is plainly indicated by the subjoined analyses given by Randau of the external layers and inner portion of an antique Roman glass vessel :—

	External Layer.	Interior Mass.
	Per Cent.	Per Cent.
SiO_2	48.8	59.2
Al_2O_3	3.4	5.6
CaO	11.3	7.0
MgO	6.8	1.0
FeO	11.3	2.5
Na_2O	—	21.7
K_2O	—	3.0
MnO	trace	trace
Loss on ignition	19.3	—

Another theory, due to von Buch and Daubree, of the origin of clay should be mentioned. It is that the felspar has been attacked by acid vapours, chiefly hydrofluoric acid, from below. Collins, in 1887, claimed to have obtained kaolinite in 96 hours by treating orthoclase with dilute hydrofluoric acid. But it is much easier to suppose that the fluorides are already present in the granite as a mica, and that the acid has been liberated by carbonic acid.

This theory is really part of a wider one, the pneumatolytic theory, which supposes post-volcanic emanations of fluorine, sulphur or boron compounds. Possibly isolated beds of clay have been formed by such means and by many other agencies, such as swamp waters alone. It is, in fact, impossible to generalise on every clay, but weathering, with or without chemical agents, is undoubtedly the safest hypothesis yet advanced.

Besides the felspathic granites, clay may also be formed from augitic, zeolitic, and volcanically metamorphosed minerals. However original rocks may differ in composition, the residual clays formed by their weathering tend to bear a striking chemical resemblance to each other, owing to the fact that the silicious aluminates are the most resistant constituents of the raw materials. The more basic a rock, the more rapid its decomposition. An increase of soda and potash accelerates weathering, the soda being more effective than the potash in this respect. Similarly lime decreases resistance more than magnesia. Increase of iron in a rock lessens resistance. Increase of alumina checks decomposition and silica lessens it. The character of the residual clay is governed by the extent to which merely physical forces have aided rock decay.

The chief difficulty in any theory of clay formation is to explain the presence of combined water in the product. Beside kaolinite, the monoclinic Al_2O_3 $2SiO_2$ $2H_2O$, there are numerous other hydrated aluminium silicates. Some, like lithomarge, nacrite, pholerite, and bentonite, have the same formula as kaolinite. Others are as follows :—

Pyrophyllite (pencil stone)	Al_2O_3.	$4SiO_2$.	H_2O	
Agalmatolite	Al_2O_3.	$4SiO_2$.	H_2O	
Allophane	Al_2O_3.	SiO_2.	$5H_2O$	Amorphous
Halloysite	Al_2O_3.	$2SiO_2$,	nH_2O	,,
Lenzenite	Al_2O_3.	$2SiO_2$.	nH_2O	,,
Newtonite	Al_2O_3.	$2SiO_2$.	$4H_2O$ + aq.	Rhombohedral
Cimolite	$2Al_2O_3$.	$9SiO_2$.	$3H_2O$ + 3aq.	Amorphous
Montmorillonite	Al_2O_3.	$4SiO_2$.	H_2O + n aq.	,,
Collyrite	$2Al_2O_3$.	SiO_2.	$9H_2O$	,,
Schötterite	$8Al_2O_3$.	$3SiO_2$.	$30H_2O$	,,

And clays are sometimes found with abnormal losses on ignition. To take a single example, a kaolin found at Passau, in Bavaria, results from the decay of ekebergite, a scapolite, of which it often retains the external forms. Its composition is: SiO_2 46.4, Al_2O_3 35.0, H_2O 18.6 per cent.

It is possible that bacterial agencies have been at work in clay formation, but though some experimenters have thought they were able to increase the plasticity of clay by inoculation, there is no real evidence yet that the weathering of felspar is promoted by microbe or enzyme.

Before leaving the geological origins of pottery materials, the more frequently occurring silicates should be mentioned.

Comparatively few of the metallic elements are found naturally as silicates. Thirteen—sodium, potassium, lithium; calcium, magnesium, barium, strontium, manganese; iron and aluminium; and (of the heavy metals) zinc, copper, and bismuth—exhaust the list. Many of them occur together with others, and it is easier for the mineralogist to group the silicates under general formulae.

The augite or pyroxene species, $R''SiO_3$, contains varieties diopside, alaite, salite, malacolite, coccolite, diallage, hedenbergite, jeffersonite, fassaite, omphacite, pyrgom, achmite, ægirine, breislakite.

Wollastonite is $CaSiO_3$; pectolite, $4CaSiO_3 . Na_2SiO_3 . H_2SiO_3$; spodumene, $Li_2O . Al_2O_3 . 4SiO_2$.

Hornblende or amphibole, like augite, is of formula $R''SiO_3$. Its varieties are tremolite, grammatite, actinolite, smaragdite, pargasite, arfoedsonite, asbestos, amianthus, uralite, nephrite.

Leucite is $K_2O . Al_2O_3 . 4SiO_2$.

Turning to the formula R''_2SiO_4 we have the olivine, peridote, tephroite, willemite, dioptase (with $1H_2O$). Garnet is $3R''_2 SiO_4 R'''_2Si_3O_2$, and idocrase much the same but with water. Nepheline has the formula $2NaKO . 2Al_2O_3 . 5SiO_2$; sodalite, $3Na_2Si_2O_8 + 2NaCl$; haüyne and nosean are like nepheline, but containing sodium or calcium sulphates. The scapolites are all silicates of lime and potash or soda.

The micas include biotite, lepidomelane, phlogopite, zinnwaldite, lepidolite, muscovite, paragonite, margarite. We have already dealt with most of them.

Chlorite is $4R''O.\ Al_2O_3.\ 2SiO_2.\ 3H_2O$, where R'' is Mg or Fe.

The basic silicates, those containing less than 40 per cent. of silica, comprise chondrodite, humite, andalusite, cyanite, staurolite, tourmaline, axinite, datholite (the last three containing borate), topaz (which has from 16 to 20 per cent. of fluorine), and the epidote group.

As Orton and Mellor have pointed out, the nomenclature of silicates is in urgent need of standardisation. Three systems are in vogue, and the confusion arising therefrom is illustrated in this table :—

Formula R''.	Pottery.		Metallurgy.		Pure Chemistry and Mineralogy.
	Molecular ratio : Base. Acid.	Name.	Oxygen ratio : Acid. Base.	Name.	
$3RO\ .\ 1SiO_2$	1 : ⅓	⅓ silicate	1 : 1½	sub-silicate	parasilicate
$2RO\ .\ 1SiO_2$	1 : ½	½ silicate	1 : 1	singulosilicate	orthosilicate
$4RO\ .\ 3SiO_2$	1 : ¾	¾ silicate	1½ : 1	sesquisilicate	octobasic trisilicate
$1RO\ .\ 1SiO_2$	1 : 1	monosilicate	2 : 1	bisilicate	metasilicate
$2RO\ .\ 3SiO_2$	1 : 1½	sesquisilicate	3 : 1	trisilicate	orthotrisilicate
$1RO\ .\ 2SiO_2$	1 : 2	disilicate	4 : 1	quadrisilicate	metadisilicate
$1RO\ .\ 3SiO_2$	1 : 3	trisilicate	6 : 1	sexi-silicate	metatrisilicate

The chemical analysis of rocks has been considerably advanced in recent years, notably in the accurate estimation of components that had previously been overlooked altogether. Instead of some half-dozen constituents, the average rock has more nearly twenty. Ordinary analytical processes are somewhat outside the scope of this book as they pertain to general chemistry, but the reader is recommended to Hillebrand's "Analysis of Silicate and Carbonate Rocks" (U.S. Geological Survey, Bull. 422, 1910).

Washington has performed a useful service (U.S. Geological Survey, Professional Papers 14 and 28) in critically examining the mass of analyses published between 1869 and 1900 and assigning to each analysis a certain value on a scale of 5. We append a few examples of analyses of British rocks which Washington regards as superior.

Name.	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O	MnO	CO_2	Sum.	Analyst.
Griesen	80.36	11.12	1.77	n.d.	0.56	0.67	1.82	2.47	1.96	..	..	100.73	L. J. Spencer
Granite	74.69	16.21	trace	1.16	0.48	0.28	1.18	3.64	1.23	0.58	..	99.55	Phillips
,, ...	67.12	20.12	3.71	0.28	0.82	1.79	1.53	3.38	1.01	..	0.03	99.84	I. Macadam
,, ...	70.65	16.16	1.53	0.52	trace	0.55	0.54	8.66	1.22	trace	..	99.83	J. A. Phillips
,, ...	70.48	14.24	3.72	n.d.	0.40	1.48	3.66	4.26	1.59	..	..	99.83	S. Haughton
,, ...	66.02	21.43	4.62	0.63	1.77	1.81	0.15	3.17	0.16	..	0.08	99.88	I. Macadam
Microgranite.........	74.39	15.55	1.35	n.d.	0.33	0.48	3.79	2.14	1.18	..	..	99.43	Holland
Ortho-felsite	68.8	14.9	0.9	4.3	1.1	1.9	2.7	2.8	2.0	..	..	99.4	J. H. Player
Granophyre	71.60	13.60	2.40	n.d.	0.21	2.30	5.55	3.53	0.70	..	..	99.89	G. Barrow
Quartz-felsite........	74.80	13.89	trace	none	0.05	2.59	5.45	2.74	0.77	..	..	100.29	G. A. J. Cole
Felsite	68.01	17.48	0.41	n.d.	0.46	trace	5.77	7.08	0.73	..	..	99.94	F. E. Tadman
Biotite-porphyrite ...	60.84	20.03	1.47	0.42	0.45	1.56	9.12	4.48	1.15	..	0.11	99.64	I. Macadam
Quartz-felsite	72.66	18.98	0.57	0.21	0.47	0.03	0.21	5.91	0.86	..	..	99.94	I. Macadam
Hornblende-porphyrite	63.41	16.92	2.67	2.96	2.08	4.32	5.18	2.36	0.64	..	..	100.54	Teall

CHAPTER II.

CLAY.

Clay has the general theoretical formula $Al_2O_3 . 2SiO_2$ $2H_2O$. There are numberless varieties of clay, but it may roughly be divided into ball clay, china clay, and fire clay; or, in other words, a plastic clay, a non-plastic clay, and a refractory clay.

CHINA CLAY, or kaolin, is a friable, non-plastic substance showing six-sided scales under the microscope. Its specific gravity is 2.2. The proportion of kaolin in granite is generally from 10–30 per cent.

J. M. Coon has recently (1911) made the mechanical analyses of the St. Austell deposits. The average of five samples gave the figures:—

	Per Cent.
Coarse quartz	37.4
Medium quartz	18.9
Fine quartz, tourmaline	2.8
Very fine quartz, coarse mica, tourmaline	2.0
Fine mica, coarse clay, tourmaline	2.6
Very fine mica, medium clay	3.3
Marketable china clay	31.5

Another sample yielded 49 per cent. of marketable clay, but this is quite exceptional.

The clay as dug up is pumped with water into narrow channels called 'micas,' which are fitted with traps that can be raised or lowered at will, so that the clay is allowed to deposit a certain amount of its heavier material, and then run into fresh micas. The mica sand deposited in the first set is waste, but that from the others is re-washed and sold as mica-clay. From the micas the clay water passes, preferably through silk lawn or wire screens, to the settling pits, and then to tanks till the clay has attained the consistency of lard, the deposits round the walls being cut up, and transferred to the kiln. The best kaolins are residual, and are found in the spot where they were produced by the decomposition of the weathered felspar.

Ball and Fire Clays, on the other hand, are sedimentary. The chief characteristic of ball clay is its plasticity on being treated with water, and of fire clay its refractoriness. The best fire clays underlie beds of coal, and are often worked in conjunction with them. They are dark in colour and contain roots of stigmariae and other fossilised plants. Fireclays are low in alkali, and therefore refractory, because they have served as soil for the vegetation which ultimately became coal. Hutchings thinks that many fire clays are not clays at all, but micas formed subsequently to sedimentation, owing to felspar being washed down as such, and yielding mica instead of kaolin on decomposition; the analyses may be read either way. Ball clays are usually dark in colour, owing to the presence of organic matter. When mined they contain about 30 per cent. of water, of which about 20 per cent. is driven off at steam heat.

A large content of chalk in a clay constitutes a *marl*, and *loams* are clays with much sand. Pipeclay, so-called because tobacco cutties are made from it, is an impure kaolin containing free silica.

Two properties of clay—plasticity and cleavage—are of prime importance to the potter. On the Cleavage depends the ease or difficulty with which the clay can be mined. Cleavage is due to the unlike cohesion in various directions of individual crystals. Only with the crystals of the regular system is there perfect equilibrium of the mutual attractive forces. In other crystals, such as felspar and mica, there is a tendency to cleavage in one or two definite directions. In the process of weathering, therefore, the break naturally takes place in those directions in which the least mechanical resistance is to be overcome—that is, along the planes of cleavage,—and the minerals are accordingly broken up into laminæ which become thinner and thinner. When at length these laminæ are washed away and deposited in some new position, it is obvious that the most stable position of equilibrium is parallel to the surface of the sediment. J. S. Owen has shown (*Geog. Journ.*, 1911, 76) that a body falls in water with the greatest possible surface horizontally disposed. The whole bed of sedimentary clay thereby assumes a plane of cleavage which was at first peculiar to the individual crystal.

PLASTICITY is the chief characteristic of ball clays, and the phenomenon has not yet been satisfactorily explained. As it is destroyed at 415°, the temperature necessary to drive off the combined water, it has been thought by some to be due to water of combination. Others have attributed plasticity to the action of bacteria, but Hecht and Kosmann failed to increase the plasticity of clays by inoculation. Stover, however, claims to have done this in 1903 by treating a thin clay with water drained from a fat clay, and he attributes the action to the specific influence of bacillus sulphureus. It is difficult to understand how a bacillus whose function is to decompose pyrites should promote plasticity except indirectly by removing salts which are detrimental to the phenomenon. In any case the smell arising from the process is likely to prevent its general acceptance. Bischof opines that felting of the particles of clay enables them to adhere to each other. Numerous other theories have been put forth from time to time, and they are comprehensively surveyed by Zschokke (*Bau materialen Kunde*, 24, 7). At present three theories contest the field—the colloidal, the soluble salt, and the molecular attraction theories.

Taking the *colloid theory* first, a colloid may be defined as anything not crystalline. Colloids exist in two characteristic forms, sol and gel. The homogeneous suspension of a colloid in a liquid is called sol; the continuous jelly with pore walls and pores filled with a liquid is called gel. Colloids are reversible or irreversible, according to whether or not they will pass back from gel to sol. The process of passing back from sol to gel is called coagulation, and the reverse process deflocculation. Charcoal is an example of a gel that has been permanently set by heat. Schloesing, in 1876, actually isolated the colloids from clay.

The attribution of plasticity to the presence of colloids appears to have been arrived at in 1903 independently by three observers—P. Rohland in Germany, and Cushman and Ries in the States. In the same year Acheson found that the addition of 2 per cent. of tannin to a lean clay materially augments its plasticity. Clays transported by water and deposited in some new place, reasoned Acheson, have greater plasticity than those found near their parent rock, and as it is unlikely that the water itself has imparted this property to the clay, it follows that the washings from the forests have been the agent that increases plasticity. Accordingly he tried the effect of several vegetable extracts on lean clays, with the result mentioned above. The discovery was immediately claimed to support the colloid theory, and it was extended by Acheson and others, such as Weber in Germany, to the use of sodium silicate, alkalies, carbonates, and some other salts for promoting plasticity, as a proof that the colloids were being deflocculated. In 1908, Harrison Ashley advanced a method for estimating the colloids in a clay by taking advantage of a property well developed in colloids, the power of absorption—that is, of taking other substances out of solution on suspension. Ashley found that colloids can be estimated by their adsorption of dyes, such as malachite green, and that when this is done the plasticity of a clay varies with its relative colloidal content. The increase of plasticity caused by the addition of caustic soda is explained by saying that enough of the gel is converted into sol to make the slip appreciably thinner, so that it can be poured freely. If the alkali be neutralised by acid, the mass again stiffens by gel formation.

The soluble salt theory was advanced by Purdy and Moore in 1907, but Seger had several times noted that there seems to be a close relationship between the amount of soluble salts in a clay and its plasticity. He found, for example, that bricks made of plastic clays are peculiarly liable to efflorescence of salts on their surfaces. According to this theory, the adsorbed or otherwise held salts form, on addition of water, a viscous solution round the grains of clay, resulting in an enveloping liquid medium of high surface tension. To account for the fact that flint or other minerals of surface factor equal to that of clay do not develop plasticity when soluble salts are added, it is supposed that clay particles have an adsorptive power far in excess of that of any other mineral substance.

A third theory of the cause of plasticity is that of Grout, which involves the notion of a molecular attraction between the clay particles and the water. When clay is made into a slip, each grain is enveloped in a film of water. If now the volume of the water be decreased by evaporation or adsorption in a plaster mould, the mass gradually passes into a stiff condition, because the particles of clay have approached each other closely enough for their mutual molecular attraction to overcome that of the water and clay. This theory is based on the fact that water is always required to develop the plasticity of a clay.

Whatever the cause of plasticity, on its existence depends the secret of clay-working. Although in the near future it is possible that this property may be artificially induced in several other materials, the pottery industry could never have originated without the occurrence in nature of plastic clays.

In the next chapter we shall deal with the chemical analysis of clay.

It need hardly be said that scrupulous sampling is essential. A bed of clay may remain constant in composition for miles. On the other hand, owing to a fault, it may alter abruptly and return to its original composition only at some spot far removed. In sampling, care should be taken that overlying strata which may be sandy or friable cannot drop into the borehole and vitiate the sample.

For accurate analysis the sample should be ground under alcohol to prevent oxidation of ferrous and other reduced salts.

CHAPTER III.

CLAY ANALYSIS.

The progress of chemistry has extended the number of ingredients to be found in clay as in all minerals. Any or all of the following compounds may occur in quantities that can be estimated :—

SiO_2, TiO_2, ZrO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_3, FeO, MnO, NiO, CoO, MgO, CaO, SrO, BaO, ZnO, CuO, K_2O, Na_2O, Li_2O, H_2O, P_2O_5, S, SO_3, C, CO_2, F, Cl, N.

Until the volumetric analysis of silicates by hydrofluoric acid is made feasible by the appearance on the market of a cheap non-silicious ware that will stand the action of acid and of heating to boiling point, the best method of ultimate analysis is the usual one of fusing 1gram. of the finely powdered substance with mixed carbonates, and subsequent precipitation of silica and alumina. Ignition of silica is facilitated by a final washing with alcohol.

TITANIA is always present in clays, generally in amounts varying from 0.01 to 0.8 per cent. It is partly precipitated with the silica, and partly with the alumina. It may be tested qualitatively in acid solution in the absence of iron by the strong yellow colouration produced with the peroxides of hydrogen or sodium. To estimate it, the weighed silica precipitate is fused with six times its weight of potassium hydrogen sulphate, and the extract added to the solution of the weighed precipitate given by ammonia. The solution is reduced with zinc, and an aliquot portion titrated with permanganate. This gives the sum of the titania and iron oxide. The titania is found in another aliquot portion by titration with a solution of methylene blue standardised against pure titanous chloride. Ferrous salts do not reduce methylene blue.

IRON OXIDE is found by difference in the permanganate and methylene blue titrations explained above.

SOLUBLE SALTS are always adsorbed by clay to some extent. Five grammes of the dried powder is boiled with water, and the whole made up to a known amount. As a plastic clay might take a week to filter completely, the soluble salts are estimated on an aliquot portion of the filtrate. Mellor recommends the use of a filter made of lightly biscuited pottery, which is said to give a clear filtrate. The salts soluble in weak hydrochloric acid should be ascertained, as limestone and similar detritus might otherwise be attributed wrongly in proximate analysis.

ALKALIES are estimated by the Lawrence Smith method, proposed in 1871. One gramme of the substance very finely powdered is mixed with 6grms. of calcium carbonate and 1-1.5grms. of ammonium chloride, both reagents being puriss. The mixture in a platinum crucible is heated for 40 minutes in a muffle to bright redness, but not to the point of fusion of any part of it. It should have shrunk to a bougie easily detachable from the crucible. To avoid partial fusion, it is well to rest the crucible in a little cupel containing sand. The contents of the crucible are then extracted twice with boiling water in porcelain dishes, glass being avoided all through the analysis. To the filtrate ammonium carbonate and a few drops of oxalate are added, and the lime precipitate filtered. The filtrate is then evaporated to dryness, ammonium salts are gently ignited off, the residue is extracted with water and a few drops of oxalate, filtered into a weighted platinum basin, evaporated to dryness and gently ignited again, and the residue from this process is taken up with weak hydrochloric acid, evaporated to dryness, heated in the air-bath, and finally weighed as RCl. The equivalent is found by titration with silver nitrate or by precipitation of potassium platinochloride, and hence the amounts of soda and potash are calculated. A blank should be conducted, as this may yield 5-10mgms.

Lawrence Smith's method has the advantage over the hydrofluoric acid method that borates are in the water-insoluble residue as calcium borate. This may not be of much consequence in clays; but in glazes borates may amount to as much as 20 per cent. of the whole, and the accurate separation of alkalies and borates is therefore important.

Hydrated Silicic Acid is determined by boiling 5grms. of the finely ground material with 120c.c. of 5 per cent. sodium carbonate solution for ten minutes. The solution is decanted and the sample again digested; the combined filtrates are acidified and evaporated to dryness, and the silica estimated as usual. A blank may yield as much as 1mgm., and should therefore be undertaken.

Carbon may be present in clay to the extent of 4 per cent., imparting a dark colour to it. It is estimated by dissolving the clay in hydrofluoric acid in the water-bath and filtering on to a tarred paper. This is best done after heating the clay in the air-bath as high as possible in order to char organic matter that may not be yet carbonised.

Vanadium, like titanium, is diffused through all granites, and may be present in clay to the extent of 0.1 per cent. It should be reported as the trioxide, as it replaces alumina or ferric iron. It occurs in basic silicate rocks chiefly.

Molybdenum, on the other hand, is confined to the more silicious rocks, and is less common than vanadium. For the analysis of these two components the reader should refer to Hillebrand.

Lime, gypsum, magnesia, barium sulphate, and pyrites are detected and estimated by the usual routine of chemical analysis.

Colloids in clay are estimated by Ashley by malachite green. 50grms. of clay are suspended in 1 litre of a 0.3 per cent. solution of malachite green. After settling, a portion of the supernatant liquid is pipetted off, and the amount of dye left in estimated colorimetrically. Assuming that equal quantities of colloid adsorb equal quantities of dye, the relative colloidal content of clays is easily calculated. Ashley takes Tennesse Ball Clay No. 3 as a unit standard of comparison. Rohland distributes the finely divided clay on a slide, and stains it with fuchsine. The colloids adsorb the stain, a micro photograph is taken, the stained portions cut out and weighed. The figure obtained gives a numerical value of the plasticity of the clay. But Ashley's has the advantage of a volumetric over a gravimetric method.

Beside the fusion method with mixed carbonates, clay can also be decomposed by hydrofluoric acid, and this method is useful when only partial analysis is required. For complete analysis it is not as rapid as the fusion method, as time is lost in evaporating off the fluorides with sulphuric acid. But when a clay is already known, and it is only a question of detecting variation in it, much time is saved by doing the loss on ignition and the loss on evaporation with hydrofluoric acid, and subsequent ingition to constant weight. The loss on ignition indicates the clay content, as clay theoretically holds 13.9 per cent. water of combination, while the evaporation with hydrofluoric acid gives a measure of the silica and any alkalies that are volatilised in ignition.

Appended are the normal losses on ignition of many clays as given by Rieke (1911) :—

KAOLINS.

	Per Cent.		Per Cent.
Amberg kaolin	11.76	Albsheim kaolin	13.09
Halle kaolin...........	9.68	Zettlitz kaolin	12.98
Bohemian kaolin	11.82	Geisenheim kaolin	6.51
Australian kaolin	12.45	Cornwall china clay ..	12.44
Texas kaolin	14.77	St. Yrieux kaolin	10.55

REFRACTORY PLASTIC CLAYS.

Lischwitz clay	13.55	English blue ball clay.	9.69
Löthain clay	11.88	English white ball clay	7.86
Halle clay	9.35	Vallendar clay........	7.04
Meissner clay..........	4.71	Grossalmerod clay	6.55

NON-REFRACTORY FERRUGINOUS CLAYS.

Bunzlau plastic clay ...	8.29	Karst brick clay......	10.44
Helmstedt clay	8.94	Brazilian clay	2.19
Agram brick clay	7.47	Velten clay	contains much $CaCO_3$

MISCELLANEOUS.

Shale containing carbon	20.34	Cornish kaolinised granite	8.50
Bohemian clay-stone ..	9.35	Berkenfeld felspar	3.18

PROXIMATE ANALYSIS.

The methods outlined above give the percentages of the various oxides present, but they do not indicate in what mineral combinations they exist. Clay, by its origin, is likely to contain felspar, quartz, and mica, in appreciable quantities, and it is the object of proximate analysis to estimate them. For this purpose the so-called " rational analysis " is the most generally used. In 1835 Forchammer used sulphuric acid to dissolve clay and separate it from felspar, and in 1844 Brongniart refers to the process as ' rational analysis.' But it was Seger, in the later 'seventies, who developed the method, although it is still far from perfect. The idea of the process is to decompose the clay with sulphuric acid, which is supposed to leave the spar and quartz untouched. The residue is boiled with alkali to remove the liberated silica, and this residue is then fused with carbonates, and the alumina in it estimated in the usual way, or else treated by the Lawrence Smith method for estimating alkalies. The felspar is calculated from either the alumina or alkalies just found. Felspar (orthoclase) has the theoretical percentage composition :—

SiO_2, 64.63 ; Al_2O_3, 18.49 ; K_2O, 16.88

the alumina being 1.085, and the silica 3.828 times the alkali, and the silica-alumina ratio is 3.5 : 1.

Clay contains theoretically

46.33 SiO_2 ; 39.77 Al_2O_3 ; and 13.9 H_2O per cent.

the silica-alumina ratio being 1.17 : 1

Having found the clay and spar, the quartz is given by difference.

Rational analysis, however, has several drawbacks. Mica was neglected by Seger, who returned his results as clay, felspar, and quartz. The modern French school goes too far in the other direction, and returns mica to the exclusion of spar. There can be little doubt that a seemingly stable bed of clay contains clay, spar, mica, quartz, rutile, hornblende, and many other minerals, all reacting with each other according to partially reversible equations, though the general tendency is towards loss of alkalies and formation of hydrated aluminium silicates such as kaolinite, halloysite, pholerite, and the simplest micas.

Further, the assumptions that sulphuric acid attacks only the clay and that spar is unaffected by alkalies are unjustified. Many micas are decomposed by the acid, and Brockmann cites two cases where 18.6 and 16.1 per cent of orthoclase were also dissolved. This was supported by Langenbeck, who states that as much as 20 per cent. of the felspar present may be dissolved with the clay. But Seger, and also Jackson and Rich, found that felspar is decomposed by acid to the extent of only 2.24 per cent., and Jackson and Rich found that the subsequent treatment with caustic soda also attacked the felspar, no end point being reached. This, they think, may account for the high results of Langenbeck; but, nevertheless, the general opinion of modern chemists is undoubtedly against the rational method. The behaviour of micas under the treatment is still a matter of uncertainty. Dana states that biotite and phlogopite are completely, and glauconite, lepidolite, and muscovite slightly, decomposed by acid. He also says that plagioclase felspars are more attacked than orthoclase. And there is no doubt that minerals richer in alkali than felspar, such as nepheline and haüyne, are completely decomposed.

It is obvious, then, that the "rational method" has not yet deserved its name, so that many chemists, including some of the various State officials in America, fall back on the ultimate analysis to calculate the theoretical amounts of clay, spar, and quartz from the alkali, alumina, and silica found. But this is only begging the question of proximate analysis. It would be better to remedy the defects of, rather than to neglect, the rational method.

That process is best carried out as follows:—Two grammes of the dried clay are heated with 50c.c. sulphuric acid and 100c.c. of water on a water-bath for four hours, and then allowed to stand over-night. The flask is then heated on a sandbath till the acid fumes strongly. After filtration the solution is analysed in the usual way, and the residue treated with 5 per cent. sodium carbonate solution to remove precipitated silica, and then treated as in ultimate analysis.

Another method of proximate analysis is that of Lunge and Schochor, but it is devised chiefly for testing the cement value of marls. In principle it is similar to the Lawrence Smith method for determining alkalies. The clay is treated with lime, which most readily attacks the combined silica and the finely divided free silica. By subsequent treatment with hydrochloric acid, and the sodium carbonate, the unlocked bases and soluble silicates are removed, and the residue is simply that which was not decomposed by lime.

It is doubtful whether any scheme of proximate analysis will ever be perfected. The various aluminium silicates concerned are so similar in chemical composition that a finely divided mineral which is supposed to remain in the residue will probably be more soluble than a coarser specimen that should dissolve in whatever solvent is being used. Before proximating, therefore, we must effect some sort of mechanical separation of the clay materials, according to their state of sub-division.

MECHANICAL ANALYSIS.

Although mechanical analysis has not yielded the results which were hoped of it, the important influence which the fineness of clay and other materials has on various physical properites, such as shrinkage, fusibility, porosity, rate and safety in drying, safety in burning, colour, plasticity, and so on, has been universally recognised. For example, if a certain percentage of quartz or flint be introduced into a body mixture, then the coarser the quartz grains the greater the reduction of shrinkage and the less the reduction of porosity, the less water required in tempering, the less the tendency to warp or crack in burning, and the fewer gas vesicles formed in the ware. Stone in a body causes the contraction to vary inversely as the diameter of the grains. In glazes the crazing tendency increases with the diameter of flint. These empirical results agree with Fick's law, based on a study of salt solutions of different degrees of concentration, which states that the amount of solute which diffuses through a given cross-section is proportional to the difference in concentration of two cross-sections lying indefinitely near to each other, or is proportional to the difference in cross-section. From which it is seen that the fineness of the raw materials governs the conduct of the body, as the area of the surface of the particles in contact is dependent thereon.

Mechanical analysis is complicated by the fact that the raw materials differ only slightly in specific gravity, as appears in this table :—

Kaolinite	2.6
Calcite	2.7
Biotite	2.7–3.1
Quartz	2.6
Felspars	2.55–2.75
Micas	2.7–3.0

The methods in use depend therefore on variety of size and shape of the particles, and not on their density or mineral composition. In all cases the clay must first be deflocculated, and a few drops of ammonia or alcohol is probably the best agent for this purpose. Schloessing (1903) recommends preliminary extraction with weak acid, and then treatment with ammonia after washing free from acid. If all colloids are present as alkaline compounds, shaking with cold distilled water alone is sufficient for deflocculation. Sodium hydroxide is more vigorous in its action than ammonia. When polyvalent bases are present, either combined with the gel or in the soluble salts, alkaline oxalates are recommended by Ashley (1910). In all these cases excess must be avoided, and the right amount to add should be determined on a separate sample. The amount usually worked on is 5-30grams. of the dried clay, and the various sediments should be dried at the same temperature as the sample—say at 100° C.

The first apparatus for mechanical analysis of importance was that of Schulze (1849). It was followed by those of Nobel (1864), Dietrich (1866), and Masure (1867), but they are of merely historic interest. Schoene, of Moscow, modified (1867) Schulze's method, and improvements of these two are still used to-day. Seger, in standardising the Schōne method, proposed a classification of the particles according to their diameter, which is generally accepted by ceramists, though agronomists prefer a wider nomenclature.

SEGER'S CLASSIFICATION.

Seger.	mm. diam.	U.S. Dept. of Agriculture.	mm. diam.
Clay	0 –0.01	Clay	0 –0.005
		Fine silt	0.005–0.01
Rock dust	0.01 –0.025	Silt	0.01 –0.05
Silt	0.025–0.04	Very fine sand	0.05 –0.1
		Fine sand	0.1 –0.25
Sand	0.04 –0.333	Medium Sand	0.25 –0.5
Coarse Sand	> 0.333	Coarse Sand	0.5 –1.0

It must be borne in mind that the nomenclature thus adopted in all processes of mechanical analysis does not necessarily refer to the chemical composition. Clay may not be aluminium silicate; sand may not be silica. But Mellor and Heath (1907) found that as the diameter of the particles increased, the substance became more silicious, which gives some basis for the classification. The various processes of mechanical analysis may be classified as follows:—

1. Elutriation—Schulze, Schoene, Hilgard.
2. Subsidence, or beaker method.—Osborne (1887), Whitney (1896).
3. Centrifugal method.—Yoder (1904).
4. Pneumatic method.—Cushman.
5. Microscopic methods.—Sizing by counting, and the use of stains.

ELUTRIATION METHODS depend on the fact that particles of various size will be transported by a moving column of water, according to the velocity of the current.

The Schulze apparatus consisted of three tapering glass or metal receptacles of different size through which a constant flow of water is maintained. The velocity is therefore greatest in the first and smallest can, and least in the last and largest; and the particles are arranged accordingly in the various cans, the coarsest being found in the first can, while much of the very fine clay is lost in the overflow. Parmelee and Moore (1909) recommend varnishing the interior of the cans to prevent the electrolytic action set up by corrosion, which causes fine clay to lodge instead of overflowing.

The Schoene apparatus is in principle the same as the Schulze, but the flow is controlled by a piezometer, which, however, may be rendered inaccurate by capillarity. Seger gives the following figures for the flow :—

	Diameter.	Velocity.	Height of Manometer.
	mm.	mms. per sec.	cm.
Clay	0 –0.01	0.18	1
Rock dust	0.01 –0.025	0.7	8
Silt............	0.025–0.04	1.5	50

The Hilgard apparatus is more elaborate than the Schoene. It substitutes a cylindrical for a tapering tube in the elutriation, and in this tube a set of arms rotates at high speed to break up flocculations.

The chief faults of the elutriation methods are the large volume of water required, which introduces soluble salts and possibly organic matter, the duration of the analysis, and the tendency to flocculation.

Subsidence Methods depend on the differing rates of fall of bodies suspended in water at rest. The whole material is introduced into the water, and after some minutes the fluid still containing particles in suspension is decanted from the larger particles which have settled. The process is repeated with longer periods of subsidence.

The drawback to subsidence methods is immediately apparent. Small particles near the bottom will reach the bottom more quickly than large ones further away. The sediments must therefore again be fractionated. But they have the advantage that flocculation occasions little inconvenience.

The Centrifugal Apparatus devised by Yoder is the standard method of the U.S. Department of Agriculture (*U.S. Bull.* 24, 1904). In it the clay group is separated from the others by centrifugal force. It consists of an electric motor mounted with vertical shaft, to which is attached a spider carrying eight trunnioned frames. The centrifugal tubes are heavy glass, 18 × 3cms., supported in the trunnioned racks. The motor is provided with a rheostat giving four different speeds. Before analysis, it is necessary to disintegrate aggregations. Five grammes of each sample are shaken for a few hours in a 250c.c. bottle containing 75c.c. distilled water and 10 drops of strong ammonia. The contents are then decanted into the centrifugal tubes, and the machine run for three minutes. A sample of the suspended material is examined under the microscope for particles larger than the clay group. If satisfactory, the clay suspension is evaporated to dryness in weighed platinum vessels. It is not necessary to use centrifugal force for further separation, as sedimentation of sand from silt is fairly rapid.

The *Pneumatic* separation proposed by Cushman is carried out on the dry particles by currents of air of differing velocity.

Microscopic and *staining* methods are occasionally useful, but as a rule the counting and measuring take too much time. If one has access to the requisite apparatus, the Hilgard and Yoder methods are best. If not, a beaker and a microscope are most useful.

SURFACE FACTOR.

Given the mechanical analysis, it is necessary to know how to read it. For example, which of the two clays, A and B, is the finer ?

	A.	B.
Clay	33 per cent.	37.8 per cent.
Rock dust	30 ,,	39 ,,
Silt	16 ,,	16 ,,
Sand	21 ,,	7.2 ,,

To answer this, W. Jackson in 1904 devised the so-called surface factor (see *Trans. Eng. Ceram. Soc.*, 1904, or *Jackson's Ceramic Calculations*). The calculation depends on the fact that the more finely divided a material, the greater is the total surface of its particles per unit mass. The average diameter of the four fractions usually obtained by elutriation are 0.005, 0.0175, 0.0325, 0.185mms. respectively, and the surfaces of equal masses of each fraction will be in the proportion

$$\frac{1}{50} : \frac{1}{175} : \frac{1}{325} : \frac{1}{1850}$$

or 3367 : 962 : 518 : 91.

To get the surface factor the percentage of each fraction is multiplied by its respective number—*i.e.*, the clay by 3,367, the rock dust by 962, the silt by 518, and the sand by 91. These products are added together, and the last two figures omitted. The number obtained is the surface factor, and the greater this number the finer the material. Thus, in A and B above, we have :—

A.		B.	
33 × 3367	111111	37.8 × 3367............	127272
30 × 962	28860	39 × 962.............	37518
16 × 518	8288	16 × 518.............	8288
21 × 91	1911	7.2 × 91..............	655
	1501		1737

Therefore B is the finer.

Purdy in 1905 (*Trans. Amer. Ceram. Soc.*, 7, 441) proposed a modification of Jackson's factor, and the Jackson-Purdy surface factor is the one used in the States. But it makes precisely the same assumptions as its predecessor, and differs chiefly in not inverting the diameters. If Jackson's factor were to trace a rectangular hyperbola, so also would Purdy's. Cushman (*Journ. Amer. Chem. Soc.*, 29, 589) shows the inaccuracy of assuming that the mean diameter of a group of particles can be obtained by averaging the extreme diameters of that group. Mellor (*Trans. Eng. Ceram. Soc.*, 1909, 9, 94) discusses the Jackson and Purdy factors, and suggests a new one :—

$$\frac{6}{s}\left(\frac{W}{e_1}+\frac{W_2}{d_2}+\frac{W_3}{d_3}+ \;-\;-\;-\;-\right)$$

Where s is the mean specific gravity of the powder, W_1. . . the respective weights of the fractions per unit weight of powder, and d_1 . . . the corresponding average diameters. He calculates the average diameter from the mean diameters d_1 and d_2 as

$$\sqrt[3]{\frac{(d_1 + d_2)\ (d_1^2 + d_3^2)}{4}}$$

It will be seen, then, that no one factor has been generally accepted.

CHAPTER IV.

RAW MATERIALS.

Silica is introduced generally as flint or powdered quartz or pure river sand. It occurs in three conditions: *hexagonal* in quartz, and its minor varieties, rock crystal, quartzite, Lydian stone, amethyst, cairngorm, smoke topaz, morion, cat's-eye, avanturine, hornstone, jasper, and bloodstone; *rhombic* in tridymite and asmanite; *amorphous* in opal, hyalite, hydrophane, sinter, and geyserite. Then mixtures of quartz and amorphous silica form flint, chalcedony, carnelian, sard, plasma, chrysoprase, agate, and onyx. Sand usually consists of quartz grains. When indurated it becomes sandstone, being cemented by lime or iron compounds with fragments of other minerals. Silica may now be obtained on the market as river sand containing 99.5 per cent. silica.

Bitstone is a coarse sharp-grained quartz which is used in saggers so that the point fused into the glaze on the bottom of a piece of ware may be as inconspicuous as possible. It should be of uniform grain to carry the ware level.

Chert is a silicious rock occurring chiefly in limestone. It is less splintery in fracture than flint, and is used not so much as an ingredient in pottery as for runners of wet grinding mills. H. L. Terry (1906) gives the following analyses of chert sold to the Potteries for this purpose:—

—	Derbyshire.		Swaledale.	Flintshire.
H_2O	0.54	0.60	1.51	1.32
SiO_2	82.53	63.40	95.69	93.56
FeO	—	—	1.02	4.52
Fe_2O_3	1.05	2.34	—	—
$CaCO_3$	15.88	33.66	1.86	0.43

A 2-ton chert runner working on flint alone lasted ten months, when it was reduced to 7cwt.

KIESELGUHR, or infusorial earth, consists of the silicious integument of lower organisms. It is best detected under the microscope. *Tripoli* is similar in origin and composition.

HYDRATED SILICA is not introduced as a raw material, but it may occur in clays, especially those of volcanic origin. Its action in a body, compared to that of crystalline silica, is to increase translucency, shrinkage in air and fire, to lower the temperature of vitrification and to form deposits of silica acid on the surface of the ware.

The SILICATES chiefly used in pottery are, besides clay, felspar, Cornish stone, asbestos, water-glass, ganister, marl, cullet, and slag. The employment of silicates is being greatly extended. Granite, syenite, felstone, eurite, volcanic ash, pozzolana, trass, santorin earth, are all making their way into pottery and building ware; but it is doubtful if the many patents taken out in various countries for mineral silicates could be upheld.

FELSPAR in commerce is usually the potash spar, generally of Scandinavian origin. Lime and soda spars do not appear on the market to any extent. According to A. S. Watts (1909), ware made with soda spar gives a wooden ring when tinkled, but such ware may have as much strength as that with a brighter sound. A good spar should be free from iron and should contain 14.5 to 16.5 per cent. of K_2O. The alkalies are estimated by the Lawrence Smith method. Bastard spars containing 9 to 14 per cent. alkali may be utilised on a cheap quotation if the necessary allowance be made in the mixings. We have already explained the mineralogy of felspar in previous chapters. Felspar often appears red in the raw powder and yet may burn quite white. This phenomenon is due to organic remains, and does not infer the presence of iron.

CORNISH STONE is a weathered granite or porphyry in which the decomposition has not proceeded to a finish. It contains 5 to 9 per cent. of alkali, and should be free from iron. Watts gives it the empiric formula—

$$\left.\begin{array}{l} 0.676\ KNaO \\ 0.293\ CaO \\ 0.030\ MgO \end{array}\right\} 1.167\ Al_2O_3,\ 8.93\ SiO_2.$$

Combining weight, 732.7.

Langenbeck has found as much as 19 per cent. soluble silica. Cornish stone is probably the most variable of potters' materials. It nearly always contains fluorine, derived from mica, up to as much as 2 per cent. Ashley says it is composed roughly of kaolin 11, quartz 22, spar 67, mechanically mixed, not in chemical combination. Both Watts and Ashley have failed to find any difference between the introduction of stone and artificial substitutes of the same composition into a body, except that the natural stone gave a brownish cast to the ware.

Ganister is a silicious rock cemented with clay, found in the lower coal measures. It contains about 90 per cent. of silica and 5 per cent. of alumina.

Sodium Silicate may be obtained as a dry powder, but is generally bought as *water-glass*, a very viscous liquid containing 45 per cent. of water when fresh, and approximating to the formula Na_2O, $2SiO_2$, $8H_2O$. The alkali content may be estimated by direct titration with acid and methyl orange.

Asbestos and Talc, each containing about 31 per cent. of MgO, and other magnesium silicates, are occasionally used as pottery material. The magnesia is estimated by the phosphate method.

Cullet, or broken glass, may vary in composition, and careful analysis is necessary if bought from outside. The colour of the glass should be watched. The origin of the material can probably be deduced from its analysis, thus—

	SiO_2.	Al_2O_3.	PbO.	CaO.	Na_2O.	K_2O.
Combustion tubing	75	—	—	10	—	15
Window glass	69	7.5	—	12.5	11	—
Crown	67.5	1.5	—	10	—	21
Flint	56	1.0	34.5	—	—	8.5

Slags containing silicates include blast-furnace slags from the production of iron, copper, and lead; tap cinder, acid Siemens' slag, and similar materials. If the slag be the chief constituent in a body, such as for building embankments, making filter beds or cast-blocks, experience has shown that it should contain about 40 of silica, 40 of lime, and 20 of alumina. Slags containing under 33 per cent. SiO_2 and 14 per cent. Al_2O_3, or over 45 per cent. CaO, are apt to disintegrate, while very silicious slags crack or fly to pieces on cooling. Manganese and iron are always present in slags, a fact which limits their employment to coloured ware. Granulated slag, as used in making slag cement, has the composition :—

SiO_2	27 to 35 per cent.
$Al_2O_3 + Fe_2O_3$	8 to 20 ,,
CaO	44 to 52 ,,
MgO	0.6 to 2.5 ,,
SO_3	1 to 3 ,,

Grog, or rough stuff, is pottery waste (often deliberate). Its composition is probably that of the body it came from. Each class of rough stuff should be kept distinct.

Marl finds greater employment in cement works than in potteries ; but it is used to some extent for making saggers. Marl consists of clay and calcareous matter.

Willemite has the formula $2ZnO.SiO_2$, which gives ZnO 73 per cent., SiO_2 27 per cent. If introduced into a white glaze it should be free from manganese, which may be present in the variety *troostite* up to 12.5 per cent., with corresponding dimunition of zinc.

NON-SILICIOUS INGREDIENTS.

These include red lead, litharge, white lead, whiting, plaster, fluorspar, dolomite, magnesia and magnesite, barium carbonate and sulphate, zinc oxide, soda ash, borax, salt, saltpetre, nitre, bone ash, boracic acid, colemanite, cryolite, silico-fluorides, and numerous stains and opacifiers which will be treated in subsequent chapters. The analytical methods for most of these materials are too well known to need description, but the standards of quality may be briefly run over. Red lead contains 95.7, white lead 86, and litharge 100 per cent. of lead as PbO. Red lead is 113 per cent. of white lead, and white lead 89 per cent. of red lead, in respect of substituting either in a mixing. Whiting should contain 98 per cent. $CaCO_3$. Theoretically, whiting is equivalent to 56, dolomite to 30.4, gypsum to 32.5, plaster to 38.5, fluorspar to 71.5 per cent. CaO ; but dolomite also contains 21.74 per cent. MgO. Grecian magnesite contains approximately 90 per cent. $MgCO_3$ and 10 per cent. $CaCO_3$. Precipitated barium carbonate may have a loss on drying of 1 per cent. (All raw materials should be periodically tested for moisture during storage.) The mineral witherite may hold some isomorphous strontium carbonate and some barium sulphate mechanically mixed. Barium sulphate rarely contains more than 96 per cent. $BaSO_4$. It should be tested for loss with hydrofluoric acid to ascertain clay, etc. Theoretically, the sulphate is equivalent to 65.7 and the carbonate to 77.7 per cent. BaO.

Borax has the composition: H_2O 47.12, Na_2O 16.23, B_2O_3 36.65 per cent. The soda is titrated with methyl orange and normal acid, then glycerine is added to one-third of the total bulk and the boric acid titrated with phenolphthalein and normal alkali (see Schaak, *Journ. Soc. Chem. Ind.*, 1904, 23, 699). B_2O_3 is multiplied by 2.731 to convert into borax. Moisture, as apart from water of crystallisation, is obtained by difference. *Boric acid* is also tested by Schaak's method. Langenbeck found (1894) 10 per cent. SO_3 as ammonium sulphate in boric acid; it was probably the brown Tuscany acid.

Jacobi (1905) gives the analysis of this as—

Boric acid	81.61
SiO_2	0.79
$Al_2O_3 + Fe_2O_3$	0.31
CaO	1.12
SO_3	8.89
R_2O	2.34
Ammonium oxide	3.99

Which means that brown acid roughly consists of 70 per cent. pure boric acid, 15 of borax, and 15 of volatile matter and objectionable sulphates. Theoretically, boric acid is 43.55 H_2O, 56.45 B_2O_3 per cent.; but as much as 50 per cent. H_2O may be present.

Colemanite is a mineral of the formula: $2CaO, 3B_2O_3, 5H_2O$. Its advantage lies in the fact that being insoluble in water it can be used dehydrated in a glaze without fritting.

Fluorspar, when finely ground, is entirely soluble in boiling hydrochloric acid. Any silica is filtered off, and calcium precipitated with oxalate. The fluorine is estimated, if at all, as in cryolite below.

CRYOLITE is composed of 32.81 Na, 12.98 Al, 54.21 F per cent., or 40 AlF_3 : 60 NaF. Several artificial cryolites are on the market, being generally mixtures of sodium and aluminium fluorides loaded with silica—*e.g.*, one had the composition AlF_3 18, NaF 50, SiO_2 32 per cent. But some artificial cryolites preserve the ratio of the natural mineral and contain only about 5 per cent. silica.

The fluorine in cryolite and other insoluble fluorides that may contain silica is estimated as follows:—One gramme of the finely ground material is fused with 4grms. of mixed carbonates. The melt is digested with 100c.c. water and filtered. The filtrate, which contains the fluorides, is evaporated until gummy, then diluted and just neutralised with nitric acid and phenolphthalein. Last traces of silica are removed by adding 20c.c. of Schaffgotsch solution. (This is made by dissolving 250grms. of ammonium carbonate in 180c.c. of ammonia (sp. gr. 0.92) and diluting to one litre, then adding 20grms. of mercuric oxide and shaking till solution is effected.) The filtrate from the Schaffgotsch treatment is boiled with large excess of calcium chloride solution. The precipitate, consisting of calcium carbonate and fluoride, is washed, dried, gently ignited and treated with dilute acetic acid till evolution of carbon dioxide ceases. The liquid is then evaporated to dryness, the residue taken up with hot water (slightly acidified with acetic acid), filtered, dried, gently ignited and weighed as CaF_2. This may be checked by heating with sulphuric acid and weighing again as $CaSO_4$. The method gives results which are 2 to 4 per cent. too low in fluorine.

SILICOFLUORIDES are now sold as by-products in the manufacture of artificial manures. In these, hydrofluosilicic acid is taken up by water and precipitated by soda or salt. The samples should be tested accordingly for chlorides. Silicofluorides are titrated by normal caustic and phenolphthalein, the equation being:—

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O.$$

The sample should contain 95 per cent. sodium silicofluoride.

BONE ASH consists of tribasic calcium phosphate, $Ca_3(PO_4)_2$, with calcium and magnesium oxides or carbonates and a little fluoride. It may be dark grey from presence of carbon, which may be eliminated by adding saltpetre to the mixing. The value of bone ash depends solely on the phosphates present, which are estimated by the ammonium molybdate or volumetric uranium methods. Edwards (1904) gives the composition of the average bone supplied for china manufacture as :—

Tribasic calcium phosphate	85.25
Calcium carbonate	2.88
Magnesium carbonate	2.45
Calcium fluoride	1.68
Ferric oxide	0.32
Silica	4.57
Loss (water and carbon)	2.85

BAUXITE is a hydrated alumina mixed with clay, iron, and titania. It contains from 45 to 80 per cent. Al_2O_3, and 15 of water. Irish bauxite contains 75, and American 90 per cent. Al_2O_3 after ignition.

CHAPTER V.

BODIES.

The composition of a body depends on its purposes and on the temperature at which it is to be fired. In determining what class of ware he is going to make, the manufacturer must be guided by the market price of the ware, by the nature of his own raw materials, and by the cost of other raw materials, including that of fuel, which influences the firing temperature. The cost of carriage to the nearest open market and the wage-rate must also be taken into account. It will be seen, then, that each locality is best fitted for the production of some particular class of ware in which it should be able to meet all competition. The most elementary type is the local brickfield, fitted with obsolete plant, and yet able to maintain its position in the immediate vicinity because the price of bricks would not pay the cost of carriage from more scientific centres. Thence we proceed by infinite gradations till we reach the hard porcelain of Germany and the bone china and decorated stoneware of England,

Besides the chemical analysis, physical tests should be made of the clays to be made up into bodies. The chief of these concern plasticity, tensile or transverse strength, drying shrinkage, firing shrinkage, refractoriness, and colour after burning.

Plasticity, which is only developed in clay when wet, is best estimated by feel. To get a numerical expression of plasticity several methods have been suggested. Stover (1905), following Bischof, suggests forcing the wet clay through a die and measuring the length of pencil extruded before it breaks by its own weight. Another method is founded on the fact that, generally speaking, the more plastic a clay the more water required to bring it to the degree of softness at which it can be worked. The proportion of water required to soften one hundred parts of dry clay expresses the plasticity. To get this, Langenbeck suggests the use of Vicat's needle, and states the proper consistency is reached when the needle under 300grams. penetrates 4cms. in 5 mins. Ashley's theoretical plasticity formula is $\frac{B \times C}{A}$, where A is the Jackson-Purdy surface factor, B the cast air shrinkage, and C the relative colloids found by malachite green adsorption.

Tensile Strength is measured by moulding the clay into briquettes, and, when dry, pulling them apart in a machine. The result is given in pounds per square inch. High tensile strength and high plasticity often go together, but not invariably so.

Transverse Strength.—Ries and Allen (1910) recommend this in preference to the older tensile test as being easier to carry out, and as giving more uniform results. The clay is moulded into bars 3.5 × 1.25 × 0.7in.; the bars are supported on round wooden edges 2.5in. apart; a steel rod $\frac{1}{16}$in. in diameter is laid across the bar half-way between the supports, and from this a pail is suspended. Shot is fed into the pail till the bar breaks.

Drying and Firing Shrinkage are expressed either lineally or cubically. The shrinkage of a clay is reduced in manufacture by an admixture of its own grog. A body should have a total shrinkage of not more than 1 in 9 lineally, else warping will probably ensue. It is better to work to 1 in 12, or even less if possible, whilst keeping the porosity low.

The pre-heating treatment of clays is said to overcome the difficulty of making a vitreous body without undue loss in manufacture or excessive cost in firing. It is the weakness of plastic clays that they give rise to cracking during drying, and if rough stuff is introduced to overcome this, the resulting biscuit is less vitreous at the same temperature of firing. But for building ware, and still more for sanitary ware, a high absorption of the body must be avoided. Bleininger (1909) found that the process of "weathering" clay, which overcomes the difficulty to some extent, can be materially hastened by heating the clay from 200-300° C. It does not follow that the more plastic the clay originally, the more it is affected by heating; each clay must be treated on its own merits, but the general rule is to heat for three to five hours to a temperature not exceeding 300° C. The range of the temperature in which the change takes place is in some cases exceedingly small. Temperature-shrinkage curves are helpful in indicating the behaviour of a clay.

Refractoriness is best tested by firing cones of the clay side by side with Seger cones. It must be remembered that these complex silicates have no definite melting point, and that the fineness of the material and the duration of firing are as important as the temperature reached. Other things being equal, the firing point is dependent on the chemical composition.

Colour.—The chief colouring impurity in a clay is iron oxide, though the depth of colour is dependent on the amount of alumina and lime as well as iron. Clays high in lime or alumina may contain over 1 per cent. of iron without affecting the whiteness of the body. The atmosphere of the kiln also influences the colour, as a reducing atmosphere forms the green or blue black ferrous colours. Standards of colour should be made for purposes of comparison. Lovibond states that pure calcium sulphate is the whitest material obtainable. The three primary colours—red, green, and violet—are matched by carmine, emerald green, and French mauve. With these four substances and lamp-black one can express any colour by the amount of each ingredient.

The Co-efficient of Expansion of the fired body should be noted, and, if possible, measured in actual scientific units. Le Chatelier has invented an instrument for this purpose. The linear coefficient of porcelain and well-fired pottery is between 0.0000044 and 0.0000070 per degree Centigrade.

Turning to the effect of raw materials on a body, we may say in general that basic oxides act as fluxes, tightening the body; acid oxides (SiO_2, TiO_2) act as refractory materials, rendering it less fusible. Sesquioxides (Al_2O_3, P_2O_3, B_2O_5, Fe_2O_3) take an intermediate position. The composition of a body or glaze is therefore expressed by grouping the various oxides to get the general formula

$1.0\ R_2O$, aR_2O_3, bRO_2. But this does not necessarily imply that the fusibility of a body can always be increased by adding more bases. The ratio of alumina to silica is important, and increase in the sesquioxide content may be requisite to lower the melting point if the silica be too high. On the other hand, if the silica be too low the sesquioxides alumina and boron trioxide function as acid oxides, and you get borates and aluminates instead of aluminium salts of substituted silicates. Boron trioxide and phosphorus pentoxide are more apt to change over to the acid oxides than alumina or ferric oxide, while titania acts a flux in a refractory body. It is impossible to classify ceramic materials into fluxes and refractories, as an excess of any component above the amount needed to form eutectics causes that component to act as a refractory.

The molecular formula is sometimes calculated to R_2O_3 as unity, thus: cR_2O, $1.0\ R_2O_3$, dRO_2, and this is the preferable method, as it brings out more clearly the intermediate position of the sesquioxides.

The present writer has devised (1909) a short system of expressing formulæ. Suppose that one wishes to describe more shortly the molecular formula R_2O, $0.25\ R_2O_3$, $3.0\ RO_2$. Multiply the number of RO_2 molecules by 1,000, the R_2O_3 molecules by 100, and add. The figure obtained is 3,025, and it is a complete expression of the formula. We ignore the second place of decimals in the RO_2 group, and the third place in the R_2O_3 group. The R_2O is, of course, unity in the molecular formula. Thus:—

The glaze 6135 would have a molecular formula $6.1\ SiO_2$, $0.35\ Al_2O_3$, $1.0\ R_2O$.

B_2O_3 molecules are added to the glaze numbers without any multiplication, so that—

The molecular formula R_2O, $0.23\ Al_2O_3$, $0.7\ SiO_2$, $0.99\ B_2O_3$ would be expressed by the number 723.99.

If a portion of the glaze has previously to be fritted, this is expressed by the minus sign. Thus:—

2116.475 − 723.99 signifies a glaze of molecular formula R_2O, $0.16\ Al_2O_3$, $2.1\ SiO_2$, $0.475\ B_2O_3$, of which R_2O, $0.23\ Al_2O_3$, $0.7\ SiO_2$, $0.99\ B_2O_3$ has previously to be fritted.

The temperature of firing can be added by giving the cone numbers with C as prefix. Thus: 306 C 010 means R_2O, $0.06\ Al_2O_3$, $0.3\ SiO_2$ fired at cone 010. Similar letters can be devised for the time of grinding (G 48), mesh of lawn (M 150), and all the other points of consideration in the preparation and firing of a glaze or body.

In the unlikely event of the alumina or boric anhydride being more than 1.0, they could be expressed by a point over the first figure. Thus 723.$\dot{0}$8 means R_2O, 0.23 Al_2O_3, 0.7 SiO_2, 1.08 B_2O_3.

Pottery Bodies may roughly be divided into porcelain, stoneware, earthenware, terra-cotta, and filters. The German "steingut" corresponds approximately to our stoneware, and "steinzeug" to earthenware, and the French equivalents are "grès" and "faience." The American "white granite" covers more or less both stoneware and earthenware; but they apply the term porcelain to tight bodies such as insulators, which we would call vitrified stoneware.

None of these divisions are perfect. Like the colours of the spectrum, pottery wares merge imperceptibly into each other. Commercial competition and the needs of advertisement are responsible for great confusion in nomenclature. In several cases—*e.g.*, enamel, faience, and majolica—the modern meanings are the precise opposite of the original. An enamel first meant a clear glaze; it now in commerce implies an opaque one.

The chief characteristics of the five divisions are these: Terra-cotta and filters are unglazed; stoneware, earthenware, and porcelain glazed. Porcelain and earthenware are white, the raw materials being so selected to give a white body. Stoneware is made from clays that do not burn quite white. Terra-cotta is still more coloured; it is the artistic evolution of common brick. The absorption is some guide to a body. Porcelain should have no absorption, stoneware 0 to 8 per cent., earthenware 0 to 10 per cent., terra-cotta up to 12 per cent., and filters from 25 to 35 per cent. The reason why earthenware is generally more absorptive than stoneware is that the content of china clay and flint is made as high as possible to keep the body white and straight. Earthenware with absorption of less than 1 per cent. would probably be called ironstone china or some similar name. It is used for toilet and table ware, and in origin is really an imitation of porcelain fired at a much lower temperature, the result being an open body with no translucency, and an adhesive glaze instead of one that is inseparably combined with the body as in porcelain. The composition of earthenware and stoneware is :—Silica, 62-70 per cent. ; alumina, 25-35 per cent. ; alkalies, 1-4 per cent.

The first native English stoneware of value was made by Dwight, who started in Wigan in 1671 and moved to Fulham in the following year. Meantime a foreign colony had sprung up in Staffordshire, Elers, a Dutchman, being sued by Dwight for infringement of patent between 1690 and 1700.

Earthenware, as now understood, originated with Wedgwood and his contemporaries (*c.* 1770), who changed the buff body coated with white slip or tin enamel for a body white throughout. The next fifty years were the high watermark of English pottery. Wedgwood also produced Jasper ware, an unglazed but impermeable body made from plastic clay and barytes, fired almost to translucence, and coloured with metallic oxides.

PORCELAIN is divided into hard porcelain and soft porcelain or china. The hard porcelain takes a natural felspathic or pegmatite glaze, and the latter a softer artificial one. The best known hard variety is the Berlin ware, which consists of 55 per cent. clay substance, 22.5 per cent. quartz, 22.5 per cent. felspar. The limits of safety in hard porcelain are :—Clay 40-66 per cent., quartz 12-40 per cent, spar 15-30 per cent., calcium carbonate 0-6 per cent.

Soft Porcelain includes the artificial (sometimes called French or frit) porcelain, Seger porcelain, and bone china.

Artificial Porcelain resulted from an attempt to reproduce Chinese ware, which came to Europe in the 15th century. Venice claims to have made it in 1519, and ware made at Florence in 1575 is yet extant. It was also manufactured at Rouen in 1673, and in England, at Stratford-le-Bow or Chelsea, in 1730. (Worcester, which still survives, was founded in 1751). Chemically, artificial porcelain is a connecting link between true porcelain and glass, as its alumina content is extremely low. It is therefore too sensitive to changes of temperature. Le Chatelier has shown that the secret of soft porcelain was known to the ancient Egyptians, who made a porcelain of the composition:

SiO_2	88.6	per cent.
Al_2O_3	1.4	,,
FeO_3	0.4	,,
CaO	2.1	,,
Na_2O	5.8	,,
CuO	1.7	,,

which is very similar to modern Sevres soft paste ware.

Bone China originated (Frye's patent, 1742) through the supply of steatite from Cornwall failing. A normal china body consists of :—Bone ash 44 per cent., Cornish stone 30 per cent., clay 26 per cent.

Seger Porcelain (1880) is based on the Japanese. In this Seger returns to the original raw materials of porcelain ; but, by using plastic white clays, is enabled to reduce the clay and increase the fluxes, thus :—Clay 25 per cent., spar 30 per cent., quartz 45 per cent., as compared to the Berlin, clay 55 per cent., spar 22.5 per cent., quartz 22.5 per cent.

Fireproof China is made by introducing much alumina, either free or as china clay. Such a ware, fired at cone 10, has the composition :—Kaolin 24 per cent., quartz 1 per cent., felspar 3 per cent., burnt stuff 3 per cent.

A feature of the last decade has been the appearance of wares which go to the extremes in what has been regarded as the usual raw materials of pottery. Formerly the chief chemical difference between pottery and glass lay in the low alumina content of the latter. But the fused silica ware containing 99 per cent. of silica, sand lime bricks which are 90 per cent. silica, 10 per cent. lime, siloxicon (a refractory compound of silicon, carbon and oxygen produced by heating ground coke, sand and sawdust to 2600° C. in the electric furnace), and, on the other hand, the corundum and other alumina articles, suggest that the name Ceramics will have to include glass, pottery, cement, and all other manufactured articles containing either silica or alumina.*

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*Many precious stones pertain to the sphere of ceramics in regard to chemical composition. Thus, amethyst and cairngorm are quartz silica, opal is hydrous silica. Corundum, ruby, sapphire, and Oriental amethyst are alumina. Turquoise is hydrous aluminium phosphate, and topaz aluminium fluosilicate. Magnesia and alumina form the spinel and ruby, and beryllia and alumina chrysoberyl and alexandrite. Zircon, jargoon, and hyacinth are zirconium silicate. Double silicates form a numerous class. Beryllium and aluminium form beryl, emerald, and aquamarine ; the garnets are silicates of aluminium with calcium magnesium or iron ; olivene and peridote are magnesium and iron, and sphene calcium titanium, silicates.

Most of these new products result from the high temperatures possible in the electric furnace. They are generally shaped upon a core of carbon or similar material, and then finished in subsequent firings.

Sand-Lime, however, is an interesting departure from clay in the direction of low temperatures. It is due to Michaelis, who subjected an intimate mixture of lime and silica to the action of high-pressure steam for several hours. The resulting product consists of sand grains cemented together by a bonding substance. Apart from the calcium hydroxide or carbonate that may be present, this bonding material consists of a mixture of at least two and most likely three calcium silicates, which may be hydrated, the bulk being calcium meta-silicate, $CaSiO_3$ or $CaSiO_3,H_2O$, and the others the ortho- and di-silicate.

The Committee appointed (1911) by the Dutch Minister of Industry and Commerce to inquire into the relative merits of building ware made from clay and from sand-lime mixtures, concluded that for buildings intended to be permanent sand-lime brick is not sufficiently durable nor does it lend itself to architectural treatment, but within these limitations it is a useful ware. Its fracture should be smooth and straight, its absorption not more than 15 per cent. The first quality should withstand a crushing force of 200 kilos. per sq. cm. (approximately 2,850lb. per sq. in.) on an average of 10 samples, with a minimum of 180kilos. per sq. cm. (2,560lb. per sq. in.). The second quality should average 150kilos. (2,130lb. per sq. in.) with a minimum of 135kilos. per sq. cm. (1,920lb. per sq. in.).

The reproduction of a body is not merely one of analysis and subsequent synthesis in terms of the raw materials at one's disposal. As we have explained before, the chemical reactions do not proceed to a finish in body firing, so that the number of possible bodies is as infinite as the number of possible sources of clay. A chemist must not be afraid to make departures from the guiding analysis which will be more suitable to the conditions in which he is placed. To ascertain the correct firing temperature, trials of the same composition are fired and drawn out at various temperatures, and the absorptions tested till one coincides with that of the original.

The following table illustrates the composition of most of the well-known pottery wares.—

BODY ANALYSES (ON FIRED WARE).

Ware.	SiO_2	Al_2O_3	FeO Fe_2O_3	CaO	MgO	K_2O	Na_2O		Analyst.
PORCELAIN:									
Sevres, 1770-1830	58.0	34.5	..	4.5	..	3.0	..		Malaguti
Sevres	59.6	32.6	0.6	4.5	..	2.0	0.7		Seger
Vienna, 1806	61.5	31.6	0.8	1.8	1.4	2.2	..		Laurent
Vienna	59.6	34.2	0.8	1.7	1.4	2.0	..		Seger
Berlin, 1808	66.6	28.0	0.7	0.3	0.6	3.4	..		Laurent
Berlin, 1877	64.3	29.0	0.6	0.3	0.5	3.6	..		Seger
Meissen, 1825	59.4	32.6	0.4	..	..	5.5	..		Laurent
Meissen	58.5	35.1	0.8	0.3	0.6	5.0	..		Seger
Nymphenburg	72.8	18.4	2.5	3.3	0.3	0.6	1.8		Seger
Chinese	70.5	20.7	0.8	0.5	0.1	6.0	..		Malaguti & Laurent
Chinese	69–73	19–23	1.2–2.0	0.3–0.8	..	2.5–3.6	2.3–2.9		Seger
Seger	77.2	17.2	..	0.3	0.2	3.8	0.8		Seger
Bristol, 1775–1780	62.9	33.2	..	1.3	..	2.6	..		Church
English soft, 1847	39.9	21.5	..	10.1	..	2.1	...	Bone 26.4	Cowper
,, 1889	41.0	23.0	0.1	..	..	2.5	...	Bone 33.1	Burton
FAIENCE:									
Persian (xiv.-xvi. cent.)	48.5	12.0	3.1	19.3	0.3	..	..	R_2O + loss 16.7	Brongniart
Hispano-moresque	46.0	18.5	3.6	17.6	0.9	..	..	,, 14.0	,,
Luca della Robbia	49.6	15.5	3.7	22.4	0.2	..	..	,, 8.6	,,
Nevers	56.5	19.2	2.1	15.0	0.7	..	...	,, 6.5	,,
Rouen	48.0	15.0	4.1	20.2	0.4	..	...	,, 12.3	,,
Delft	49.1	16.2	2.8	18.0	0.8	..	...	,, 13.1	,,
MISCELLANEOUS:									
English earthenware (cream)	63.1	33.1	2.1	1.1	0.1	0.2	..		Burton (1889)
,, (granite)	70.9	27.2	1.0	1.0	..	0.1	..		,,
Lambeth stoneware	74.0	22.0	2.0	0.6	0.2	1.1	..		Salvetat
Wedgwood stoneware	66.5	26.0	6.1	2.0	0.2	0.2	..		,,
Palissy ware	67.5	28.5	2.0	1.5	..	..	...		Brongniart

CHAPTER VI.

GLAZES.

To protect and decorate a body it is covered with an impervious vitrified coating called a glaze, which differs from glass only in the higher alumina content necessary to meet the differing conditions. Historically, glazes originated before either glass or pottery. The earliest relics are pebbles glazed in a fire by woodash. Glass then arose through the working of the glaze into beads, and pottery by substitution of an artificial clay body for the pebble. Glazes may be clear, opaque, or crystalline, and they may or may not be coloured. Opaque glazes we shall treat subsequently as enamels; they are glazes containing an undissolved material in suspension. The development of colour in glazes by the addition of stains will also be discussed later.

In dealing with glazes we are on firmer ground than with bodies, and one can give definite formulæ with the prospect of achieving the same results from raw materials of different origin. The essential oxides, apart from stains, are practically confined to those of lead, sodium, potassium, calcium, barium, magnesium, zinc, aluminium, boron, silicon, phosphorus. Fluorides also are introduced into glazes and enamels for the purpose of softening them, but their exact behaviour is not yet settled. Some observers say that the whole of the fluorine goes off in the fire as silicon tetrafluoride, while others maintain that some fluoride always remains in the matured glaze. Mayer and Havas (1911) state that the amount of fluorine remaining in an enamel depends principally on the nature of the compound in which the fluorine was introduced. Thus when 5 and 10 per cent. of various fluorides were introduced into a glass of the same composition in each case, they found the percentage loss of fluorine to be as follows :—

	5 per cent. added.	10 per cent. added.
Fluorspar	33.8	33.6
Aluminium fluoride	37.4	36.1
Sodium fluoride	15.8	14.2
Cryolite	14.4	16.1

They state also that borates cause additional loss of fluorine by volatilisation as boron trifluoride. These experiments of Mayer and Havas were done on quickly-fired enamels which only take an hour or two to mature, so that it would be quite compatible with their results to find no fluorides at all in glazes which have been fired for a week in the kiln.

The constituent oxides must be chosen to meet the requirements of the glaze. As we shall see, there is much confusion about the order of bases in regard to fusibility and the other physical properties, and organised research is badly needed on these points.

A glaze must have practically the same coefficient of expansion of the body, so that it will neither craze nor peel. It must not devitrify either in a prolonged fire or subsequently. It must be sufficiently viscous when molten to hold on to vertical bodies, and yet fluid enough to flow smoothly on flat ones. It must admit of the use of metallic oxides and pigments for purposes of colouring. In constructing glazes certain conventions should be observed; the chief of these are the ratio of the bases to silica, of alumina to both, and of silica to borate. According to Seger, practical glazes are confined to those which do not in silica exceed a tri-silicate nor fall below a bisilicate. But this ruling is too severe. Binns (*Trans. Amer. Ceram. Soc.*, 1900, 2) showed that monosilicate glazes are often superior to others, especially when used raw. As in the case of bodies, we are likely to see an extension of the limits of glaze formulæ in the near future.

The glazes that decompose most easily in air are those low in alumina, high in phosphate, alkalies (10 per cent.)

or lead oxide (20 per cent.). Boro-silicates are most steadfast provided that they are not too rich in borate. At least two bases should be present in a glaze or devitrification follows.

With regard to fusibility, Seger says that bases stand in the order of fluxing power according to their equivalent weights—*i.e.*, PbO, BaO, K_2O, ZnO, Na_2O, CaO, MgO, Al_2O_3; but it is more than doubtful whether any such law can be upheld. Richter and Bischof state that MgO is a greater flux than CaO; Seger himself puts ZnO after Na_2O; Kraze and Popoff (1911) give the order of fusibility as Cu, Co, Sr, Fe''', Ba, K, Mn, Na, Ca, Mg, Ni, Cr. So that each class of glaze should be studied on its own merits, especially with regard to the number of oxides present and to the predominance of one or more of them.

The same remark applies to coefficient of expansion to which Seger applied the same law of equivalents, with hopeless results. Damour gives the order as ZnO, PbO, CuO, CaO, BaO, Na_2O; Hovestadt gives ZnO, PbO, BaO, CaO, K_2O, Na_2O; Winkelmann and Schott (1894) B_2O_3, MgO, SiO_2, ZnO, Li_2O, BaO, PbO, Al_2O_3, CaO, K_2O, Na_2O; and Kraze and Popoff (1911) Co, Cu, Cr, Mn, Fe, Zn, Ba, Ca, Mg, Sr, K, Na. We shall return to the matter of expansion in treating of enamelling on metal, where the question of fitting glaze to body is rendered acute, because the coefficient of iron is nearly twice that of pottery.

Glazes may be applied by dipping, spraying, or vapourising, the first two being done before the fire, the last during it. Vapour glazing includes the reduction colours obtained by controlling the atmosphere of the kiln, the smeared ware fired in a plumbiferous atmosphere, and, chief of all, salt-glazing.

SALT-GLAZE was formerly thought, by Church for example (*Cantor Lectures*, 1881), to have a definite formula, $Na_2O, 7SiO_2$; but Barringer showed (1902) that the composition of salt-glaze depends on that of the body behind it. To take a good salt-glaze a body should be silicious. Langenbeck says that the best alumina-silica ratio is 1 : 8. Barringer finds that these limits may be widened to 1 : 4.6 – 12.5, but anything more silicious than 1 : 9 is impracticable for reasons of plasticity and strength.

Soluble salts may be present in a body up to 3 per cent. without interfering with a good glaze.

The process of salting is endothermic, and the temperature of the kiln rapidly drops. To prevent chilling, salting is either done in two or three stages about half an hour apart, or else resin and crude oil are mixed with the salt.

CLEAR GLAZES, beside salt, include those for china, earthenware, stoneware and Bristol. Hard porcelain glaze is merely felspar or pegmatite—lime spar in the case of Berlin—fired to such a temperature that glaze and body become inseparable. In every fired ware there is an intermediate layer where the glaze has attacked the body to form a semi-vitrefied mass intermediate in composition between body and glaze, but except in porcelain this layer is extremely thin. Porcelain glazes conform to the general formula: R_2O, $0.5-1.25\ R_2O_3$, $5-12\ RO_2$, and glazes for earthenware, etc., to: R_2O, $0-0.4\ R_2O_3$, $1.6-4.0\ RO_2$.

Sevres stoneware glaze, for example, has the formula: $0.3\ K_2O$, $0.7\ CaO$, $0.32\ Al_2O_3$, $2.0\ SiO_2$. Purdy (1906) gets a Bristol maturing at cone 6 from the formula:—

$$\left.\begin{matrix}0.4\ K_2O\\0.4\ ZnO\\0.2\ CaO\end{matrix}\right\}0.55\ Al_2O_3,\ 3.3\ SiO_2$$

CRYSTALLISED GLAZES really include Parian, or matt, and opalescent glazes besides those named crystalline, in which clusters of crystals appear in a clear uncrystalline glaze. They are all effects of crystallisation, but opalescent and "crystalline" glazes are due to supersaturation, while mattness is caused by a general separation throughout the glaze. For convenience we will call the whole group "crystallised," and retain the usual name "crystalline" for the sub-variety.

Opalescence is due to the refraction of light by particles of matter suspended in the glaze matrix. The composition of the suspended matter seems immaterial, but it should be a separation from the cooling glaze and not a coarse addition which would produce opacity instead of opalescence. Purdy (1907) states that glazes high in silica and borate, and fully matured, give good opalescent effects. Stull and Radcliffe (1910) attribute opalescence to a separation of a silicate of boron. According to Edwards and Wilson (1904) the phenomenon occurs when the molecular ratio $B_2O_3 : SiO_2$ is greater than 1 : 6. Purdy gives the formula :—

$$\left.\begin{array}{ll}0.125 & \mathrm{Na_2O}\\ 0.125 & \mathrm{K_2O}\\ 0.5 & \mathrm{CaO}\\ 0.25 & \mathrm{PbO}\end{array}\right\} 0.2 \quad \mathrm{Al_2O_3} \quad \left\{\begin{array}{ll}2.62 & \mathrm{SiO_2}\\ 0.66 & \mathrm{B_2O_3}\end{array}\right.$$

fired at cone 5 for an opalescent glaze. Whitmer (1909) gives :—

$$\left.\begin{array}{ll}0.15 & \mathrm{K_2O}\\ 0.15 & \mathrm{Na_2O}\\ 0.4 & \mathrm{CaO}\\ 0.3 & \mathrm{PbO}\end{array}\right\} 0.2 \quad \mathrm{Al_2O_3} \quad \left\{\begin{array}{ll}1.49 & \mathrm{B_2O_3}\\ 2.97 & \mathrm{SiO_2}\end{array}\right.$$

fired at cone 1.

Crystalline Glazes, the sub-variety, may be obtained by the addition of zinc oxide, titania, or manganese oxide to suitable glazes. Purdy and Krehbiel (1907) found that manganese gave the best effects, zinc gave good crystals in local areas, while titania tends to mattness, producing crystals that are small and evenly distributed throughout the mass. In producing crystalline glazes Heinecke makes one glaze run over another by dipping the ware in one and putting the raw materials of the other in a cover, which is fitted on the ware so that the second glaze when melted runs down over the first. It is doubtful whether such a process could be a commercial success. Amongst the bases, those of low atomic weight favour crystallisation, lead and barium retarding it. Amongst the acid oxides the reverse is true ; the relatively high silicates, titanates, and phosphates favour, while borates are prejudicial to, the effect. As in all crystallisation, slow cooling is favourable to good effects. Purdy and Krehbiel give 0.3 – 0.6 ZnO, 0.7 – 0.4 KNaO, 0.8 – 1.9 SiO_2, 0 – 0.3 TiO_2, and manganese up to 0.9 equivalents as good formulæ. Alumina and borate are absent from nearly all recipes of crystalline glazes.

Matt Glazes include Parian and, when leadless, Carrara. The separated flakes decrease in size with increase of silica and with decrease of alumina and lime. Barium oxide is more potent than lime in producing flakes. Zinc oxide is almost essential to mattness. Just as a false opalescence may be obtained by a slight addition of insoluble matter to a glaze, so a false mattness is the result of firing a glaze below maturity to get a dull surface. True opalescent and matt glazes have been fired to complete fusion and have separated subsequently.) Matt glazes are apt to crawl, which can be overcome by substituting dolomite for whiting, or by putting a small addition of gum in the slop. Claflin (1910) gives good matts, without the use of gum, burned at cone 1, as :—

$$\left.\begin{array}{r} 0.45\ PbO \\ 0.15\ ZnO \\ 0.1-0.15\ K_2O \\ 0.4-0.3\ \ CaO \end{array}\right\} 0.34\ Al_2O_3.\ \ 1.31-1.62\ SiO_2$$

Stull recommends (1909) :—

$$\left.\begin{array}{l} 0.33\ Na_2O \\ 0.33\ MgO \\ 0.33\ ZnO \end{array}\right\} 0.43\ Al_2O_3,\ 3.4\ SiO_2$$

fired at cone 8 as a good opaque glaze for stoneware.

In selecting a glaze to be fired at a given temperature it is a useful guide to ascertain the composition of the corresponding Seger cone, but glazes should be fired 90° above their actual melting point in order to reach full maturity. A better method is to analyse a ware which is known to fulfil the desired purpose. The glaze is chipped off, if possible; if not, the body behind must be ground away. The analysis is conducted as with clay, but borates must be looked for in the insoluble residue of the Lawrence Smith alkali treatment and estimated by Schaak's method. Fluorides are estimated as described under cryolite, and phosphates by molybdate or uranium nitrate.

CHAPTER VII.

ENAMELS.

Enamels comprise (*a*) all glazes, whether opaque or translucent, on metal; (*b*) opaque glazes on pottery; (*c*) clear glazes separated from a pottery body by a non-transparent undercoat or engobe.

Enamelled brick dates from Babylonian times. Enamelled metal is not found before the Roman dominion of Egypt—it is probably of Indian origin. The opacity in early enamels is due to an excess of the colouring agent over what the flux will dissolve. Thus the black enamel of Egypt and Greece may be reproduced by firing equal parts of natural magnetite with a flux made from 55 parts of sand to 45 of soda ash. The undissolved iron oxide here renders the enamel opaque.

Artistic enamelling on metal and pottery was practised in England at Battersea in 1730, though a previous attempt to transplant it from Limoges had been made in the Middle Ages. The earliest known English patent for cast iron is that of Hickling in 1799.

Chemically, an enamel does not differ from a glaze, though the suspended material may slightly alter the coefficient of expansion and fusing point of the glazes. Enamelling pottery is therefore not appreciably different from glazing pottery, and it is performed in precisely the same way. But enamelling metal is rendered more difficult through the disparity in coefficient of expansion between metal and enamel; and also because the potter cools his ware slowly, while the enameller immediately exposes his to normal temperatures. Industrially, the most important metal for enamelling is iron, both cast and sheet. Cast iron is used for baths, steam-jacketed pans, and the like, and sheet iron for cooking utensils, advertisement signs, etc.

The best compositions for these are :—

——	Sheet Steel.	Cast Iron.
Sulphur	0.04 – 0.05	—
Phosphorus	0.03 – 0.09	1.0 – 1.8
Silicon	.01	2.0
Manganese	0.04 – 0.06	0.5 – 0.7
Carbon	0.10	3.5

But Grünwald gives the manganese for sheet metal as 0.23–0.35 per cent.

The metal, before enamelling, must be pickled or sand-blasted.

An enamel on metal must fuse between 850-1000° C. It must mature in a few minutes and be fluid enough to lie evenly. It must withstand sudden changes of temperatures, and fit the iron as nearly as possible. And according to its purpose, it must be more or less acid-proof.

In order to lower its melting point, it is made very rich in fluxes, and the ingredients are previously fritted. The coefficient of expansion must be raised as much as possible. Iron has the coefficient of cubical expansion $(3\alpha) \times 10^{-7}$ of 4.2, and copper is greater still. Pottery and glazes, on the other hand, are 2.0-3.0; so that the constituents of an enamel require judicious selection to fit a metal. Winkelmann and Schott's figures (1894), revised and extended by Mayer and Havas (1911), and confirmed practically by Wolf (1911), are as follows for the expansion of the various oxides in a glaze or enamel, as compared with the 4.2 of iron :—

Na_2O	10.0	PbO	4.2	ZnO_2	2.1
K_2O	8.5	TiO_2	4.1	SnO_2	2.0
NaF	7.4	Fe_2O_3	4.0	As_2O_5	2.0
Na_3AlF_6	7.0	Nio	4.0	Li_2O	2.0
Cr_2O_3	5.1	Sb_2O_5	3.6	P_2O_5	2.0
CaO	5.0	BaO	3.0	ZnO	1.8
Al_2O_3	5.0	CaF_2	2.5	SiO_2	0.8
CoO	4.4	MnO	2.2	MgO	0.1
AlF_3	4.4	CuO	2.2	B_2O_3	0.1

From these figures the expansion of a glaze which is suitable in other respects may be calculated.

It will be seen that very few of these oxides have coefficients greater than iron, and as a matter of fact it is impossible to produce a stable and practicable enamel that will have a coefficient as high as 4.2. Recourse is therefore had to the ground or undercoat, an unfused or only very partially fused body which acts as a compromise between metal and enamel. If the enamel has a coefficient 33 per cent. less than the metal, then the undercoat might be made only 20 per cent. less, the disparity being therefore diffused. German practice insists on the use of cobalt oxide or nickel oxide in the undercoat. In fact, Grünwald "safely asserts" that all recipes without them "may be regarded as humbug." Despite this, other nations are able to dispense with these oxides, although cobalt is useful by giving a blue tint which neutralises any yellowness in the cover enamel. Shaw gives the formula for undercoats as :—

$$\left.\begin{array}{ll} K_2O & 0.15\text{–}0.75 \\ Na_2O & 0.\ \text{–}0.6 \\ CaO & 0.14\text{–}0.64 \\ CoO & 0\ \ \text{–}0.06 \end{array}\right\} \quad Al_2O_3 \quad 0.1\text{–}0.5 \quad \left\{\begin{array}{ll} SiO_2 & 1.1\text{–}1.7 \\ B_2O_3 & 0.2\text{–}0.5 \end{array}\right.$$

The CaO here being probably introduced as fluoride. Randau gives a mixing for an undercoat as :—Flint 30, felspar 30, borax 25, fused together and ground with 10.75 of clay, 6 of spar, and 1.75 of magnesia. Several recipes have been published for cover and ground enamels containing lead, but lead enamels, especially for cooking utensils, should be prohibited. Considering that T. and C. Clark's patent for leadless enamel dates from 1839, there can be no hardship in this. A similar remark applies to those whose opacity is caused by arsenic.

We now return to the cover enamel, of which there may be as many coatings as desired. Shaw gives a formula to cover his previously mentioned undercoat as :—

$$\left.\begin{array}{ll} K_2O & 0\text{–}0.6 \\ Na_2O & 0\text{–}0.65 \\ CaO & 0.2\text{–}0.6 \end{array}\right\} \quad Al_2O_3 \quad 0\text{–}0.5 \quad \left\{\begin{array}{ll} SiO_2 & 1.0\text{–}1.8 \\ B_2O_3 & 0.2\text{–}\,? \end{array}\right.$$

Given another base present, it is not important whether potash or soda or both be used. The upper limit in B_2O_3 was not reached by Shaw with regard to appearance and workability, but it is obvious that the resistant qualities of the enamel to acids and juices would suffer by too high a content of B_2O_3. Grünwald gives the following mixings of two white enamels, the first being easily fusible :—

	1	2
Felspar	60kg.	46kg.
Borax	42	47
Soda	15	1.4
Saltpetre	2	—
Clay	—	4.5
Cryolite	—	16.2
Tin Oxide	12	—
Antimony Oxide	—	9.2

According to Randau, a cover enamel suitable for cooking utensils is made from : Flint 20, glass 20, borax 28, tin oxide 21, soda 2, saltpetre 10, magnesia 5, clay 2 ; add in grinding 1.8 per cent. of flint, 1.8 of magnesia, 1.0 of soda.

Riddle (1907) chooses an enamel for cast iron with the composition :—

$$\left.\begin{array}{ll} PbO + BaO & 0.4 \\ K_2O & 0.15 \\ CaO & 0.15 \\ ZnO & 0.05 \\ Na_2O & 0.25 \end{array}\right\} \quad 0.15\ Al_2O_3 \quad \left\{\begin{array}{ll} SiO_2 & 1.0 \\ B_2O_3 & 0.2 \\ SnO_2 & 0.2 \end{array}\right.$$

Enamelled metal tubes are often required for locomotive boilers, as the smooth surface allows the fur to be removed with ease, and also for carrying acid liquors in mines and works. Amtmann enamels iron pipes with the following formula :—

	Ground.	Cover.
Quartz	34	19
Borax	15	24
Soda	2	9
Felspar	—	34
Fluorspar	—	4
Saltpetre	—	3
Tin Oxide	—	16

Enamelling on metals other than iron need not detain us long. Copper or copper deposited on another metal is the chief, and it is applied only to artistic decoration. The scientific principles of getting a smooth-fitting surface are the same as in iron. Böttcher employs an enamel for copper consisting of : Felspar 48, unburned gypsum 48, borax 4. The amateur in artistic enamelling is best advised to buy powdered glass as his flux.

OPACIFIERS.

The chief opacifying agent is tin oxide, but the market price rules extremely high. Arsenic, antimony oxide, or sodium metantimonate are sometimes used as substitutes, with or without the addition of zinc oxide, and zirconia and titania have also been suggested. But the present price of zirconia is twice that of tin oxide, and it requires a content of 15 per cent. to produce the requisite opacity, so that its use is not likely to extend for many years to come.

Tin oxide may be rapidly tested for loss with nitric acid, and loss with hydrofluoric acid. In enamels on metal, which mature at 900° C., tin oxide is almost insoluble, not more than 0.01 equivalent going into solution. Opacity may be produced by the addition of 0.13–0.25 equivalent to the molecular formula, which means about 7–10 per cent. of the mixing. But more tin dissolves in higher fired glazes to form a silicate which is not opaque, and therefore pottery enamels in general require more opacifier than those of iron.

Lomax (1912) states that it is possible to make a transparent glaze containing as much as 15 per cent. tin oxide. To do this, the basic side must be chiefly soda, and the alumina equivalent should not be more than 1.5 times the bases. For opacity the converse is therefore true, that the alumina should exceed the bases by half an equivalent.

Antimony oxide should be tested for insoluble matter and for arsenic. Arsenic is separated from antimony either by potassium sulphide or silver nitrate, both of which dissolve the former. According to Landrum (1910), only arsenic comes down if sulphuretted hydrogen be passed through a strong hydrochloric acid solution packed in ice. The filtrate is then treated with a current of air to remove H_2S, 5 grammes of tartaric acid are added, the liquid is made up to 250c.c., and 25c.c. taken, neutralised with bicarbonate and titrated with starch and $\frac{N}{10}$ iodine. 1c.c = 0.006 grammes Sb.

ENGOBES.

There remains the production of enamelled brick, etc., by a clear glaze over a slip or engobe. These may be reproduced from :—

$$\begin{array}{llllll} \textit{Engobe} & K_2O & 0.1\text{–}0.16, & Al_2O_3\ 1.0, & SiO_2\ 4.0\text{–}4.8 \end{array}$$

$$\textit{Glaze}\quad \left.\begin{array}{ll} K_2O & 0.3 \\ CaO & 0.6 \\ ZnO & 0.1 \end{array}\right\} \quad Al_2O_3\ 0.4,\quad SiO_2\ 3.8$$

The engobe remains as an only partially fused material separating glaze from body and hiding the latter by reason of its immaturity. In composition it is very like the earthenware bodies of North Staffordshire. It is applied to the body by dipping in a similar manner to the glaze.

Let us suppose, now, that we are required to reproduce the glaze or enamel of the general molecular formula :—

$$\left.\begin{array}{ll} a & PbO \\ b & Na_2O \\ c & K_2O \\ d & CaO \\ e & ZnO \\ f & BaO \\ g & MgO \end{array}\right\} \qquad \begin{array}{ll} h & Al_2O_3 \\ k & B_2O_3 \end{array} \qquad \left\{\begin{array}{ll} l & SiO_2 \\ m & B_2O_3 \\ n & F_2 \end{array}\right.$$

although so many bases in one glaze would be unlikely. The first step would be to multiply each quantity by the molecular weight of the oxide in order to obtain the parts by weight, thus 223a of PbO, etc. If the raw materials were theoretically pure, this would be unnecessary, as the calculations could be made molecularly. Lead oxide would then be calculated into the bisilicate frit favoured by the Home Office, and the corresponding amount of silica would be accounted for. Then the potash would be calculated into felspar, and allowance made for the alumina and silica thereby introduced. Excess of potash over alumina would require nitre, and excess of alumina over potash, clay ; while excess of alumina over both potash and silica would have to be introduced as bauxite. B_2O_3 would go in as borax, excess of B_2O_3 over Na_2O as boric acid, and excess of Na_2O over B_2O_3 as soda ash, or soda spar if alumina be sufficient. B_2O_3 might also be introduced with CaO as colemanite, but CaO generally goes in as whiting or fluorspar, unless the P_2O_5 is sufficient to hold it as bone ash. Magnesia, zinc, and barium may be introduced as silicates or as oxides or carbonates. Any excess of silica over all the bases is added as flint. Fluoride may pair with CaO as fluorspar or with sodium and aluminium in cryolite.

CHAPTER VIII.

THE PRODUCTION OF COLOUR.

Owing to the high and protracted firing to which pottery is subjected, it is impossible to employ organic stains for the production of colour. We are, therefore, confined to the few metals which form coloured salts and to complex inorganic stains similar to ultramarine or the masses formed when zinc or aluminium salts are heated on charcoal with a cobalt solution. But though we lose in palette by the temperature of firing and the elimination of organic dyes, we gain considerably by the permanence of the ware thus produced. The process is very similar to the natural process by which minerals are coloured. The chemistry of glazes is not materially affected by the added stains, owing to their low content. As they are mostly bases, they will form silicates and will make the glaze slightly more fusible with greater tendency to craze. But a glaze must already have too great a tendency in any direction if the added stain deteriorates it. The metallic oxides include those of copper, cobalt, iron, manganese, chromium, nickel, uranium, antimony, titanium, selenium, iridium. The colour produced depends largely on the composition of the glaze and on the atmosphere of the kiln. Zinc and borates in a glaze are peculiarly liable to spoil colours, and lead also to a smaller extent. Perhaps soda is the best developer of colour, but a high content of soda is made at the expense of the durability of the glaze. A reducing or oxidising atmosphere influences the red or green of copper, the green or brown of iron, and the green or yellow of chromium.

The stains employed to produce specific colours are as follows :—

White :—Barium sulphate (permanent white), zinc oxide (Chinese white), tin oxide.

Blue :—Cobalt, Thenards' blue, smalt. Cerulean blue is a mixture of oxides of tin and cobalt.

Matt Blue :—Zinc-alumina-cobalt colours.

Turquoise :—Copper.

Green :—Copper, chrome, ferrous iron, Rinman's green, Guignet's green.

Yellow :—Antimony oxide, lead (Naples yellow) or potassium antimonite and antimonate, ferric oxide, uranium oxide, sodium uranate, selenium, silver and cadmium oxides, tungsten, molybdenum.

Cream :—Titania.

Violet :—Manganese oxide.

Brown :—Nickel, uranium, rutile, ferric oxide, manganese. Vandyke brown is bituminous peat-earth, and Cologne earth is the same calcined.

Pink :—Chrome-tin colours.

Red :— Iron-alumina, iron-chrome, iron-zinc colours, sodium- and tin-gold chlorides, purple of Cassius.

Black :—This may be obtained from 1 part of copper oxide to 1.07 of cobalt oxide and 1.64 of manganese dioxide, all very intimately mixed. Black is also obtained by reducing organic salts to carbon.

Orange :—This comes from mixtures of yellow and red. Similarly, a very large selection of colours may be produced by mixing the above stains in various proportions.

An artist's wheel is undoubtedly a useful aid in matching colours, but it has dangers when working with glazes. A glaze containing say 2 per cent. of copper may be green, and one might think that diluting the stain would produce a lighter green. But probably the result of 0.2 per cent. copper would be a light blue. Conversely, strengthening a blue might yield a green. There is also the fact that many of these complex artificial stains only act when present in a certain amount, otherwise they are decomposed by the glaze and do not form any colour. Thus a lime-tin red diluted would not yield a pink, it would simply give no colour at all; so that the colours produced in a glaze by any stain can only be used with safety to assist in matching other colours when the same amount of stain is kept in. It follows that the artist's wheel must be supplied with the tints caused by each stain in varying amounts, which might conveniently increase by 0.1 per cent. up to 4 or 5 per cent.

Stains do not, of course, all have the same colouring power, nor are they equally soluble in a glaze. The solubility is important, as an enamel, and not a more deeply tinted glaze, is formed by excess of stain. Ramsden gives the solubilities of the metallic oxides in glazes maturing at 1,000°-1,100° C. as: nickel oxide not more than 1, manganese oxide 1-4, chromium oxide, not more than 1, iron oxide 3-14, copper oxide 3-8 per cent. The particular stain to be used depends also on the temperature of fire. Thus copper turquoise is destroyed above 1,200°, the best temperature for it being 1,040°. Tin-gold reds and crimsons, also, cannot be used at the highest fire.

Colours may be produced in the glaze or overglaze or underglaze, and they may be developed by an oxidising or a reducing atmosphere. But it is obvious that the atmosphere could not greatly influence an underglaze colour. Overglaze effects, on the other hand, are generally intended to be sensitive to the air condition of the kiln. The rouge-flambe and sang-de-bœuf ware, for example, may be produced by reducing an overglaze containing copper; but more permanent colours are obtained, though with greater difficulty, when the copper is reduced in the main glaze. Generally, overglaze effects obtained by reduction which include all the lustre wares, are less permanent than others. As overglaze may be made exceedingly thin, it is possible to employ stains which would otherwise be too costly. The reduction effects of platinum, iridium, and similar metals are thereby produced. Both with overglaze and underglaze the stain is first mixed or fritted with a fusible glaze which may conveniently be $1.0\ PbO$-$0.5\ SiO_2$, $0.5\ B_2O_3$. There is obviously room for a great number of combinations of clear glaze over coloured glaze, one coloured glaze over another, glaze over enamel, or glaze over coloured body. Most of the artistic pottery in existence falls into one or other of these classes. Thus faience is a coloured body covered with a clear glaze, majolica a coloured body concealed by an opaque enamel or coloured glaze. But the chemistry of the processes is much the same in all.

The most difficult colours to obtain in pottery are the pinks and reds. No metallic oxides by themselves will give either colour; ferric oxide, which comes nearest to red, has always a shade of brown or yellow in its effects. At Sevres they obtain a coral red by firing 28 parts of lead chromate with 75 of a flux made of 85 of minium and 15 of flint. Otsuki gives the following analysis of a blood-red Chinese glaze :—

SiO_2 59.6, SnO 0.32, CuO 1.2, PbO 8.2, Fe_2O_3 1.4, Al_2O_3 8.4, CaO 11.1, MgO 1.7, K_2O 2.74, Na_2O 5.27, MnO trace.

To produce purple, carmine, and pink, gold is used at low temperatures. Stannic ammonium chloride (pink salt) is added to dilute gold chloride solution to obtain a purple, and this may be rendered deeper in colour by adding stannous chloride. Gold-purple was formerly supposed to have the formula SnO_2, 2 Au, but modern thought regards it as a mixture of colloidal gold and colloidal stannic acid in different proportions. For these colours Heubach suggested a flux composed of: PbO 0.65-0.8, Na_2O 0.2-0.25, K_2O 0-0.12, SiO_2 0.5-1.0, B_2O_3 0.4-0.5. To prevent the colours turning violet a small percentage of silver carbonate or chloride is added. The ware is fired in an oxidising atmosphere at 800° C. For higher fire chromium-tin stains are used either in glaze or underglaze. Heubach gives the following formulæ for the stains themselves :—

	Dark Red.	Pink.	Lilac.
K_2O	0.0047	0.013	0.45
CaO	0.9768	0.987	—
PbO	0.0184	—	—
Cr_2O_3	0.011	0.013	0.45
SiO_2	1.11	2.26	—
SnO_2	1.12	1.31	14.28
B_2O_3	0.005	—	1.10
Na_2O	—	—	0.55

Chrome red can exist only in basic glazes and fluxes, assuming here that boric anhydride is not an acid. The basicity should be as great as possible and produced chiefly by means of lead oxide. Firing should be short and cooling rapid.

Red colours fired higher than cone 9 are obtained from chromium-aluminium compounds. The stains should be prepared at a higher temperature than the ware will be fired at. A violet-red fired at cone 14 is produced from 1.0 K_2O, 16.53 Al_2O_3, 1.0 Cr_2O_3, 3.27 B_2O_3, and an underglaze salmon from 0.046 K_2O, 0.658 MgO, 0.296 ZnO, 0.722 Al_2O_3, 0.046 Cr_2O_3, 0.08 B_2O_3.

Lethbridge states that the presence of zinc chromate makes chrome-tin-lime pinks more brilliant. He gives the formula SnO_2 72, Cr_2O_3 1.0, CaO 26, for a pink. The lime lowers the temperature of development. Purdy uses the general formula for chrome-tin pink and red glazes :—

$$\left.\begin{array}{ll} \mathrm{PbO} & 0.22 \\ \mathrm{CaO} & 0.59 \\ \mathrm{KNaO} & 0.19 \end{array}\right\} \quad \begin{array}{ll} 0.16 & \mathrm{Al_2O_3} \\ x & \mathrm{SnO_2} \\ y & \mathrm{Cr_2O_3} \end{array} \quad \left\{\begin{array}{ll} 2.1 & \mathrm{SiO_2} \\ 0.47 & \mathrm{B_2O_3} \end{array}\right.$$

Of colours other than red, little need be said. The composition of the glaze is of course important. Chrome greens are spoiled by zinc, probably through formation of chromate. Copper greens are easily obtained. Silica and borates may be present to any extent in the glaze, but more than 0.25 equivalent of alumina gives a yellow cast to the copper green. Barium favours copper blue, and soda is essential to torquoise. But barium spoils brown, which is best developed by rutile, with potash and magnesia or lime as bases.

Uranium is often used as a stain because antimony compounds are uncertain with regard to reduction by the fire-gases. But although 0.006 equivalent of U_3O_8 gives a strong colour, its high molecular weight makes it a weak stain, and the price per pound makes it an expensive one. The colour of uranium in glazes depends chiefly on the lead content of the glaze. Presence of lead induces orange, and absence, lemon. The " yellow uranium " of commerce is not uranium oxide, but sodium uranate. Owing to the peculiarity of uranium salts in re-dissolving in an excess of sodium carbonate, the commercial uranate is generally free from heavy metals, and samples from bulk need only be tested for sodium carbonate, the sodium uranate being taken by difference. The amount would probably be 90-95 per cent.

Nickel oxide is not used extensively, because the presence of lead and of borates is detrimental to its regular coloration ; it shades from brown to green. But it may be serviceable in alkaline glazes free from borate.

Manganese is generally purchased as the expensive dioxide in order to ensure a standard of purity regarding other chromogenic oxides. For claret colours it must be free from iron, but where brown tints are desired it may be introduced as umber, which contains 16-20 per cent. manganous oxide and 30-38 per cent. ferric oxide, but also quantities of gypsum. Sulphates should always be avoided in pottery as much as possible, as they cause bubbling in the kiln unless fired in a reducing atmosphere.

There are many preparations of iron ochre (Venetian red, Mars red, Indian red, Sienna, etc.) on the market, of various bright colours. These are prepared by precipitating iron from its liquors with lime and roasting the precipitate. The colour of the roast depends on the proportion of lime to iron, but its effect in a glaze is precisely what the equivalent amount of iron would achieve, and the presence of sulphate renders its use dangerous.

In spite of the extra initial expense it is generally safest to buy all stains in the purest commercial condition, even where two stains are going to be mixed together.

Owing to the powerful colouring action and to the high price of many of these stains their analysis is of importance, especially with regard to the presence of other colouring oxides. Thus cobalt should be tested for nickel, and vice versa. But as they pertain to ordinary inorganic chemistry the methods of analysis need not be enlarged on here.

CHAPTER IX.

FIRING OF THE WARE.

The proper supervision of the burning of the ware is an important item in an efficient and economical factory. Weight for weight, the proportion of fuel to pottery burnt in a kiln is from 25 to 70 per cent., according to the nature of the ware. And a kiln requires fuel of certain value, chiefly with regard to high volatile matter and calorific power. A fuel of low volatile content does not furnish a flame sufficiently long to penetrate through all the kiln, and much of the ware is accordingly under-fired. But with the best intentions, there is probably no process of manufacture which wastes so much fuel as pottery burning. The contents of the kiln are often so valuable—representing hundreds, and perhaps thousands of pounds—that it is false economy to risk deterioration of ware from first to second quality in order to reduce the fuel bill. The chemist must therefore steer a middle course between undue prodigality and economy in fuel. Much is to be hoped of gas-fired regenerative kilns, but these are still a long way from superseding the older type of potters' kiln. A continuous kiln might only burn $5\frac{1}{2}$ tons of fuel to the 10 in an up-draught and the $6\frac{3}{4}$ of a down-draught kiln, and there is a saving in sagger loss of 50 to 80 per cent., but the wear and tear of a continuous kiln, especially where the gas impinges on the brickwork, is enormous. The most prominent gas-fired kilns for ceramic purposes are the Hoffman, Buehrer, Mendheim, Ehrenwerth, Venier, Steinmann, Lehse, and Czerny-Deidesheimer. For details the reader should refer to special works on the subject; but they all follow the general principles of producer gas furnaces. Most ceramic kilns of this sort are built on the recuperative and not the regenerative principle. Regeneration consists of heating brickwork flues by passing hot exit gases through them, and subsequently passing the combustion air through the same passages so that the brickwork can communicate its heat. In recuperation the hot exit gases pass outside pipes, through which the combustion air flows, preferably in the opposite direction.

Whatever type of kiln be used, three properties are requisite: (*a*) To obtain the temperature required in a proper interval of time and to hold it at pleasure; (*b*) to control the temperature throughout the kiln by being able to advance or steady the heat in its different parts; (*c*) to control at will the chemical character of the flame, whether oxidising, reducing, or neutral. A kiln fired by coal should be constructed on the down-draught principle—that is, the flame should be made to travel up and then down the kiln after striking the crown, so that heat is conserved which would escape in the exit gases in an up-draught kiln. In an up-draught kiln there is probably an excess of air of 50 to 100 per cent.; in a down-draught only 30 to 50 per cent. But in china biscuit ovens an excess of 50 per cent. is said to be necessary in order to avoid discoloration of the ware—an example of the quality of the ware being more important than economy in fuel. Bleininger and Seligmann give the following figures for the distribution of heat in a down-draught kiln for firing bricks:—

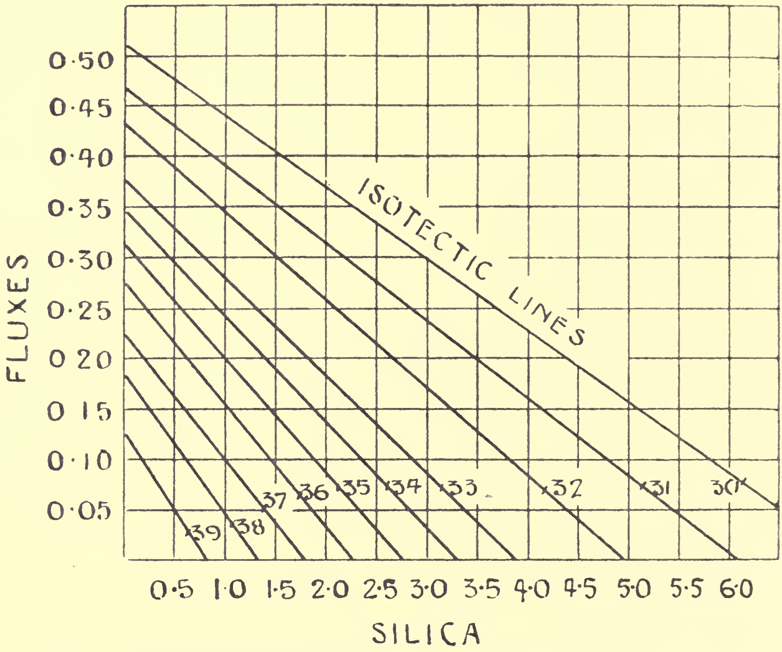
	B. Per Cent.	S. Per Cent.
Theoretical heat required to burn the bricks	19.6	25
Heat lost by unburnt carbon in ash	3.5	1
Heat lost by exit gases	27.3	59
Heat stored by kiln and ware and recovered for drying purposes, through suitable plant	28.1	
Heat lost by radiation and left in kiln and ware unused	21.5	15

In muffle kilns, for artistic ware, the theoretical heat is a still smaller percentage of the actual heat used up, as the gear absorbs much that would be utilised in burning bricks or pipes. We may say that burning the crudest pottery costs at least three shillings a ton of finished ware, and that this figure may increase to pounds for the most delicate art ware. An important point is to utilise every possible space in the kiln. Empty spaces often amount to 50 per cent. of the total content of the kiln. Another point in economy is that the kiln should be built on well-drained ground, preferably with a cement foundation. The capillary movement of moisture from wet ground through porous bricks may cause very serious loss.

Burning the ware is the chemical operation to which pottery is subjected in order to achieve its final character of permanence and rigidity in the body and of vitrification of the glaze with the development of colour. The temperature range in which chemical and physical changes may proceed in a clay body extends from atmospheric temperature to 1,850° C., at which point the most refractory clays are affected. At ordinary temperatures we have colloidal action, at 200° the changes induced by the so-called pre-heating treatment, at 440° to 500° dehydration has almost ceased, and plasticity is lost beyond recovery. According to Witt and Knote, $Al_2O_3 . 2SiO_2 . 2H_2O$ decomposes on dehydration into water, and the silicates $Al_2O_3 . SiO_2$ and $Al_2O_3 . 3SiO_2$ or some higher silicate, and not into the monosilicate and free silica as formerly supposed. Mellor states, however, that the endothermal change shown at 500° corresponds with the decomposition of kaolinite into free silica, free alumina and water. Proceeding to higher temperatures the density decreases, but suddenly increases at 950°, where an exothermic reaction obtains. Thence changes occur in clay bodies which are much the same in all, but take place at different temperatures according to the refractoriness of the body. But under sufficiently severe heat every body assumes a crystalline structure similar to the sillimanite in porcelain. At still higher temperatures vitrification proceeds to a finish, accompanied by an increase in specific volume.

The melting point of a body or glaze depends chiefly on its chemical composition and on its physical subdivision. Many formulæ have been advanced purporting to give the fusibility or its opposite, refractoriness, of a body from the chemical composition. Bischof, Richter, Seger, Kocks and Seyfert, Ludwig, Simonis, have all attempted to establish such relations. Three classes may be formed for purposes of calculation: (*a*) Firebricks and other refractory bodies which should not soften below cone 30; (*b*) ordinary pottery bodies which should attain a close texture between 1,100° to 1,400° C.; (*c*) glazes whose melting point is required to obtain the proper firing temperature, which should be three cones above the melting point.

The best theoretical method for calculating the refractoriness of a fire-brick or similar body is that of Ludwig, who has constructed a chart for the purpose. The composition is first expressed as the molecular formula: $a\ R_2O,\ 1.0\ Al_2O_3,\ b\ SiO_2$. The silica is plotted on the abscissa, the fluxes on the ordinate. Ludwig found that clays of equal fusing point occupy "isotectic" lines. By putting the Seger cones whose compositions are known into the chart, the fusing point of any refractory clay body may be found. The numbers on the isotectic lines on the chart here given are those of the corresponding Seger cones.



LUDWIG'S REFRACTORINESS CHART.

The second class, pottery bodies, may be studied by the formulæ of Simonis (1908), which applies to bodies containing not more than 10 per cent. of alkalies, and therefore also to the refractory class above. Simonis works from the proximate analysis, and obtains a refractory index *p* which corresponds with certain Seger cones. When k (kaolin) $> \frac{1}{3}$ q (quartz), $\rho = k - \frac{1}{3} - f$ (felspar) $+ 60$. When $k < \frac{1}{3} q$, $\rho = \frac{2}{3} q - k - f + 60$.

The melting point is then found from this table :—

....	17.5	22.6	28	33.7	39.2	44.6	50	57.6	65	72	80	89	102	114	127
Cone	14	15	16	17	18	19	20	26	27	28	29	30	31	32	33

In the third class, Barrett (1909) has advanced a method for calculating the melting point of a glaze. According to him, one equivalent of CaO is equal in fluxing value to $\frac{1}{6}$ equivalent of Na_2O and K_2O, $\frac{1}{2}$ equivalent of ZnO, and 1.0 of BaO. He therefore calculates all bases into their fluxing equivalent of CaO, and brings the alumina to units. It is then found that the glaze 10 SiO_2, 1 Al_2O_3, $6\frac{3}{7}$ RO melts at 1,200°, and that 1 equivalent SiO_2, neutralises $\frac{2}{7}$ RO in point of fusibility, so that 9 SiO_2, 1 Al_2O_3, $6\frac{1}{7}$ R_2O would also melt at 1,200° C. Also, by deducting $\frac{1}{7}$ equivalent of RO, the melting point is raised 5°, so that 10 SiO_2, 1 Al_2O_3 6 RO would melt at 1,215°.

Such are three methods for calculating melting point, but they must be regarded as only approximations to the truth, and they require that other conditions shall be equal.

PYROMETRY.

Undoubtedly the most convenient pyrometer for kilns is the Seger cone. Heintz suggested in 1886 that glass mixtures of varying fusibility would make better pyrometers than the alloys made by Prinsep in 1828. Seger took the matter up and made a series of cones which, revised, serve all practical purposes. Seger instituted cones 1 to 35, of which 4 to 35 consisted of clay, quartz and spar or whiting, while in 1 to 3 iron oxide was used as flux. Then Cramer prepared the more fusible series 01 to 010 by adding boric acid, and Hecht extended them down to 022 with the aid of lead oxide. These cones, as left by Seger, were subject to two serious inaccuracies: cones of the same number did not always go down together, and the gradations in temperature between consecutive numbers was not uniform. However, Simonis calibrated them in 1908, and the official Berlin cones may now be regarded as fairly reliable. But those containing iron oxide are dubious in action if heated quickly or in a reducing atmosphere. Cone 1 melts at 1,150° C., 2 at 1,170°, and so on by intervals of 20° up to 36 (1,850° C.). Then the downward series goes from 0.01 to 010 (1,130° to 950°), and thence by gradations of 30° to 022 (590°).

Cones should be placed in various parts of the kiln, protected from direct contact with the flame and from draught from the eyehole. They are often stuck in wads of wet clay, but should be gummed on to pieces of burnt tile to avoid the shrinkage of the clay sagging them over.

The chief weakness of cones is that they afford no indication of the temperature till the lowest bends over. But the capability of holding a kiln at low temperatures on the upward fire is sometimes most essential, and for this a thermo-electric pyrometer is perhaps the most useful indicator. Though far from perfect—its reading may be altered 100° C. by external currents, such as those generated by rubbing the case—it may be carried to any part of the kiln and gives the temperature in a few moments.

FIREBRICKS.—The kiln must be built, of course, of refractory bricks, which should be able to withstand cone 31 without shrinkage or vitrification. Sand decreases drying and firing shrinkage, especially the latter, but increases porosity. A silica content of 55 to 70 per cent. is the best for making good refractory bricks, the alkalies and iron being as low as possible. Titania is best absent, as it acts as a flux under these conditions. Ries notes that the fusibility of a firebrick could be reduced 5 cones by grinding the raw materials to pass a 100 sieve.

CHAPTER X.

LOSS IN MANUFACTURE.

Loss in manufacture may occur at any stage from cracking during drying of the thrown or moulded clay to delayed crazing or peeling months after the ware is drawn from the kiln. The different kinds of loss are: Cracking, stunting, and blowing on bodies whether glazed or unglazed; efflorescence on unglazed bodies; peeling or shivering; and crazing, creeping, bubbling, pinholing, blistering, shelling, spit-out, spotting, running, and bare or dull surface of glaze. Some of these glaze defects may be cured by re-firing, which, however, adds to the cost of manufacture without ensuring the prevention of further loss.

Crazing and Peeling depend on the difference of coefficient of expansion between body and glaze.* If the coefficient of the body be greater than that of the glaze, the body will contract on cooling more than the glaze, with the consequence that the glaze "peels" off. On the other hand, when the glaze has the greater coefficient, it crazes—*i.e.*, it is covered with a network of cracks. The proper treatment of unequal coefficient depends on how the glaze stands with regard to fusibility. The following table sums up the remedies, changes being made in the glaze unless otherwise stated.

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* Although one uses the ordinary phrase, coefficient of *expansion*, it would be more correct in this case to say co-efficient of *contraction*, as it is in the contraction of the ware during the cooling down of the kiln (and subsequently) that the defect arises. What happened during the up-fire, before the glaze was properly matured, does not concern the matter.

	Glaze too fusible.	Not fusible enough.	Right.
Crazed	Add flint, or substitute PbO or BaO for CaO or Na_2O.	Add spar, [or substitute B_2O_3 for SiO_2.†]	Replace clay by flint and spar or alkaline earth bases by ZnO or add flint to body.
Peeled	(Not likely to occur.) Replace spar by clay [or B_2O_3 by SiO_2.†]	Substitute flint for clay or CaO or Na_2O for PbO or BaO.	Add clay or reduce spar or alter body by reducing, or using coarser grain of silica.
Right	Substitute spar with clay and flint.	Add spar or reduce clay.	—

Loss through unequal coefficients may not occur immediately. Glazes have some elasticity, and this may delay any slight tendency to craze or peel till after the ware has been sold to customers. But sooner or later the glaze will tire and the defect appear. Probably no glaze and body can be exactly fitted to each other, which accounts for the invariable crazing or peeling on all old pottery. Reproductions of such ware as Persian are deliberately crazed, but it is doubtful whether the original in coming from the kiln was not as free from defect as our modern pottery.

Crazing can be lessened by a second fire; the glaze takes up silica from the body. Peeling, on the other hand, is induced by return to kiln.

Bubbling, blowing, pinholing, blistering, and spitting all arise from the evolution of gas either from body, engobe, or glaze in one or other of the fires to which the ware is

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† The substitution of B_2O_3 for SiO_2, or *vice-versâ*, is Seger's suggestion, but many ceramists of to-day dispute the accuracy of the statement.

subjected. Blowholes or blisters in the body are due to steam or carbon dioxide or oxides of sulphur. If the gas does not escape through the body, but through the glaze, the difficulty will lie in assigning the real cause of the trouble to body, or engobe, or to immature glaze. The danger of gas from the glaze can be minimised by previously fritting all the raw materials which give off volatile constituents. Pinholing is due to bubbles bursting without the glaze being sufficiently fluid to flow over the place. The other terms are loosely used, there being no general agreement as to their meaning except over small areas. Blistering is merely a pronounced form of bubbling, which applies to the unburst excrescences. Spitting, or spit-out, in so far as it differs from general bubbling, is confined to the evolution of gas during the enamel fire of china, or of any glaze that is to be fired twice. The glaze on its first fire has not been completely matured, and the bubbles imprisoned in it escape during the subsequent fire.

Efflorescence on an unglazed surface is due to soluble salts, probably chlorides and sulphates, drying out in the fire. The chlorides cannot be prevented, but will wash off fairly easily. Calcium sulphate, however, is difficult to remove without the use of acid. The sulphate scum can be prevented by adding a barium salt to the body mixing. The insoluble barium sulphate cannot dry out. An insoluble chloride is of course not commercially feasible.

Efflorescence on a glazed surface means the decomposition of the glaze. Increase of alumina content is the probable remedy.

Shelling is sometimes mistaken for peeling, but the term should be applied to the faulty adhesion of the glaze through a dirty or greasy surface of the body, or through the use of too infusible a glaze. The glaze thereby strips off in pieces.

Creeping, or crawling, unless due to a greasy body, occurs most frequently in immature matt glazes, or in glazes composed almost entirely of frits. The glaze has never been sufficiently fluid to form an even surface after slight separations of the glaze powder have been caused by the expulsion of moisture from the body and glaze. The adhesion of a frit may be increased by adding 2 or 3 per cent. of china clay in the grinding. Matt glazes may be cured of creeping tendencies by the addition of a little gum to the slop, or by a suitable composition of the glaze. Dolomite is alleged to be useful as a raw material in this respect.

Running of glaze over its proper limits on vertical surfaces is caused by excessive fusibility or fluidity of the glaze.

Stunting, or dunting, of the body may be due to rapid cooling of the kiln, but is most liable in bodies nearly vitrified. In more open bodies those having a high flint content tend most in this direction, the reason being the curious curve of flint in thermal expansion and contraction. Generally, non-plastic ingredients tend more to stunting than plastic ones.

Cracking during drying is caused by uneven thickness of the ware or by irregular drying.

Dipping is another cause of loss before going into kiln. It may be the fault of the dipper or of the glaze. " Ropey " glazes are too viscous, and do not throw excess glaze off the biscuit after dipping. Mayer states that this can be remedied by the addition of 0.4 – 0.8 per cent. magnesium sulphate to the slop.

Crooked Ware results from uneven temperature in the kiln, or from excess of magnesia, lime or soda in body; also from uneven support of the ware in kiln.

Stuck Ware also results from bad placing in kiln.

Sulphur, whether in the coal, or as pyrites, or sulphate in the body, or as sulphates in the glaze, must be avoided as much as possible, especially in the glaze. The sulphur oxides are not driven off till a high temperature has been reached, with the almost inevitable consequence of bubbling or pinholing. A reducing fire helps to cure this fault, as sulphur dioxide more easily escapes than the trioxide. The Berlin porcelain works formerly introduced their calcium as gypsum with some success, owing to the reducing fire employed.

The best way to avoid body losses is by a slow and regular burning of the kiln, especially on the up-fire, with regard to evolution of gas, and on the down fire for loss by thermal contraction.

CHAPTER XI.

INDUSTRIAL DISEASE.

Allied to the expense caused by loss in manufacture is that arising out of industrial disease. Potters are peculiarly liable to two forms of disease, lead poisoning and lung troubles, caused through the inhalation of dust and flint, clay and other raw materials. Of these, lead poisoning is the more notorious, but its prevalence not nearly so great. Taking the actual number of excess deaths of potters over other artisans in North Staffordshire, between thirty and forty die annually from lung diseases to one from plumbism; and, taking the rate per 1,000 exposed to risk, the former are eight times more fatal than the latter. Obviously, the only cure for lung disease is the prevention of dust by installation of exhaust fans and provision of respirators to workpeople.

The elimination of plumbism is more difficult. Lead silicates have a higher refractive index than the silicates of other metals, the appearance of lead glazes being thereby enhanced. The compulsory adoption of leadless ware would therefore entail the loss of the highest-class trade against competitors who were not so handicapped. A compromise has been suggested in the introduction of lead into glazes as insoluble bisilicate. Experience has shown that this eliminates plumbism, but many potters still maintain that the use of "fritted" lead does not conduce to a high standard of appearance. They prefer to use "raw" lead in the form of red or white lead, and to pay compensation to their workers when plumbism occurs.

The history of the movement against lead poisoning is quite modern, and is concerned as much with white lead and paints as with pottery. But we must confine ourselves here to consideration of the last.

In 1891 Oliver's Goulstonian lectures, subsequently published in book form, dealt with the subject as studied by him at Newcastle, a centre of white lead manufacture. Seven years later Thorpe and Oliver, appointed by the Home Office, recommended the compulsory adoption of fritted lead glazes having a solubility of less than 2 per cent. in acid representing the strength of the gastric juice. The potters found themselves unable to accept this standard, and offered instead a 5 per cent. standard for white and lightly coloured glazes. The offer was refused and withdrawn, and in 1901 the question was submitted to the arbitration of Lord James of Hereford. His award rendered it optional for manufacturers to accept the 5 per cent. standard, but those who did were exempted from compensation in case of plumbism.

The Workmen's Compensation Act of 1907 destroyed this privilege—which was insubstantial, because plumbism does not occur with low solubility—but the recent Home Office Commission (1908-11) could not find sufficient support to insist on low-solubility glazes because the majority of potters alleged that fritted lead does not conduce to the highest class of ware.

The problem is one of practical ways and means, the chemistry of the subject being fairly simple. Lead is used in glazes because lead silicates have a higher refractive index and more lustre than other silicates, besides being better suited to pottery treatment in regard to fusibility, resistance to fire and so on. Glazes containing lead can be rendered almost insoluble in the gastric juice by introducing the lead as an artificial silicate. The most practicable frit is the bisilicate $PbO . 2SiO_2$, no frit more basic than this being resistant to acid. Other compounds may be introduced into the frit, but, with the exception of alumina, these tend to lessen its stability in acid. Alumina is a useful component when polysilicates are fritted as it reduces the melting point, any pure lead silicate above $PbO . 2.5 SiO_2$ being difficult of formation and tending to a suspension of silica in the bisilicate.

The official Home Office test for solubility is to agitate 1gram. of the dried glaze material with 1 litre of 0.25 per cent. HCl* for one hour at ordinary temperature. The liquid is allowed to stand for an hour and then filtered. The filtrate is evaporated to convenient bulk, and the lead in it estimated, preferably by precipitation with H_2S, solution by HNO_3, evaporation with 1 – 2c.c. H_2SO_4† and weighing as $PbSO_4$, which is calculated to PbO and must not exceed 5 per cent. for classification as a low-solubility glaze.

Thomason (1910) studied this test with a view to ascertaining how far it accords with the conditions in the human system, where also lactic and acetic acids, enzymes, food of all kinds, and a higher temperature may increase or diminish the solubility of lead. He found that the small amounts of other acids present in the gastric juice are unimportant and that in this respect the official use of hydrochloric acid is sound. The rise to body temperature increases solubility in the ratio of 5 : 3, but pepsin retards the solubility of lead in acid, the proportion being 9 : 10, and if albumin be also present, as 8 : 10. Other food substances, such as bread and milk, also retard solubility slightly in presence of pepsin. It follows, therefore, as these experiments were done at body temperature, that the official procedure is as good an indicator of the solubility of a frit in the stomach as can be obtained in a laboratory. The change from the stomach to the upper bowel is, chemically, that from an acid to an alkaline solution with a change of enzyme. Under these conditions, with pancreatin, food and an alkaline solution of sodium carbonate, practically no lead absorption takes place, and it follows that the poisoning effect of lead glazes is confined to the stomach. The presence of carbon dioxide slightly lessens the solubility of lead.

Thomason then proceeded, as raw lead glazes differ from those made with fritted lead in that the whole of their lead content is soluble in excess of acid, to examine the influence of gastric juice, enzymes and food on the solubility of white lead in acid. No appreciable retardation in solu-

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* The official German and Dutch solvent is acetic acid.

† The Dutch precipitate as chromate.

bility is observed in presence of pepsin alone, but when foodstuffs are present the effect varies with the proportion of acid, food and lead present. The percentage solubility of white lead in the stomach varies with the acidity and inversely as the amount of lead and of proteid food present.

It must be remembered that under industrial conditions the amount of lead absorbed in the system is not more than 3mgms. a day, so that the acid of the stomach is always in excess, a condition which promotes the absorption of lead by the system. This may be checked to some extent by the continual presence in the stomach of foodstuffs, of which the most effective are those high in protein, such as beef and mutton.

CHAPTER XII.

TESTING OF FINISHED WARE.

Decorative pottery that is intended for no other purpose requires no test except that the glaze should be stable and the colours permanent. But all pottery intended for useful purposes has to meet specifications of various sorts. Unfortunately, there are at present no standard specifications. Consequently the manufacturer is harassed by varying requirements of quite minor importance in every order he has to fulfil.

Most pottery that is not of a purely ornamental character is made for building or sanitary purposes. It must meet requirements with regard to absorption and crushing strength. If glazed, the glaze must be adhesive, resistant to the corrosion of smoky towns and to chance blows, and must not be of a rough surface that will hold dirt. The ware must be free from efflorescence, and must withstand extremes of temperature in winter and summer.

Absorption is best tested by boiling a previously dried piece in water for an hour and calculating the percentage gain in weight. A variant of this test, not so good, is to soak the weighed piece for one or more days in cold water. The boiling test gives the whole absorption in a very short time, and also eliminates errors caused by surface tension.

Langenbeck states that in testing absorption a corner of the piece should be left unimmersed so as not to seal the pores but to leave a means for the air to escape. It is doubtful whether this makes any difference.

Crushing strength.—A piece of certain length is supported at the two ends, and weights are applied to the middle till the piece ruptures.

Freezing test.—This refers to the adhesion of the glaze under the strain of water in the body expanding to ice just under the glaze.

It is not generally practicable in laboratories to have a freezing chamber, and crystallisation is therefore resorted to. The ware is dipped, glaze first, to the extent of an inch in a saturated solution of some highly crystallising substance, such as aluminium sulphate, ammonium nitrate, copper nitrate, or sodium dichromate.

Corrosive tests.—The resistance of glaze to a liquid is best studied by applying the liquid to the surface with a brush or, in the case of vessels, by boiling the liquid in them. Resistance to vapour is tested by placing the ware in a bell-jar filled with the vapour. A crucible filled with strong hydrochloric acid placed in a bell-jar will soon detect instability in a glaze. If the glaze is untouched after half a week of such treatment it will stand the atmosphere of any town.

Percussion.—Shots of known weight are dropped on to the surface of the ware from different heights. Enamels on sheet iron that are to be used for automobile tags are liable to percussion from flying stones, and this test should be especially applied to them and to advertisement signs made of enamelled metal.

Surface tests of the glaze are made by rubbing lamp-black on to it, or by soaking the body in a coloured liquid, such as red ink. Holes or crevices are immediately detected by the retention of the dirt, or the stain of the liquid creeping up from under the glaze.

Soluble salts, which are a measure of the liability to efflorescence, are found by crushing a weighed piece of the ware, boiling in distilled water, filtering, evaporating to dryness, and weighing the residue. If it be not desirable to crush a piece, a minimum figure can be obtained by allowing distilled water to percolate through the whole brick, or whatever ware it is, placed in a basin.

Change of temperature, apart from freezing action, is not sufficiently marked to produce much influence on building ware. But enamels on iron, especially in cooking vessels, must be prepared for extremes of temperature. To test their reliability, they are heated to dull redness and plunged into cold water. They should withstand such treatment at least twice.

Solubility of lead or other poisonous salts must be tested for, especially in cooking ware. In fact, such ware should be compulsorily free from such ingredients. The ware should be boiled in acetic or hydrochloric acids to test lead solubility. For the attack on other ingredients, a 1 per cent. solution of sulphuric acid boiled in the vessel for fifteen minutes is sufficient. Shaw suggests (1910) that the loss in weight per square inch of enamelled surface should not be more than 0.008grams. under the treatment.

CHAPTER XIII.

CLASSIFICATION OF POTTERY.

Before finishing this book a word should be said on the classification of pottery. Brogniart's scheme is the most widely known, but neither that nor any other yet propounded can be said to be satisfactory.

Brogniart divides pottery into three main classes :—

I.—Bodies fusible at porcelain heat but burned soft enough to be scratched by a knife.

II.—Bodies hard, non-transparent, that cannot be scratched by a knife.

III.—Bodies hard, translucent, high in alkali.

Each of these classes is sub-divided, but roughly. The first class consists of bricks, pipes, tiles, ancient pottery, and the cheaper forms of common pottery; the second comprises good earthenware and stoneware; and the third, the various porcelains.

The scheme has obvious drawbacks. A softly-burned cup or dish would go into Class I.; another of precisely the same make burned in a different part of the same kiln might go into Class II. By making it sufficiently thin the same body might gain an entrance into the third class.

In Germany, Knapp divides pottery into two classes, dense and porous. The first includes china and stoneware; the second, earthenware, or bricks, tiles, etc. Kerl divides this second class into (*a*) bricks, tiles, terracotta; (*b*) refractory ware; (*c*) art ware; (*d*) common pottery; (*e*) earthenware; (*f*) faience; (*g*) pipes.

To the mind of the present writer the most sensible classification is the most obvious, that some bodies are unglazed, some glazed in various ways, some consist entirely of glaze—*i.e.*, glass,—also that bodies can be grouped into three main divisions according to their absorption. One would then get a table which could be filled in *ad lib.*

	Absorption 0 to 0.5 per cent.	Absorption 0.5 to 10.0 per cent.	Absorption over 10 per cent.
I.—All glaze	Glass		
II.—All body	Fused silica	Terracotta bricks	Filter candles, roofing tiles, etc.
III.—Body and glaze			
(*a*) Clear glaze	Porcelain Chemical stoneware	Stoneware Bristol Salt-glazed pipes	
(*b*) Crystalline glaze		Parian Carrara	
(*c*) Clear over engobe		Persian white glazed ware	
(*d*) Enamel	Enamelled metal	Majolica proper	
(*e*) Reduced glaze over glaze		Lustres	

The table can be extended indefinitely to include all the variations of glaze over glaze or glaze over coloured body, etc., which were pointed out in Chapter VIII. (page 61)

CHAPTER XIV.

RESEARCH.

The chief problems in ceramics on which research is needed trench on the sciences of geology, chemistry, and physics. The origin of clay from rocks other than felspathic, the exact composition of such clays, the presence of combined water, the cause of plasticity, the influence of subdivision and of the presence of small quantities of impurities, the proximate analysis of clay, the physical chemistry of fusing silicates—all these should be elucidated quite apart from the technical difficulties of manufacture. The latter are vital from the commercial point of view, and as the future of English pottery is concerned with the highest class of ware, the following statistics—for which I am indebted to the courtesy of Professor Orton, the Secretary of the American Ceramic Society—of ceramic endowment in the United States are worthy of attention :—

Place	Equipment. £	Annual Maintenance. £
Ohio State University	9,500	1,700
Illinois University	6,300	1,700
New York State School of Ceramics	5,250	700
New Jersey State University	3,150	1,100
Iowa State College	3,000	?
U.S. Government Research Laboratory, Pittsburg	2,000 +	2,300

Other States, North Dakota in particular, are also founding courses in Ceramics. We must bear in mind that these are recognised courses of training, including chemistry, physics, and engineering, and leading to University degrees. The British Government is loth to endow scientific research, and little can be hoped in that direction, but the Universities should lose no time in taking up the study of Ceramics as an applied science.

CHAPTER XV.

BIBLIOGRAPHY IN ENGLISH.

Mr. Solon has published a bibliography of books dealing with Ceramics, and Vice-president Branner, of Stanford University, one of articles on Ceramics, both to be recommended. The chief books and journals are these :—

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2. Langenbeck, Chemistry of Pottery (1895).
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4. Hillebrand, Analysis of Silicate and Carbonate Rocks (1910).
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7. C. F. Binns, Ceramic Technology.
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10. Transactions of the American Ceramic Society (1899), *et seq.*
11. Journal of the Society of Chemical Industry. Collective Index.
12. Burton's Article on Pottery in Thorpe's Dictionary of Applied Chemistry and on Ceramics in Encyclopædia Britannica XI.

[THE END.]

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