DEPARTMENT OF MINES
SOUTH AUSTRALIA

CLAY.

MINERALOGY, PROPERTIES & USES WITH A SUGGESTED CLASSIFICATION.

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1 INTRODUCTION

In the course of a State wide evaluation of clay resources, the need has become apparent for a clearer understanding of the fundamental properties of clays in order that their behaviour during processing may be forecast. The present account reviews the whole subject. A classification based on types of clay, uses, origins and approximate clay mineralogical content is appended. It is hoped at some future date to provide a classification based on the type of clay mineral or minerals present which would be related to the specific uses of the clays. After a mineralogical examination of clay, it would then be possible to suggest its most suitable use.

2 DEFINITIONS

The word "clay" has been used with varying shades of meaning by different authors; perhaps it is best retained as the name of a rock group. Twenhofel (1937) defines clay as a rock with over 50 per cent of particles of clay size. He also stipulates that the particles should consist in the main of clay minerals. There has unfortunately been little agreement as to the maximum dimensions of the clay size. The boundary of clay to silt size has been fixed at 0.001 m.m. by Hopkins in 1899, 0.002 m.m. by A. Herberg in 1903, 1/128th m.m. by Udden in 1914, 1/256th m.m. by Wentworth in 1922 and 0.005 m.m. by the U.S. Bureau of Soils. According to Ries (1937), the term clay is usually applied to certain earthy rocks whose most prominent property is that of plasticity when wet. Grim (1942) suggests that the word "clay" (or clay material) has three implications. (1) that it is a natural material with plastic properties, (2) that it is composed essentially of particles of very fine size and (3) that these particles are fragments of crystalline minerals. In this context a plastic material is one which can be kneaded by the fingers but which retains its shape when the pressure is removed. The crystalline fragments are clay mineral particles (essentially hydrated aluminium, or more rarely, magnesium silicates).

3 CLASSIFICATIONS

With the growth of the clay industry there as emerged a nomenclature and classification based upon the needs of the clay worker. Clays are chiefly named after their uses; thus one reads of fireclays, brick clays, stoneware clays, slip clays etc. A modern and comprehensive use classification after Parmelee is given by Ries (1937)

The value of a clay for a particular use depends upon such properties as colour, plasticity and bonding strength, and density, temperature of burning, absorptive qualities, etc. Unfortunately standards differ from place to place and in any case properties such as plasticity are extremely difficult to measure accurately. The factors affecting properties are numerous and complex. Thus two clays put to different uses, may have individual names yet may have similar fundamental composition.

The study of clay deposits in their geological settings invokes questions of origin. Such a genetic classification after Ries (1937) is:-

A. <u>Residual clays</u> (by decomposition of rocks in situ)

  1. Kaolins or china clays (white burning)

    (a) Veins, derived from pegmatite
    (b) Blanket deposits, derived from extensive areas of igneous or metamorphic rocks.
    (c) Pockets in limestone, as Indianaite.

  11. Red-burning residuals, derived from different kinds of rocks.

B. <u>Colluvial clays</u>, representing deposits formed by wash from the foregoing and of either refractory or non-refractory character.

C. <u>Transported clays</u>,

  1. Deposited in water

    (a) Marine clays or shales. Deposits often of great extent.

      White-burning clays. Ball clays.

      Fireclays or shales. Buff Burning.

      Impure clays or shales (calcareous
                              (non-calcareous

(b) Lacustrine clays (lakes or swamps)
    Fireclays or shales
    Impure clays or shales, red burning
    Calcareous clays, usually of surface character.

(c) Flood-plain clays, usually impure and sandy.

(d) Estuarine clays, mostly impure and finely laminated.

11. Glacial clays; either red or cream-burning.

111. Wind-formed deposits (some loess)

IV. Chemical deposits (some flint clays)

Such a classification stresses the nature of the occurrence of a clay deposit in the field which is often a matter of uncertain geological interpretation, for example the origins of loess and kaolin have occasioned much discussion. A genetic classification is unsatisfactory in that it makes no provision for the particular nature and uses of the clay and furthermore is impracticable when only the hand specimen in the laboratory is available for consideration. A clay of identical composition may arise by differing processes.

The classification advocated here is mineralogical. This is at once more practical in that it dispenses with the interpretation of field evidence in naming a clay. It is well suited for laboratory work as only the hand specimen is needed. The duplication of names for similar materials is avoided. The properties of a clay, upon which its uses are dependent, must relate to the fundamental mineralogy, and any modifications to that mineralogy. Thus the economic side of the clay classification is brought into focus.

The chief difficulty of a mineralogical classification is in its application. The nature of clay materials is such as to make extremely difficult, if not to exclude, normal mineralogical investigation. The grain size of clay materials has been a cominant influence in the past. Compared with the coarser grained sediments, clays and shales are of far greater abundance yet relatively little is known about them. Methods have now been evolved by means of which it is possible to study materials of clay grain size so that to-day a mineral classification is possible.

4 CLAY MINERALOGY

4.1 Mineral Groups (Chemical)

Classification into mineral groups may be based on chemical affinities or lattice structure. Following a discussion of these two methods individual mineral groups are discussed. Ther appear to be three main groups of clay minerals:-

1. Kaolinite Group $(OH)_8Al_4Si_4O_{10}$

    kaolinite)
    nacrite) polymorphs
    dickite)
    halloysite (hydrated)
    metahalloysite (dehydrated halloysite)
    anauxite
    allophane

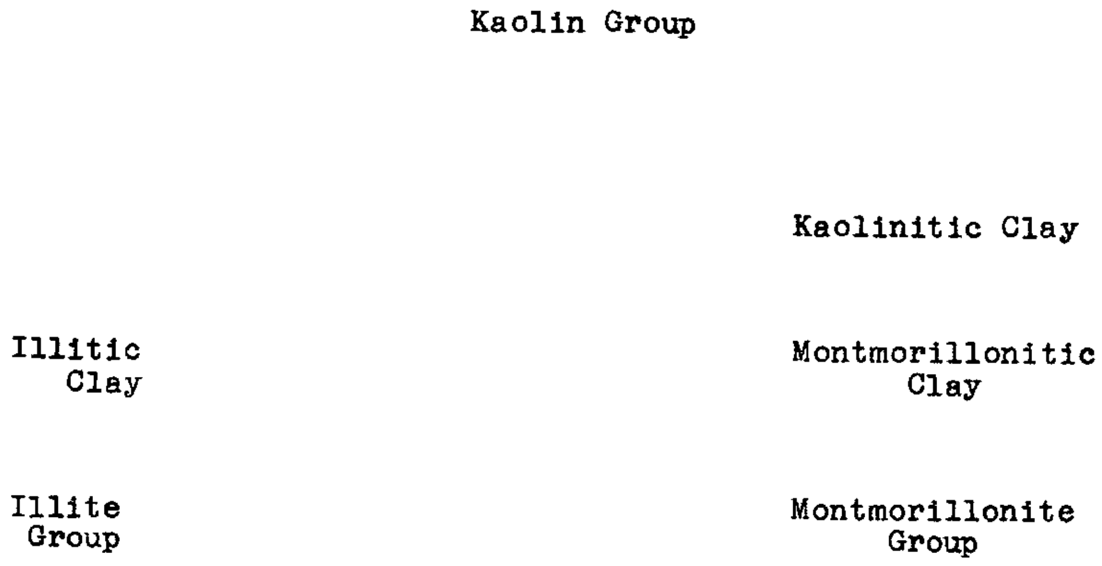
2. Montomorillonite Group $(OH)_4Al_4Si_8O_{20}nH_2O$

    montmorillonite
    sauconite
    nontronite
    hectorite
    beidellite
    saponite

3. Illite Group $(OH)_4Al_{4-a+b}Mg_aFe_cK_2Si_8Al_yO_{20}$

    illite
    sericite
    bravaisite
    brammallite

The primary division of the mineralogical classification of clays is on the basis of the dominant clay group present:-



A clay mineral group present, other than the dominant group, may be used to prefix the name of the clay material. If the constituent minerals of the dominant mineral group are known these may be stated to give greater precision.

e.g. A clay with:-

Nacrite 45% of total clay content
Illite Group 20% of total clay content
Montmorillonite Group 30% of total clay content.

would be named:-

A montmorillonitic kaolin clay (nacrite) with accessory illite group minerals.

4.2 Lattice Structures

Another primary classification of clay minerals is based upon the study of lattice structures. The most modern and comprehensive classification of the clay minerals is that of Grim (1953):-

1. Amorphous
   Allophane group

11. Crystalline

    A. Two-layer type (sheet structures composed of units of one layer of silica tetrashedrons and one layer of alumina octahedrons).

       1. Equidimensional
          Kaolinite group
            Kaolinite, nacrite etc.

       2. Elongate
          Halloysite group

    B. Three-layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer).

       1. Expanding lattice
          Montmorillonite group
          a. Equidimensional
               Montmorillonite, sauconite, etc.
               Vermiculite

          b. Elongate
               Nontronite, saponite, hectorite.

       2. Non-expanding lattice.
          Illite group

C. Regular mixed-layer types (ordered stacking of alternate layers of different types)

Chlorite group

D. Chain-structure types (hornblended-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing A1 and Mg atoms)

Polygorskite Group

Attapulgite
Sepiolite

Two structural units are involved in the atomic lattices of the clay minerals. One is the alumina or aluminium hydroxide unit, which consists of two sheets of closely packed oxygens or hydroxyls between which aluminium atoms are embedded in such a position that they are equidistant from six oxygens or hydroxyls. Actually, only two-thirds of the possible aluminium positions are occupied in this unit, which is the gibbsite (A1(OH)3) structure. The mineral brucite (Mg(OH)2) possesses a similar structure except that all possible aluminium positions are occupied by magnesium. The second unit consists of a sheet of tetrahedral silica (SiO_4) groups linked to form a hexagonal network of the composition Si_4O_{10} when repeated indefinitely. This unit may be viewed as a sheet of loosely-packed oxygen atoms with each oxygen linked to two silicon atoms directly beneath. The silicon atoms are in tetrahedral positions, three valences being satisfied by linkage to three oxygens in the overlying sheet. The fourth silicon valency is satisfied below by an oxygen atom such that silicon valency is analogous to the common hydroxyl group of gibbsite.

<u>4.3 Kaolinite Group</u> $(OH)_8Al_4Si_4O_{10}$

The composite layer of the kaolin group consists of a hexagonal network os SiO tetrahedra with a superposed layer os A1-O, OH octahedra, which shares the oxygen atoms at the apices of the tetrahedra. Diagrams appear in "X-ray Identification and Crystal Structures of Clay Minerals" published by the Mineralogical Society (1951).

This publication also gives the detailed structures of the minerals making up the group. It may not be out of place to mention here the nomenclature to be used concerning halloysite of which hydrated, dehydrated and partially hydrated forms exist. The general term is halloysite which can be particularized by speaking of hydrated halloysite, dehydrated halloysite, glycerohalloysite etc. Metahalloysite may be used for the largely hydrated form this being only an approximate term. The grouping of anauxite is difficult as although the X-ray diagrams are closely similar to those of kaolinite, analysis gives a SiO_2: Al_2O_3 ratio up to 3 : 1. The ratio typical of kaolinite is 2 : 1. Allophane is shown by X-ray diffraction studies to be essentially amorphous. Chemical analyses show that the SiO_2: Al_2O_3 ratio varies. These facts suggest that the mineral is a solid solution, mainly of silica, alumina and water.

4.4 Montmorillorite Group $(OH)_4Al_4Si_8O_{20} \cdot n\ H_2O$

Of the montmorillonite group, montmorillonite has been the mineral most studied. Since single crystal photographs cannot be made, the structure must largely be obtained by inference from better known structures, and there is thus considerable room for uncertainty. The most generally accepted structure is that proposed by Endell, Hofmann and Wilm (1953), and modified by Maegdefrau and Hofmann (1937) and others. Grim (1942, p.239) shows a diagram; in this interpretation the structural units are one gibbsite sheet between two sheets of silica tetrahedral groups. The structural unite are stacked one above the other in the direction of the C axis, and, according to Maegdefrau and Hofman without orientation in the a and b directions. Hendricks and Ross (1938) however, on the basis of optical and defraction data, indicate some orientation in the a and b directions. The units are loosely held together in the direction of the C-axis with water present between them. The amount of water between the units varies, and there is a correlated variation in the C-dimension, so that the mineral is said to have an expanding lattice.

Without water between the structural units the lattice is like that of pyrophyllite ($Al_2(OH)_2Si_4O_{10}$) except that the height of the cell is 9.6Å as against 9.2Å for pyrophyllite. The increased height of the montmorillonite cell is explained by the presence of cations between the units. Replacement of Al^{+++} gibbsite positions by Mg^{++} and Fe^{+++} leads to saponite and nontronite respectively. I t has been suggested that Si^{++++} may be replaced by Al^{+++}, and Marshall (1935) believes that beidellite is the member of the montmorillonite group in which such replacement has been appreciable.

4.5 Illite Group $(OH)_4Al_4-a + b\ Mga\ Fe_cK_2\ Si_{8-y}Aly\ O_{20}$

The structure of illite is similar to that of montmorillonite as suggested by Hofmann and others, except that about 15% of the Si^{++++} positions are replaced by A_1^{+++}, and the resulting excess charges are satisfied chiefly by K^+ ions between the silica sheets of two successive units. The K^+ions appear to act as bridges binding the units together so that they do not expand in the presence of water. The illite structure is similar to the structure of muscovite suggested by Pauling except that in muscovite one fourth of the Si^{++++}positions are occupied by Al^{+++} and the number of K^+ is proportionately greater. In illite Mg^{++} and Fe^{+++} can substitute for Al^{+++} in the octahedral sheet. There is some doubt (grim, 1942) that Mg^{++} can occupy all the possible positions, that is , substitutions of 3 Mg^{++} for 2 Al^{+++}. According to Maegdefrau and Hofmann (The Mica Clay Minerals", 1937) the substitution of Mg^{++} for Al^{+++} can be compensated for by substitution of (OH) for O, thereby partly explaining the higher water content in illite than in muscovite.

4.6 Chlorite Group alternations of $(OH)_4(Al\ Si)_8(Mg\ Fe)_6O_{20}$ & $(Mg\ Al)_6\ (OH)_{12}$.

Only recently (Mac Ewan, 1948) have chlorites been recognised as important constituents of many clay materials and it is likely that this clay mineral is much more abundant in clay materials than is now recognised. It is frequently very difficult to detect small amounts of chlorite when it is mixed with other clay minerals. The identification of chlorite is particularly difficult when kaolinite is also a constituent of the clay mineral being studied.

The variation from one chlorite to another is to be found in slight modifications of intensities or lattice spacings due to small variations of unit-cell dimensions and population of various cation positions. The identification of the various forms of chlorite is very difficult and may be impossible unless chemical and optical data are available to supplement the X-ray analysis.

4.7 Polygorskite Group - Attapulgite and Sepiolite - Attapulgite $(OH_2)_4\text{-}(OH)_2\ Mg_5\ Si_8\ O_{20}\ 4H_{20}$. Sepiolite $Si_4O_{11}(Mg.\ H_2)_3\ H_2O.2\ (H_2O)$

The minerals of this group may well be much more abundant and widespread than is now considered to be the case. They are easily missed in clay-mineral analysis. They are very soluble in acids and frequently occur in calcareous material. They would be destroyed if solution of the carbonates by acids preceded attempts at clay-mineral identification.

5. METHODS OF STUDY OF CLAY MINERAL

The minerals present in raw clays have been determined by a combination of methods including X-ray diffraction, thermal analysis etc; There methods are outlined below:-

5.1 X-ray Analysis

When a clay contains several minerals in comparable proportions, unless the components can be separated by physical and/or chemical means, it is not suitable for detailed crystallographic study. In the cases of clays to be classified the main objective is to identify the component minerals in as much detail as possible. It is comparatively simple to recognize the main types of mineral present largely from a consideration of their low-order reflections, but to obtain more specific information the whole X-ray diagram must be studied is as much detail as possible. It is generally desirable to combine with X-ray analysis, auxiliary techniques (mechanical, thermal, Chemical) either to effect a partial separation of the minerals, or to modify them in characteristic ways.

The direct comparison of standard photographs of typical single minerals with those of unknown materials is a simple and firect way of tackling the problem of clay material composition. The obvious limitation is the variability of clay minerals. The standard photographs used will depend upon the type of work undertaken, and they should be taken with the same equipment as will be used to photograph the unknown materials.

In preliminary diagnosis basal reflections and long spacings are particularly useful. As one moves towards the smaller spacings of the powder diagram, the complexity increases and the immediate diagnostic value of the lines diminishes. A tentative interpretation of spacings greater than about 3 kX (1 kX unit multiplied by 1.00202 equals 1 Å) should be attempted in the first place (consult Table XlV, p320 in "X-ray Identification and Structures of Clay Minerals," edited by G.W. Brindley, the Mineralogical Society 1951). This list gives all reflections from spacings greater than 3 kX having at least medium intensity from clay and associated minerals.

In work following the initial stages of analysis reference should be made to the more detailed information given in the chapters on the mineral groups in the book referred to in the above paragraph.

The reflected intensities from minerals vary with their composition and with such factors as the degree of orientation of the crystals in the powder specimen. If an apparently abnormal intensity cannot be explained on these grounds, then consideration should be given to the possibility of over-lapping reflections, thus cameras giving good resolution of lines should be used. The intensities of reflections may also give information regarding the amounts of the constituent minerals presen (t in a mixture. Difficulties are likely to arrise, due to differential adsorption effects, when one component is much more coarsely crystalline than the other. Errors may also arise, due to preferential orientation of the clay minerals, but this may be less troublesome than might be anticipated if a mixture is employed containing a mineral such as quartz which does not show preferential orientation. Other factors important are the degree of perfection of the crystalline material and the nature and extent of isomorphous substitution. Recording spectrometers with Geiger-Muller counters measure the X-ray intensities more easily and accurately than the older photographic and microphotometric methods, but the fundamental problems remain unchanged. When standard mixtures are used, they must be made up with considerable care and with due regard for all the many factors influencing the intensities of reflections by mixed powders. Further investigations are required before the possibilities of quantitative analysis by X-rays in the field of clay mineral studies can be assessed.

5.2 Thermal Analysis

Small quantities, about half a gram, of the material to be examined, and a neutral substance such as calcined china clay or alumina, are packed separately into two adjacent holders and heated in an electric furnace. A suitable holder is a hold drilled in a block of nicket (Norton, 1939). This is heavy and serves to reduce steep thermal gradients. A thermocouple with one junction in each substance records temperature differences between the substances arising from reactions in the one under investigation. Since clays are hydrated alumino-silicates, they lose water of constitution (generally hydroxyl groups in the crystal structure) when heated, and this loss is usually an easily observed endothermic process characteristic of the particular clay.

Absorbed water is generally lost at lower temperatures and also produces endothermic effects. Recrystallization phenomena often occur at higher temperatures, giving rise to exothermic effects. A second thermocouple records the total temperature of the neutral substance.

Automatic recording is generally employed with a time or temperature scale horizontal and a temperature difference scale vertical. In so far as a thermal reaction proceeds in a definite manner, irrespective of such variables as the particle size of the material, the method is very valuable for indication the types and quantities of minerals which are present. The peak temperatures recorded by this method depend on factors such as the size of the specimen (Norton op. sit.) and the rate of temperature increase, but when these are standardized the method is applicable to the analysis of mixtures. It is highly desirable that such techniques should be standardized so that results obtained in different laboratories are directly comparable. In the past different heating rates have been employed, these produce large variations in the dimensions of the peaks on analysis curves, so that some investigators have missed thermal reactions found by others using a greater vertical exaggeration.

Thermal analysis does not give the same amount of detailed information as with X-ray analysis. However its usefulness may be illustrated by the example of gibbsite. This mineral gives a large endothermic peak at about 300°C, whereas its presence may be overlooked by X-ray analysis due to the predominance of reflections from other components.

In applying the thermal method to quantitative analysis a definite measure of the heat effect must be used. As a basis for this measurement the height of the peak on the curve gives the maximum temperature difference between the test sample and the neutral body. Small changes in the heating rate produce large variations in the dimensions of the peaks; experience shows however that the area below the peaks is not affected, nearly so much. Complications may occur when in the analysis of mixtures of different clay minerals the peaks on the curves are at the same positions. There is a distinct influence caused by particle size. In general the position of a peak does not vary, but when the mineral is very fine grained the curve comes back very quickly to the zero line, indicating that heat transformations occur more rapidly. Thus, in quantitative analysis specimens should be uniformly ground. Grim and Rowland (1942) suggest that quantitative analysis of mixtures cannot hope for an accuracy of more than 10%. Papers by Dauffmann and Dilling (1950), and Grim and Bradley (1940) should be consulted for analysis curves and apparatus used.

<u>Kaolin minerals</u> have endothermic reactions at 550° - 600°C. and exothermic reactions at 950 - 1000°C., corresponding to dehydration and formation of a spinel respectively. Hydrated halloysite ($4H_2O$) shows the same thermal reactions with the addition of an endothermic reaction at 100 - 150°C accompanied by the loss of water and the transition to the form containing $2H_2O$.

<u>Illite group minerals</u> show endothermic peaks at 100-200° 500-650° and at about 900°C, and also an exothermic peak immediately following the third endothermic peak. The 500-650°C. reaction accompanies the loss of most of the water from the lattice and the 900°C. is interpreted as being associated with the final destruction of the illite structure. The exothermic reaction is probab ly associated with the formation of spinel.

<u>Montmorillonite group minerals</u> show endothermal peaks at 100-250°, 600-700° and at about 900°C., The first peak occurs with a loss of water held between the basal planes of the lattice structure, and is larger and extends over a wider temperature range than that of the illite group minerals. The second peak at 600-700° is associated with a loss of lattice water and occurs at about 100°C. higher than the corresponding change in the illiods. The final breakdown of the lattice with an endothermic peak at about 900°C. precedes an exothermic reation accompanying the

formation of spinel.

The endothermic reation at 500-600°C of the kaolins is sharper and about ten times as intense as that of the illite and montmorillonite group minerals. Because of this defference is reaction intensity the resistance in the galvanometer circuit must be varied to alter the vertical exaggeration. Standard curves of mixtures of illite with montmorillonite, and illite with kaolinite are given in a paper by Grim and Towland (Op. cit.)

Another thermal method which may be used in the study of clay materials is to study changes in weight with rise of temperature. The amount and temperature at which water is lost varies from one mineral to another. Whereas in the differential method a fast rate of heating is employed of the order of 10° C/minute, in the dehydration method the specimen may be brought to equilibrium at each temperature to which it is heated, or its weight may be recorded continuously as the temperature rises, or the specimen may be weighted after heating for equal periods at a series of temperatures, for example at 50° intervals, or the water vapour pressure may be measured. It should be noted that weight changes may not always be due to loss of water; losses can occur due to evolution of CO_2 and H_2S, and gains due to oxidation of ferrous to ferric iron.

6.3 Optical Examination.

The value of optical methods in studying the clay minerals has been the subject of much discussion. Some students of clays assert that optical methods are worthless for such fine-grained materials, while others plead for their universal use and base detailed clay-mineral determinations solely on optical studies. Optical methods are frequently of value but they must be used with caution. An optical examination can be made in a very short time and the chance of obtaining valuable data usually justified the expenditure of the required time. Also, after some experience has been gained in the study of clay minerals under the microscope, more can be done with them than would be supposed at first. It is usually possible to determine with fair accuracy the indices of refraction and birefringence of clay-mineral samples.

Certain of the clay minerals frequently have distinctive appearances under the microscope which aid in their identification. Thus, aggregates of the montmorillonite clay minerals often appear as a large single crystal that have been strained. The individual particles of montmorillonite either cannot be seen or else are indistinct and tend to merge into each other. The attapulgite-sepiolite minerals may also have a somewhat similar appearance. Aggregates of the other clay minerals have the appearance of being made up of discreet particles, even though the individual particles are less than one micron in diameter and the particles have a high degree of uniform orientation.

The presence of non-clay minerals, such as quartz, calcite and feldspar, may cause considerable difficulty if these minerals are present in particles of about the same size as the clay minerals. An abundance of extremely fine quartz or calcite makes optical methods valueless in many cases. Sometimes the presence of such non-clay minerals will produce an unusual appearance or strange optical characteristics which suggest that some such material might be present. However, in many cases, the non-clay material would be undetected by optical methods.

The presence of even relatevely small amounts of extremely fine-grained carbonates makes optical study of the clay minerals impossible, because of the high birefrigence of these non-clay minerals. Further, it is not possible to remove the carbonates inall cases by dissolving them, because of the susceptibility of some of the clay minerals to acid attack. Certain of the clay minerals are relatively insoluble in acid, but others are quite soluble. Unfortunately, many calcareous materials also contain the more soluble clay minerals so that in a study of such material it is necessary to determine the clay-mineral composition by non-optical methods.

Organic material and ferric iron compounds may mask the optical characteristics of the clay minerals. The organic material can frequently be removed by solvents or by mild oxidants, such as hydrogen peroxide, without altering the clay minerals. Some organic material, particularly that in the older sediments, is not affected by such reagents and can be removed only be vigorous oxidising agents or by heating to elevated temperatures. Unfortunately if there is iron present, it may be oxidised in the process, so that it may then conceal the characteristics of the clay minerals.

Sometimes the free iron compounds can be removed by reducing e.g. by hydrogen sulphide and then dissolving the ferrous iron. Again gaution must be used because of danger of attack on the clay minerals, particularly those of the montmorillonite and polygorskite groups, by the reducing agents.

Optical methods, of course, are of value in determining the non-clay minerals present in a clay material. In general, minerals found in particles as small as five microns in diameter can be identified. If the mineral has particularly distinctive optical properties, considerable finer particles can be identified.

The petrographic microscope is, of course, useful in studying the texture of clays as revealed in thin sections. Identification of the clay-minerals in thin sections is usually difficult and often impossible.

The optical properties of the clay minerals are given below:-

A very useful table listing the optical properties of the various clay minerals is reproduces by Grim (1953,p.279)

5.4 Electron Microscopy.

The use of the electron microscope has permitted the precise determination of the shape of the particles of various clay minerals and has shed light on the range of particle size of the components of clay and on the degree to which the particle size can be reduced when the clay is worked mechanically with water.

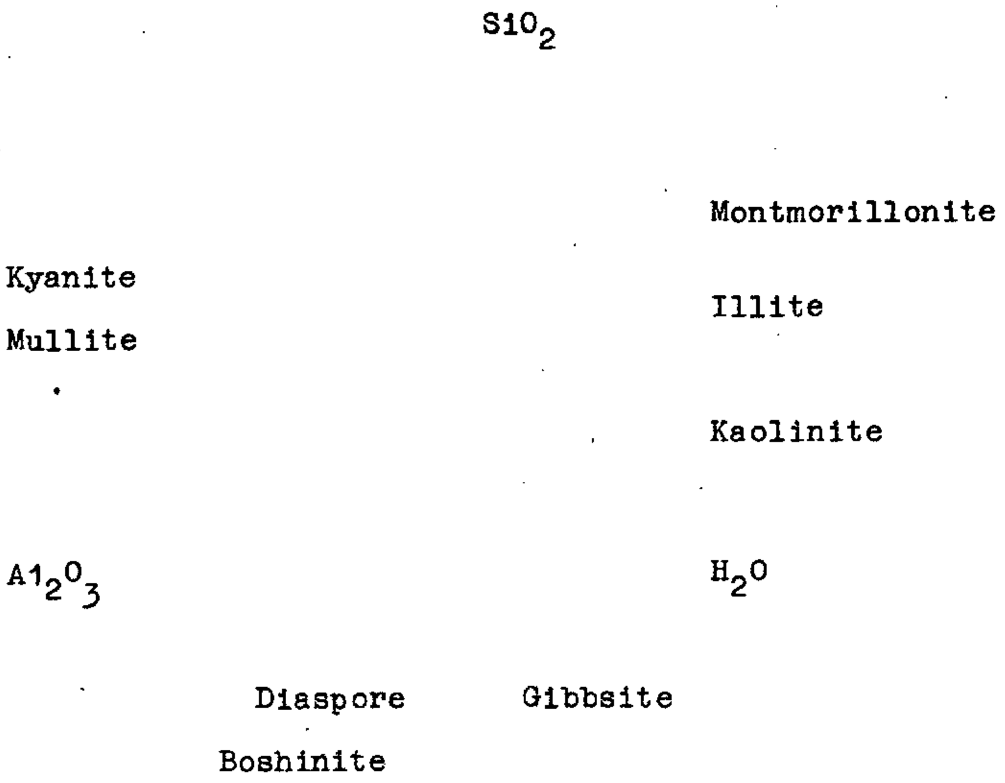
In electron microscopy, the image formation is due to the scattering of electrons as the electron beam passes through the sample. In the early work, the clay-mineral particles were mounted directly in the electron beam without any treatment. In later work the shadow method of preparing samples has been used frequently in order to show the thickness of the units better and to increase the contrast of the particles against the background. In the shadow method mounted specimens are placed in a metal evaporator where some metal, frequently uranium or beryllium is evaporated onto the specimen mounts obliquely. The angle of deposition of the metal is varied according to the thickness of particles in the sample. Angles of about 10° are used for thin particles, while angles up to 30° are used for thicker particles. Direct magnifications of from 3,000 to 15,000 are obtained and these are increased from three to five times by photographic enlargement.

In electron microscopy the specimens become heated by energy absorption. Since heating to low temperature (60° to 100° C.) causes dehydration reactions of some of the clay minerals e.g. halloysite, vermiculite and montmorillonite, care must be taken to register the original character of these minerals.

Data and excellent photomicrographs of the various clay minerals are given in Grim (1953, pp. 108-125).

5.5 Chemical Analysis.

Quantitative chemical analysis is of limited value in assessing the mineralogical content of the clay. If, however, the nature of the principal minerals has already been determined by X-ray or other methods, the bulk chemical composition may be interpreted in terms of the relative quantities of the component minerals, but how accurately this can be done depends largely on the kind and number of minerals involved, and especially on the variability of their composition due to isomorphous replacement.



CLAY MINERAL COMPOSITION (Norton: Elements of Ceramics 1952)

5.6 Base Exchange.

Base exchange is the alteration in cation constitution when a substance is in contact with a salt solution. This is expressed quantitatively in the "base exchange capacity" and measured in terms of milliequivalents per 100 gms. Numerous methods have been suggested for determining the base exchange capacity, none give results very accurately - ± 2 m.e. in 70 m.e.. A clay mateial may be treated to give a clay slip which is then electrodialzed in a three compartment cell (Norton, 1952), the absorbed ions being replaced by hydrogen. The hydrogen-clay slip is then titrated with a base such as NaOH, and the pH of the slip measured. The curve so obtained gives the base exchange capacity which is taken at the inflection:-

Milliequivalents of NaOH.

The graph also shows another method in which the electrical conductivity of the hydrogen slip clay is plotted against the base.

Base exchange capacity in m.e./100 gms. :-
(taken at pH)7.

Montmorillonite	80-150
Illite	10-40
Sepiolite-attapulgite-polygorskite	20-30
Kaolinite	3-15
Halloysite $2H_2O$	5-10
Halloysite $4H_2O$	40-50
Vermiculite	100-150
Chlorite	10-40

The extent of the exchange reaction varies with the concentration of the solution and there may be other factors. Free aluminium or ferric ions in the clay tend to clog exchange positions and to reduce the base exchange capacity. This is also reduced by extended acid leaching or salt treatment tending to remove aluminium or ferric ions from the lattice to exchange positions. There is a series giving the relative ease of replacement of cations:-

Li^+ Na^+ ....k^+ Rb^+ Cs^+ Mg^{++} Ca^{++} Sr^{++} Ba^{++} H^+

This at equivalent concentrations Ca^{++} will displace a greater fraction of Li^+ than K^+ ions. The divalent ions are more tightly held than the monovalent. The cation exchange - ability is not the same for all the clay minerals. Actually there is an exchangeability series for each mineral, so it is important to work on pure known clay minerals.

5.7 Staining Tests.

The adsorption of various organic substances by natural and chemically altered or heat-treated clays can produce colour changes in the clay. Frequently such changes vary, depending on the identity of the clay mineral and its composition. The colour changes, therefore, provide a possible basis for identifying the clay-mineral components of clay minerals. A staining test has the advantage of being rapid and simple to perform, even in the field.

In general, the reation and resulting colour change are slight or absent for clay-minerals of low adsorptive capacity, such as kaolinite, but typically are pronounced for highly adsorptive clay minerals, such as montmorillonites. Two mechanisms have been proposed to explain the colour reactions obtained with clay minerals and various reagents: (1) an acid-base reaction in which the natural or acid-treated clay reacts as an acid and (2) an oxidation-reduction phenomenon in which certain ions, mainly ferric iron contained in the clay mineral lattice, cause an oxidation of the reagent. Substances probably causing colour changes by the acid-base reation include triphenylmethane azine and azo dyes. Substances probably changing the colour of the clays by the oxidation reduction reaction include benzidine and other aromatic arsines.

The general applicability of staining tests for the identification of the clay minerals is restricted, because the development of characteristic colour reactions can be inhibited, augmented or masked by several common ingredients of clay material other than the clay minerals. Caution must therefore be used in applying any staining test indiscriminately to clay minerals.

A very large number of reagents have been suggested and tried for clay-mineral staining tests. In recent years the tendency has been to use several reagents separately in a test, so that the deficiencies of one can be compensated by the value of another for a given material.

5.8 Heat of Wetting.

A dry clay material evolves heat when placed in water and this phenonemon is known as the heat of wetting. Heat is also evolved when clay materials are placed on some liquids other than water e.g. alcolhols and various organic liquids. There is much work to be done on the heat of wetting values for fired clay material. There is some data for the minerals montmorillonite, kaolinite, illite and attapulgite. For montmorillonite, there is a sharp drop in heat of wetting after firing at the temperature where hydroxyl water is lost from the lattice. Kaolinite shows a slight reduction in the amount of heat evolved when heated to temperatures somewhat in excess of that required for the loss of hydroxyl water. The heat of wetting of attapulgite increases greatly on firing up to about 550°C. and then decreases, so that after firing at 900°C. The same value as that for the unfired mineral is obtained. (The reason for the changes in heat of wetting for the various clay minerals when heated to these particular temperatures is not clear.)

6. PHYSICAL PROPERTIES OF RAW CLAY

6.1.Colour

Colour is an important factor in the useability of clay-materials. Clay minerals are colourless or rarely tinted, the body colour of clay materials generally depending upon the presence of small amounts of pigmentary substances. In lattice interspaces the most common pigment is iron oxide which gives varying shades of yellow, pink, red and brown. The best white burning clays contain less than 1% Fe_2O_3; 2% may give a light cream colouration. The mode of distribution of the pigment is important in affecting the body colour. Thus a Buff clay-material may contain from 1 - 5" ferric oxide depending upon its state of subdivision. If a clay is burnt in a kiln under reducing conditions, the iron content may impart a bluish or bluish-black colour to the product. Furthermore, in the process of "bluestoning", reactions occur in which ferrous silicate forms at certain temperatures. The presence or organic matter may give a grey or black and rarely a pink colouration to unburnt clay materials. A creamy tint may be due to the presence of titania, present in about 2%. According to Ries (1914), clays containing soluble vanadiates, if not burned at a sufficiently high temperature will show on the surface of the ware a green discolouration which though it can be washed off with water will continue to return as long as any of the salt is left in the brick.

6.2 Porosity

Porosity is defined as the colume of pore space relative to the total volume. The Apparent Porosity is the relation between the volume (or weight) of a mass and the volume (or weight) of the water absorbed on immersion. This is the measure normally used and differs from the True Porosity by the colume of the pores which remain unfilled upon immersion in water.

In raw clay materials the pores are all open but of variable size. In fired materials the pores are open or closed, the latter being formed by the expansion of gasses during fusion. Porosity in the raw clay material has an important influence upon drying properties - large pores allowing the quick excape of water. In fired materials properties such as strength are affected.

6.3 Specific Gravity

Three types of Specific Gravity may be distinguished. The True Specific Gravity is the ratio of solid material, excluding pores, to an equal volume of water. In this measurement the sample is powdered. The Apparent Specific Gravity is the ratio of volume of solid material, including closed pores, to an equal volume, of water. The Bulk Specific Gravity is the ratio of the entire volume of material to an equal volume of water. The True Specific Gravity is affected by the minerals present, and so might be useful in analysis, and in fired materials by silica inversion, chemical reactions, fusion and crystallization etc. The Apparent and the Bulk Specific Gravities are affected also by the porosity.

6.4 Strength.

Cohesion if the force which holds a mass together. The dry or green strength of clay materials is an important property in aspects such as the handling of ware prior to hardening in the kiln. The strength of clay materials may be determined by tensional, compressional or trasverse tests. The latter is most commonly used and is expressed in terms of the modulus of rupture. The test is carried out on dried material at 110°C. The clay is thoroughly wedged and aged in the plastic state until it is as nearly as possible in a homogeneous condition. A small square-section bar (e.g. $\frac{3}{4}$" x $\frac{3}{4}$" x 3") is then cut from the mass, with as little deformation as possible and carefully dried. The bar is supported on a pair of knife edges and a load is applies by a third knife edge across the central upper part of the bar. By steadily increasing the applied load at a rate of 5 lb. per minute the value at rupture is obtained.

The modulus of rupture (also known as Transverse strength) M in lb/sq.in. is then given by :-

$$M = \frac{3}{2} \times \frac{W \times 1}{B \times d^2}$$

W = load in lb. at rupture

= distance between the knife edges (quoted at 1.95")

b = width of test bar

d = depth of test bar

High dry strength implies good bonding power and is thus a direct indication of the ability of the material to stand up to handling in the unfired state without breakage. In general, clays of high dry-strength retain good mechanical properties during the early part of the firing process i.e. up to 700°C particularly if the rate of rise and temperature is very low.

The modulus of Rupture is usually decreased by the addition of sand or ground flint; however sometimes this is not so as the addition prevents minute drying cracks thus revealing the true strength of the clay material. The Transverse Strength (or Modulus of Rupture) is widely variable - from a few lbs. / sq inch to over 1000 pounds/ square inch: see table below. The stronger clays probably contain some montmorillonite.

The Tensile Strength, is given by the following equation:-

Tensile Strength $= \frac{P}{b\ d}$, where

P = load in lb. (at rupture)

b = width of test bar in inches

d = depth of test bar in inches

In clay technology, tensile strength refers to the air-dried body.

Dried Strength of Clays:-

	Modulus of Rupture (lb./sq.in)
Washed kaolin	75-200
Sedimentary kaolin	100-150
Ball clays	150-1200
Glass pot clays	300-1300
Sewer pipe clays	200-600
Sagger clays	100-500
Brick clays	100-1000

("Elements of Ceramics" Norton, 1952, P. 35.).

Adhesion (as an aspect of strength may be important when layered or glazed articles are being produces. Binding or bonding strength is the power of a clay to hold together particles of non plastic materials such as sand. In certain types of work the bonding strength of the material used must not be below that which is necessary for good modelling or moulding. It may be necessary to strengthen a clay material by mixing in one of high bonding strength. Again the clay materials with the greatest bonding powers are those rich in the montmorillonite minerals.

7 CHANGES EFFECTED BY WATER

Penetrability is the ease with which a liquid is drawn into the pores of a body by capillary action without attendant chemical change. Permeability is the readiness with which a substance permits a fluid to flow through it and is measured by the rate at which a standard fluid flows through a mass of unit area and depth. The pressure must also be expressed. The softening effect of water on clay materials is known as slaking. Slaking times vary but may be reduced if the water used is slightly alkaline. Slaking is usually accompanied by volume and heat changes. The volume increase by "swelling" may be considerable and pressures up to one ton/sq. inch exerted. Clay materials with greatest swelling are those richest in montmorillonite group minerals. The "heat of wetting" is known to increase with decreasing grain size.

Plasticity is one of the most typical attributes of clay materials; it is the property of a material by means of which it can be deformed or changed in shape and yet retain that shape when the deforming force is removed. Clay materials are almost unique in that they retain shape but not plasticity when they are dehydrated. There does not appear to be any universally acceptable method measuring plasticity. A method for determining the "plasticity index" of a clay as used in Engineering Geology is given in Lambe (1951, p/p/24-26) and could possible be used more widely. However, gaskin and Samson (1951,pp.9 - 10) state that "little weight can be attached to the values obtained "by this method. A practical method consists of extruding small cylinders from a simple piston-type pug-nill at constant rate and plotting the extrusion pressure against the moisture content of the clay. However highly plastic or "fat" clay minerals, such as ball clays and bonding clays, may be distinguished from poorly plastic or "lean" clay materials. Plasticity may be reduced by adding non plastic material and also in some cases by preheating the material at 100-300°C., It is generally agreed that plasticity depends upon the interply of the attractive force tending to hold the clay mineral flakes together, the thickness of the water film keeping the flakes apart and the lubricating properties of that film. The thickness of the water film will vary according to the structure composition of the particles and also to the exchangeable base factor. A clay material composed of flakes with high attractive power and thin water film should yield a sticky mass. A less sticky mass should contain a clay mineral with low attractive for ce or a high attractive force reduced in effect by a thick water film. Clay materials rich in montmorillonite minerals are the most plastic whilst those rich in kaolins are the least.

Sticky Point When even a small proportion of water is added in excess of that required to develop the maximum plasticity of a clay material paste the mass adheres to the fingers and becomes "sticky". Thus there is a sticky point which is the amount of water needed to render a clay material "sticky".

Water Content - in clay materials a distinction may be made between mechanically held water and that which is chemically combined. The "water of plastcity" is the sum of the "shrinkage and pore water". "Shrinkage water" is the water evaporating from a plastic clay at room temperature until air shrinkage ceases and constant weight is obtained. "Pore water" is the water left in the intergranular spaces and may be driven off at 100°C. "Micella or hygroscopic water" is that retained on the surface of the clay particles as a film of molecular dimensions, being tenaceously held and may not be driven off until 200°C. The evolution of "chemically combined water" which forms part of the hydrous aluminium silicate clay minerals has been considered in previous paragraphs on thermal analysis. Clay materials can be very hygroscopic: water may amount to as much as 10% of the dry weight. There are cases in which relationships of the above measures find empirical applications in industry, for example in the manufacture of crucibles and glass pots the best clay materials are said to have the ratic $\frac{\text{shrinkage water}}{\text{pore water}}$ equal to one.

Shrinkage - an important aspect of the drying of clay materials is shrinkage. Air shrinkage occurs as the material dries and continues until the particles are all in contact. The amount of shrinkage varies with the water content and the type of clay material. It is the highest for thos materials which have the largest volume increases by "swelling", these are the heavy plastic clays rich in the montmorillonite group minerals. The open porous clay materials dry much more easily. If articles do not dry evenly throughout stresses will be set up which may cause rupturing. Shrinkage can be measured by linear changes but volume measurements are more accurate and volumeter should be used.

Volume of
Clay

Volume of
Water.

In the above shrinkage curve A to B is considered the "normal shrinkage", this is long for plastic clay materials and short for sandy ones. At B the moisture content is low enough to allow air to enter the pores, the particles being almost in contact. From B to O the shrinkage is reduced, this is termed the "residual shrinkage". It does not occur in china clays and some other very lean clays.

Air Shrinkage of Clays ("H Ries: Industrial Minerals" P.214)

Clay	Linear %	Volume %
Crude kaolin	5.0 - 7.6	14.11 - 20.92
Washed kaolin	3.0 - 11.0	20.0 - 29.0
Georgia kaolin	4.5 - 12.5	7.5 - 36.46
Ball clays	5.25 - 12.	22.0 - 32.0
Flint clays	0.78 - 6.5	2.3 - 21.0
Sagger clays	3.01 - 11.0	9.0 - 25.
Paring brick clays	0.9 - 6.0	3.5 - 18.0
Sewer Pipe clays.	3.5 - 10.5	16.12 - 22.9

Theoretically, the ratio of volume shrinkage to linear shrinkage is approximates to 3:1 (for small changes in volume).

8 FIRING CHANGES.

The heat changes occurring when clay materials are fired have been discussed in the paragraphs on thermal analysis. When pottery or other clay suffers complete drying the soluble salts tend to be deposited at the surface. Not only is this unsightly but it may interfere with glazing and also crystallization within pores may cause disintegration. In some cases barium compounds are added to precipitate and so render salts untransportable. Heat changes occur when volatiles are lost. Water vapour is removed by the driving off of chemically combined water carbon dioxide, the temperatures at which some other impurities decompose are given below:-

Reaction	Breakdown Temp.
$FeS_2 + O_2 \quad FeS + SO_2$	350-450 ° C.
$4\ FeS + 7O_2 \quad 2Fe_2O_3 + 4502$	500-800
$Fe_2(SO_4)_2 \quad Fe_2O_3 + 3SO_3$	560-775
$C + O_2 \quad CO_2$	350
$S + O_2 \quad SO_2$	250-920
$CaCO_3 \quad CaO + CO_2$	600-1050
$MgCO_3 \quad MgO + CO_2$	400-900
$FeCO_3 + 3O_2 \quad 2Fe_2O_3 + 4CO_2$	800
$CaSO_4 \quad CaO + SO_3$	1250-1300

("Elements of Ceramics", Norton, 1952) p 131.
Gypsum, (CaSO4 - 2H20) 110°C Plaster of Paris ($CaSO_4$ ½H_2O) 204°C Anhydrite, CaSO4, 1250 - 1800°C. - $CaO+SO_3$

Clay materials soften slowly with rise in temperature. Impure materials fuse earlier whilst kaolin clays require a much higher temperature. Thus, kaolin clay materials are useful refractories. When a material fuses, a glass is first formed which then attacks and dissolves the remaining mineral grains forming a solution of molten glass. The measurement of temperatures during firing is important as some materials easily overfire, they are said to have a short firing range. The method of thermometry often adopted is to employ <u>Seger cones</u>. These are artificial mixtures, similar to porcelain, of known composition and melting point shaped as pointed cones. A series of these is places in the oven, the members which melt and those remaining unaffected give the temperature on such a scale.
A list showing complete list of cones and fusion points is given below:-

No. of Cone	Fusion Point		No. of Cone	Fusion Point	
	OF	OC		OF	OC
022	1094	590	16	2642	1450
021	1148	620	17	2678	1470
020	1202	650	18	2714	1490
019	1256	680	19	2750	1510

No. of Cone	Fusion Point	
	°F	°C
018	1310	710
017	1364	740
016	1418	770
015	1472	800
014	1526	830
013	1580	860
012	1634	890
011	1688	920
010	1742	950
09	1778	970
08	1814	990
07	1858	1010
06	1886	1030
05	1922	1050
04	1958	1070
03	1994	1090
02	2030	1110
01	2066	1130
1	2102	1150
2	2138	1170
3	2174	1190
4	2210	1210
5	2246	1230
6	2282	1250
7	2318	1270
8	2354	1290
9	2390	1310
10	2426	1330
11	2462	1350
12	2498	1370
13	2534	1390
14	2570	1410
15	2606	1430

No. of Cone	Fusion Point	
	°F	°C
20	2786	1530
21	2822	1550
22	2858	1570
23	2894	1590
24	2930	1610
25	2966	1630
26	3002	1650
27	3038	1670
28	3074	1690
29	3110	1710
30	3146	1730
31	3182	1750
32	3218	1770
33	3254	1790
34	3290	1810
35	3326	1830
36	3362	1850
37	3398	1880
38	3434	1910
39	3470	1940

The cone numbers (with temperatures) used in the different branches of the clay-working industry in the United States are approximately as follows:-

	Cones	Temp (°C.)
Common brick	012 - 01	890 - 1130
Hard burned common brick	1 - 2	1150 - 1170
Buff front brick	5 - 9	1230 - 1310
Hollow blocks and fire proofing	03 - 1	1090 - 1150
Terra cotta	02 - 7	1110 - 1270
Conduits	7 - 8	1270 - 1290
White earthenware	8 - 9	1290 - 1310
Fire bricks	5 -14	1320 - 1410
Porcelain	11 -13	1350 - 1390
Red earthenware	010 -05	950 - 1050
Stoneware	6 - 8	1250 - 1290
Electric porcelain	10 -12	1330 - 1370

9 EFFECTS OF QUARTZ, LIME AND MAGNESIA ON FIRING

Quartz is an important anti-shrinkage agent, which greatly diminishes the air shrinkage, plasticity and tensile strength of clay, its effect in this respect increasing with the coarseness of the material. The brick maker recognises the effects mentioned above and adds sand or loam to his clay and the potter brings about similar results in his mixture by the use of ground flint. However, a good deal of coarse quartz is undesirable in the manufacture of tiles, as the grains may aggregate to give planes of weakness. Ultra fine quartz, however, appears to have little adverse effect.

Lime The presence of over 2% of lime in bricks and probably 1% in tiles may be deleterious to the ware. Danger of splitting is not likely if the lime is in a finely divided condition and evenly distributed throughout the brick or tile. If, however, lime is present in lumps, swelling of these on heating may split the ware. Another effect of lime if present in sufficient quantity is to cause the clay to soften rapidly, thereby sometimes drawing the points of incipient fusion and viscosity within 41½%C. of each other. This rapid softening of calcareous clays is one of the main objections to their use and on this account also it is not usually safe to attempt the manufacture of vitrified products from them (though the presence of several percent of magnesia will counteract this effect.)

Magnesia. The effect of magnesia if present in sufficient quantity, is to act as a flux and make the clay soften slowly, instead of suddenly as in the case of calcareous clays. An important characteristic of magnesian clays is that they can be made into wares of extreme length and very thin walls, which may be nearly vitrified without warping.

10. TYPES OF CLAY AND USES.

KAOLIN OR CHINA CLAY

Definition: A clay derived by decomposition of an aluminous mineral such as feldspar, mica etc.

Chemical Analyses

	1.	2.	3.	4.	5.
SiO_2	45.78	44.32	44.90	45.12	46.54
Al_2O_3	36.46	39.42	37.94	39.25	39.50
Fe_2O_3	0.28	0.67	1.68	0.71	
Feo	1.08	-	-	-	
CaO	0.50	0.68	0.39	0.49	
MgO	0.04	0.21	0.26	0.14	
K_2O Na_2O	0.25	-	-	-	
TiO_2	-	1.29	0.89	0.89	
H_2O	13.4	13.95	14.14	14.13	13.96
Moisture	2.05	-	-	-	
CO_2	-	-	-	-	
SO_3	-	-	-	-	

1. Washed laolin, Webster, North Carolina.
1. Kaolin, Georgia (J.M. Stuber Corporation)

3. "Hard" clay (Kaolin), South Carolina
4. Pure kaolinite.

Uses.

Paper (filler and surface coating)
rubber (reinforcing and stiffening, pigment)
refractories
white earthenware
porcelain of all kinds
adhesives
cement
insecticides
linoleum
oilcloth
paint

BALL CLAY

Definition: plastic, transported clay which, when fired in an oxidising atmosphere to the temperature of certain pottery ovens ca. 1150-1200°C., have a white or nearly white colour. The modules of rupture exceeds 600 lb/sq. in.

Chemical Analyses

	L.	2.	3.	4.	5.	6.
SiO_2	50.76	45.80	55.00	46.11	45.57	45.97
Al_2O_3	32.50	35.16	31.19	39.55	38.87	36.35
Fe_2O_3	1.17	0.75	1.17	0.35	1.14	1.08
FeO	-	-	-	-	-	-
CaO	0.86	0.66	0.74	-	tr.	1.14
MgO	0.09	-	0.26	0.13	0.11	1.09
K_2O	n.d.	n.d.	n.d.	-	0.16	1.84
Na_2O	n.d.	n.d.	n.d.	-	-	
TiO_2	0.10	0.56	1.25	1.20	1.30	-
Combined Water	11.08	13.98	9.36	13.78	14.10	12.36

1. Devon ball clay
2. Devon ball clay
3. Devon ball clay

4. Ball clay, Edgar, Florida (U.S.G.S. Prof. Paper 11, p. 39)

5. Ball clay, Woodbridge, New Jersey (N.J.G.S. Fin. Rept. V1, P.443)

6. Ball clay, Regina, Missouri (M.G.S., X1 p. 566)

Notes:- silica range from 45.57 to 55.00
alumina range from 31.19 to 38.87

Uses:-

Chiefly as one of the ingredients of whiteware and for other purposes where a refractory clay of good bonding power is required. Addition of a ball clay to a china clay imparts plasticity to the latter. The darker burning varieties of English ball clays and the more siliceous varieties are used for the manufacture of various types of coarse ware, such as salt-glazed stoneware, drain-pipes, flooring and other tiles, ornamental blocks such as copings and common bricks. The more refractory dark burning clays are used for the manufacture of firebricks, both as straight clays and as bond clays employed in conjunction with non-plastic refractory clays, while they are similarly utilised, in certain instances in making saggers and in bonding abrasives such as carborundum. The so-called "pipe clays" are used for the manufacture of tobacco pipes, which is one of the oldest uses of these clays, while "household" clay is made into blocks for whitening steps.

FIRECLAY

Definition a clay capable of withstanding a high degree of heat (it is a term which has been most loosely used and many plastic materials which have absolutely no claim to refractoriness have been included under this heading).

Chemical Analyses

	1.	2.	3.	4.	5.
SiO_2	74.25	62.89	51.92	61.44	63.69
Al_2O_3	17.25	21.49	31.64	26.18	23.01
Fe_2O_3	1.19	-	-	0.30	2.40

	1.	2.	3.	4.	5.
FeO	-	1.81	1.13	0.36	-
CaO	0.40	0.38	0.03	0.12	0.65
MgO	tr.	0.56	0.44	0	-
K_2O	0.52	-	0.40	-	1.08
Na_2O		2.52		0.02	0.25
TiO_2	-	1.82	1.16	1.39	1.18
H_2O	6.30	7.58	13.49	9.07	6.00
Moisture	-	1.16	-	0.77	1.97

1. Fireclay, Bibbville, Alabama. Ala. Geol. Surv. Bull, 6 p. 152.
2. Lower Kittanning clay, New Brighton, Pannsylvania. Pa. Geol. Surv., M.M., P. 262.
3. Bolivar flint fire-clay, Salina Pennsylvania, Ibid,P259.
4. Fireclay, Piedmont, West Virginia. W.Va. Geol. Surv.,111
5. Fireclay, Corbridge Northumberland, England.

Notes SiO_2 and Al_2O_3 percentages vary quite considerably.

Uses

Mainly for the manufacture of the various shapes of fire-brick, but also wholly or in part in the manufacture of gas and zinc retorts, locomotive and furnace linings, crucibles, floor tiles, terra cotta, conduits, pressed and paving bricks.

STONEWARE CLAY

Definition a refractory or semi-refractory clay with sufficient plasticity and toughness to permit its being turned on a potter's wheel. The tensile strength should be 125lb. per square inch or over; low fire shrinkage and good vitrifying qualities are desirable.

Chemical Analyses

	1.	2.	3.	4.
SiO_2	64.26	68.30	60.34	69.23
Al_2O_3	22.95	20.10	20.55	18.97
Fe_2O_3	1.28	1.0	3.53	1.57

	1.	2.	3.	4.
Feo	-	tr.	0.49	0.55
CaO	0.45	tr.	0.38	0.12
MgO	0.37	2.4	1.12	0.36
K_2O	1.96	tr.	2.89	2.27
Na_2O	-	0.60	0.73	0.33
TiO_2	-	1.20	0.92	1.50
H_2O	6.74	6.6	6.42	5.46
Moisture	2.05	-	2.35	-
P_2O_5	-	-	0.55	-

1. Akron, Summit County, Chio. Ohio Geol. Surv., V11, p.94.
2. Elmendorf, Bexal County, Texas.
3. Bridgeport, Harrison County, West Virginia, West Virginia Geol. Surv., 111, p. 162.
4. Huntingburg, Indiana; Indiana Dept. Geol. and Nat. Res., 29th Annual Report, p. 508.

Notes: SiO_2 and M_2O_3 percentages fairly constant.

Uses

In addition to all grades of stoneware, these clays are used also for yellow ware, art ware, earthenware and even for terra-cotta.

ROOFING TILE CLAYS.

Definition plastic coloured clays, capable of easy extrusion. Very uniform shrinkage is desirable. Warping and cracking on firing should be absent. The firing temperature is approximately 980°C. The approximate chemical composition should be:-

Insolubles (SiO_2, etc.)	70%
Al_2O_3	12 - 15%
CaO	not a trace
MgO	a trace
Fe_2O_3	6%
Loss on ignition not	7%

(information supplied by Wunderlich's Ltd.,) Notes Wunderlich's state that the so-called Indian (roofing) tiles are thinner than the Wunderlich tile and have been fired at a lower temperature. Water absorption may amount to 14%. These tiles are quite suitable and durable for roofs with a pitch 30° or more, provided they are securely fixed.

WALL TILE CLAY white-burning clay which is not burned to vitrification, but is usually hard enough to resist scratching with a knife. Wall tiles are moulded in dry-press machines and burned first in saggers in an up draft kiln. The tiles are then glazed and fired at a much lower temperature. About three-quarters of wall tiles used in Australia are imported from overseas; of these most come from England, followed by Germany. The English tiles are recognised as the best.

FLOOR-TILE CLAY.

Definition clay without surface cracks after air-pressing, should also be free from any tendency to warp or split in burning.

Notes white floor-tiles are commonly made of a mixture of white - burning clays, flint and feldspar. Buff coloured tiles are usually made from fireclays, while red ones are often made from a red-burning clay or shale. Floor tiles are moulded by the dry-press process, the raw material being first carefully ground and mixed. In burning, tiles they are placed in saggers and burned down draft kilns.

TERRA-COTTA CLAYS

Definition buff burning, semi-fire clays or a mixture of these with a more impure clay or shale - these give the best results at a temperatures (cone 6 - 8, i.e. 1250 to 1290°C) usually attained on firing. An absence of soluble salts is most desirable.

Only one analysis of a Baltimore, Maryland, terra-cotta clay has been found viz -

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$K_2O + Na_2O$	Loss on Ignition
68.30	21.27	1.43	0.52	0.80	0.20	7.55

Use

For manufacture of structural decorative work (moulded by hand).

SEWER PIPE CLAYS

Definition generally a clay high in fluxes and iron: a high percentage of soluble salts is not desirable.

Chemical Analyses

Definition generally a clay high in fluxes and iron: a high percentage of soluble salts is not desirable.

Chemical Analyses

	1.	2.	3.	4.
SiO_2	57.10	55.60	63.00	59.96
Al_2O_3	21.29	24.34	23.57	18.76
Fe_2O_3	7.31	6.11	1.87	7.72
FeO	-	-	0.46	-
CaO	0.29	0.43	0.44	0.60
MgO	1.53	0.77	0.89	0.93
K_2O	3.44	3.00	2.40	3.66
Na_2O	0.61	0.09	0.29	-
TiO_2	-	-	1.10	-
H_2O (total)	8.30	9.40	6.45	7.70
SO_3	-	-	-	0.73

1. Shale, Canton, Ohio. Ohio Geol. Surv., V11, p. 133.
2. Shale, and fire-clay mixture. Ibid.
3. Underclay, Mecca, Parker County, Indiana. Ind. Dept. Geol. and Nat.Res., 29th Ann. Rept., p.114.
4. Laclede mine clay, St. Louis, Missouri, Mo. Geol Surv., X1 p. 570.

Notes: SiO_2, Al_2O_3 and K_2O percentages fairly constant.

Use

Manufacture of sewer pipes.

BRICK CLAYS.

These may be divided into two classes, namely (a) common brick clays and (b) pressed brick clays.

(a) Common Brick Clays

Definition usually low grade clays and in most cases red-burning. They should mould easily and burn hard at as low as temperature as possible (this depending on the domposition of the clay used) with minimum loss from cracking and warping. Common bricks are rarely burned any higher than cone 05 (1050°C) The process of manufacture consists of mixing the clay in a pug-mill with water, extruding the material through a die and then cutting by means of wire cutter)

	1.	2.	3.	4.
SiO_2	66.67	52.30	56.50	56.81
Al_2O_3	18.27	18.85	19.31	20.62
Fe_2O_3	3.21	6.55	5.89	6.13
CaO	1.18	3.36	1.00	0.65
MgO	1.09	4.49	1.85	0.58
K_2O	2.92	4.65	5.98	4.47
Na_2O	1.30	1.35	-	-
TiO_2	0.85	-	-	
H_2O (total)	4.03	5.30	9.47	10.24
CO_2	-	3.04	-	-

1. Pleistocene clay, Little Ferry, New Jersey, N.J. Geol. Surv., V1, p. 220.
2. Saline shale, Warness, New York N.Y. State Museum, Bull. 35., p. 830.
3. Carboniferous shale, Grand Rapids, Michigan, Mich. Geol. surv. V111, pt. 1, p. 41.
4. Residual clay, Greensboro, North Carolina. N.C. Geol. Surv. Bull. 13, P. 114.

Note: Al_2O_3 percentages fairly constant; other constituents variable.

(b) Pressed Brick Clay

Definition a clay, clay-shale or weathered slate showing uniformity of colour in burning, freedom from warping or splitting, absence of soluble salts and sufficient hardness and low absorption when burned at a moderate temperature. Presses bricks are frequently fired to cone 7 or 8 (1270 to 1290°C) In Australia, the dry-press method is normally used. The material is powdered and then pressed into steel moulds. Air drying is eliminated.

	1.	2.	3.
SiO_2	68.28	63.11	65.78
Al_2O_3	18.83	23.30	14.79
Fe_2O_3	2.60	2.23	8.03
CaO	0.70	0.73	0.54
MgO	0.13	0.97	1.42
K_2O	2.29	0.93	2.82
Na_2O		0.49	0.97
TiO_2	0.27	-	1.00
H_2O (total)	7.23	7.82	4.98
SO_3	-	0.24	-

1. Clay used for white brick, Grover, North Carolina. N.C. Geol. Surv., Bull. 13, P. 81.

2. Clay from Hocking Valley, Ohio.

3. Shale from Cayuga, Vermillion County, Indiana. Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept., p. 503.

Notes: SiO_2 percentages fairly similar; other constituents variable.

PAVING BRICK CLAY

Definition a clay with fair plasticity, good tensile strength and a range of not less than 250°F. between the points of incipient vitrification and viscosity (impure shales are generally used). They show considerable range in chemical composition.

FIREPROOFING AND HOLLOW-BRICK CLAYS

Definition clays having sufficient plasticity to flow smoothly through the peculiar shape of die used in making them, fair tensile strength and burn to a good hard but not vitrified body at a comparatively low temperature 1050° - 1130°C - cones 05 to 01.

Chemical Analyses.

	1.	2.	3.
SiO_2	52.22	57.57	51.95

	1.	2.	3.
Al_2O_3	29.43	21.70	18.34
Fe_2O_3	2.78	2.26	7.56
FeO	-	4.11	-
CaO	0.88	0.32	4.14
MgOo	0.72	1.12	3.36
K_2O	2.10	2.16	1.43
Na_2O	0.75	0.33	2.69
TiO_2	-	1.10	-
H_2O (total)	11.10	6.78	7.81
CO_2	-	1.75	-
SO_3	-	-	2.76

1. Nation Fireproofing Co., Keasbey, New Jersey. N.J. Geol. Surv., Final Report, V1, p. 282.
2. Underclay below coal 11, Connelton, Indiana. Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept. 338.
3. Representative clay-shale, Iowa, Ia. Geol. Surv., X1V, p. 232.

<u>Notes:</u> SiO_2 percentages fairly similar; percentages of other constituents very, sometimes widely.

SLIP CLAY

<u>Definition</u> a clay containing such a high degree of fluxing, impurities and of such texture that at a low cone it melts to a greenish or brown glass, thus forming a natural glaze. It is fine-grained, free from lumps and concretion, has a low air-shrinkage and is mature in burning at as little above cone 5 (1230°C) aspossible.

	1.	2.	3.
SiO_2	63.63	38.08	57.01
Al_2O_3	13.57	11.36	12.85
Fe_2O_3	7.77	2.60	3.02
CaO	2.55	23.70	9.56
MgO	1.47	tr.	1.20
K_2O	2.63	0.58	0.75
Na_2O	0.88	1.60	2.01

	1.	2.	3.
TiO_2	-	0.70	1.13
H_2O	4.75	3.06	4.00
CO_2 (and moisture)	2.90	18.80	8.00

1. Brimfield, Ohio. Ohio Geol. Surv., V11, p. 105
2. Leon Creek, near San Antonio, Texas.
3. Alazan Creek, near San Antonio, Texas.

Notes: Al_2O_3 percentages fairly similar; other constituents widely variable.

GUMBO CLAY

Definition a fine-grained, highly plastic tenaceous clay with high shrinkage used for the manufacture of railroad ballast.

RETORT CLAY

Definition a dense burning,plastic, semi-refractory clay used chiefly in the manufacture of gas and zinc retorts.

POT CLAY

Definition Clay used for the manufacture of glass pots and consequently representing a very dense-burning fireclay.

SAGGER CLAY

Definition clay used a misture for making the saggers in which the white ware (products having a white or nearly white porous body, usually covered with a glaze.) and other high grades of pottery are burned. Commonly rather siliceous. A common mixture for saggers is 75% Silliminite, 10% Talc, 15% clay.

BENTONITE

Definition a clay produced by the alteration of volcanic ash in the situ and largely composed of montmorillonitic clay minerals. These clays are generally highly colloidal and plastic. It has the unique characteristic of swelling to several times its original volume when placed in water and forms thixotropic gels with water even when the amount of bentonite in such gels is relatively small.

Uses

In decolourising oils, in the manufacture of catalysts, in bonding, moulding, sand, in the preparation of oil well drilling muds and in other relatively minor uses.

FULLER'S EARTH

Definition this name is used for any natural earthy material which will decolourise mineral or vegetable oils to a sufficient extent to be of economic importance. (In England, the term is a stratigraphic one and is used for certain beds long used as commercial bleaching clays.)

11 CLAYS AND SHALES FOR LIGHTWEIGHT AGGREGATE

Physical and Chemical Properties in a Clay or Shale.

(1) It must contain a compound that will dissociate with the formation of gas or gases at the temperature at which the material is in a pyroplastic condition.

(2) It must have a high viscosity when in this condition so as to trap the gases and so that the surface tension of the particles is great enough to draw each particle mass together and minimise agglomeration of the particles into a clinker.

(3) It must have a wide vitrification range to allow easy temperature control below the temperature at which sticking and agglomeration become excessive.

A fraction of 1% of gas-forming compound is all that is necessary for good bloat, therefore condition (1) is not so important as high viscosity and wide vitrification range.

Desirable properties in expanded aggregate.

(1) Light weight - approx ½ the weight of the standard aggregate is replaces.

(2) Strength

(3) Absence of sharp edges and corners

(4) Low water absorption to avoid dehydration of the cement

(5) Uniform size gradation

(6) Chemical inertness

(7) Low production cost.

(1) Light weight is desirable in order to make a concrete that

effects a worth while saving inweight; the light aggregate should not weigh more than half as much as the standard aggregate it replaces. Because rock or gravel aggregates have a bulk density of approximately 100 pounds per cubic foot, that of the ideal light weight aggregate should be less than 50 pounds per cubic foot;

(2) Strength is essential and the individuel particles of aggregate should be as strong as possible. For a concrete of a given strength, a stronger aggregate will require less cement than a weaker one, resulting in a saving of both cost and weight.

(3) Absence of sharp edges and corners is preferred for the ideal aggregate should have a well-rounded, preferable spherical surface. Aggregate particles having sharp corners or an oblate configuration make a rather harsh concrete mix, which is difficult to work into forms around reinforcing bars and also tends to honey comb;

(4) Low water absorption is desired because, when made into concrete, an aggregate with a tendency to absorb water tends to dehydrate the cement, with a resulting deleterious effect upon the setting of the concrete. Pre-soaking can compensate, however, to some extent for any short comings the aggregate might have with respect to water absorption;

(5) Size gradation is a rather important requirement to ensure good work ability, as the aggregate must be composed of a range of sizes, including sufficient quantity of fines. This is particularly important where it is necessary to work the concrete into complex forms or around reinforcing bars;

(6) Chemical inertness of the aggregate is an advantage, and compounds that would tend to react with the cement and affect its setting should not be present;

(7) The cost of the aggregate is the ultimate factor that

determines its acceptability. The initial extra cost per cubic yard over sand, gravel and crushed rock aggregates must be offset either by savings in weight that permit elimination of some reinforcing steel and lighter-weight forms or the attainment of better thermal and soun-insulation qualities. A saving in foundation can be made, or an increase in height of a building made.

Laboratory testing of clays and shales to determine bloating properties.

(1) C.S. & I.R.O. method by R.D. Hill and F.A. Blakey.

Small quantities of clay being tested are heated in an oil-fired stationary kiln capable of extremely rapid heating (up to 200°C per minute) so that a heating schedule and kiln atmosphere similar to that which would occur in practice can be obtained. The extend and temperature of bloating can be determined and quick tests can be made to determine the effect of additives on poor bloaters. Clays considered suitable as a result of the small-scale tests are then processed on a larger scale in a pilot rotary kiln.

Clays with suitable bloating properties are tested for the production of aggregate.

The clay or shale is partly dried and ground to ensure uniformity of composition, and then formed into pellets in a rotary cylindrical pelletiser. (A fine spray of water is played on the dried powder as the pelletizer rotates and round pellets of clay are formed around the droplets by the rotary action. The size of the pellets is varied by varying the proportion of water, size of drops and rate of rotation).

Pellets for coarse aggregates are produced from $\frac{3}{4} - \frac{1}{2}$" and $\frac{1}{2} - \frac{1}{8}$" and fine aggregate is made from pellets from $\frac{1}{8}$"

down.

Each size range is forced separately with a different firing schedule in a pilot rotary kiln 8" in diameter and 9 feet long. The rotary kiln method of production was chosen in preference to the sinter grate process because the approximately spherical coated aggregate from the rotary kiln produces concrete of higher strength weight ratio and better workability than the crushed angular aggregate from the sinter grate process. These advantages probably out-weight the higher cost of the coated type aggregate.

Many clays or shales which will bloat in the stationary furnace are not suitable for expansion in the rotary kiln because of their tendency to stick together before the bloating temperature is reached.

(2) U.S. Bureau of Mines investigation 4401 by Conley and others.

Clay or shale sample dried and reduced to uniform size by means of crusher and rolls and quartered down to 400 or 500 grams weight. This portion then reduced to minus 20 mesh. From the ground portion a few grams removed for chemical analysis and pH tests. Remainder dried at 110°C overnight. 100 gram portion given the Atterburg test to determine the water of plasticity. Small briquettes are hand-moulded to approx. 1" x 1½" x ¼". These are then allowed to dry out at room temperature or in 105°-110°C oven. Degree of drying or time has little effect or bloating.

Bloating characteristics are tested in globar electric furnace to approximate performance in rotary kiln i.e. slow rise in temperature then sudden flash heat. In laboratory two separate heat treatments for clay.

(a) Specimens are heated from room temperature to bloating temperature in about 2 hours, trials withdrawn between 982°C and 1371°C.

(b) Once furnace is clear of slow run (a) specimens it is not allowed to cool but kept at high temperature. Another set of specimens is inserted quickly and removed at intervals of 5, 10 and 15 minutes or longer. This flash heat treatment is repeated for several diffence temps. Between 982°C and 1371°C, to cover bloating range of clay in question.

Study of both slow-run specimens and the flash-heat specimens is then made. Most naturally bloating clays will show some signs of bloating during slow run, but usually considerably more in flash-heat treatment.

Many clays that bloat well under flash treatment show no indication of bloating under slow-run.

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Appendix 1 - Glossary

Binding power	- property clay possesses of uniting with non-plastic material and water to form a uniform plastic paste.
De-airing	- a process for improving plasticity of a clay and removing air bubbles from it. The extruded clay is not so easily broken when de-aired. The de-airing equipment if connected to an ordinary pug-mill and a vacuum of about 27 pounds/per square inch pressure is produced.
"Fat" clays	- clays with high binding power
Flux	- a substance added to a clay to assist fusion; any material which reduces the fusing - point of a clay to which it is added. It usually refers to lime, magnesia, soda, potash and their compounds but has really a much wider meaning and may include almost any impurity present in a fireclay.
Grog	- burned glays used to reduce shrinkage of plastic clays. Grog is an important ingredient in the manufacture of refractory goods as it enables then to with-stand sudden changes in temperature.
"Lean" clays	- clays deficient in binding power.
Refractory	- implying a difficulty in fusion (dictionary definition.) In technology usually refers to material used in the construction of furneces, flues, crucibles etc., on account of their resistance to heat.
Saggers	- oval or cylindrical receptacles made of fireclay with a flat bottom about 20 inches in diameter and a height of about 8 inches; they are used for protecting the ware (tiles, porcelain and other pottery) in the kilns.
Salt-glazing	- represents the simplest form of glazing. The wares are placed in the kiln unprotected from the flames. As soon as the kiln has reached its highest temperature, salt is put in the fireplaces at regular intervals of time. When the salt is placed in the fires heat volatilises it and the vapours in passing up through the kiln units with the ware, forming a glaze on the surface.
"Short" clay	- refers to a clay which does not possess a great deal of plasticity on extrusion.
Slip or slip-clay	- a clay containing such a high percentage of fluxing impurities and of such texture that at a low cone it melts to a greenish or brown glass, thus forming a natural glaze. It must be fine-grained, free from lumps or concretions, show a low air-shrinkage and mature in burning at as little above cone 5 (1230°C) as possible.

APPENDIX 2 - SUGGESTED CLASSIFICATION OF CLAYS.

Clays arranged in order of purity or refractoriness

1. HIGHLY REFRACTORY CLAYS

Name	Types	Mineralogical Constitution	Mode of Origin	Notes	Uses
	Residual		final product of weathering of granites, pegmatites and other feldspathic rocks	coarser grained, less plastic, lower strength and firing shrinkage compared with sedimentary kaolins; clay pseudomorphs after feldspar	Finest china ware e.g. Wedgewood china
a. KAOLIN	semi-kaolinitic material	kaolinite, plus quartz, mica and other resistant minerals	partial weathering of granites etc.	plasticity absent or slight; little combined water	porcelain, china ware, refractories when suitable, with decreasing purity, pottery and structural clay products
b. BALL CLAYS		kaolinite or kaolin minerals as chief constituents	apparently deposited in swampy lakes	plastic, dark clays; burn to white or cream body. Finest grained of transported clays. Distinguished from kaolin by greater toughness and plasticity, better bonding power and lower refractoriness.	china, fine earthenware and as bonding material for harder and less plastic clays in refractories and stoneware. In whiteware bodies they play and dual role in increasing the plasticity of the raw mix and the content of flux.
	refractory bond clays	? each of clay minerals in substantially pure form (no data available)	probably deposited in swampy lakes	essentially ball clays with long range vitrigication, high final fusion and plasticity.	glass refractories, graphite crucibles and similar products; sanitary ware and to give plastic and fired strength to various non-plastic or weakly plastic materials
	flint fireclays	well-crystallised kaolinite in extremely small particle sizes	dynamically metamorphosed or compacted shale variety of original finely divided plastic clay	represent a dynamically metamorphosed or compacted shale variety of finely divided plastic clay. Hard anddense and break with conchoidal fracture. Little natural plasticity.	mixed with plastic clay, they act as a grog (highly burnt clay) in firebrick manufacture
c. FIRECLAYS	refractory shales	chiefly mellorite	deposition of sedimentary clays with subsequent consolidation by pressure	intermediate between refractory bond clays and flint fireclays	firebricks
	common fireclays. (low heat duty)	either kaolinite or illite or a mixture of these. If fireclay is calcareous, illite sole component	coal measure environment (swampy)	buff or light brown firing colour, represent impure residual or sedimentary kaolins	firebricks and refractories that do not have to withstand vary high temperature, May also be used for structural ceramics

2. SLIGHTLY REFRACTORY CLAYS

Name	Types	Mineralogical Constitution	Mode of Origin	Notes	Uses
a. RESIDUAL CLAYS.	montmoril	montmorillonitic, illitic and kaolinitic minerals, plus quartz, feldspar, mica, rutile and ziron	weathering of rocks in situ	coloured clays, low refractoriness	with the exception of the montmorillonitic clays, used for a wide variety of structural clay products, pottery, terra cotta and the better types for low duty firebricks
				alluvial-soft, usually plastic materials little or no fissil, structure	give a variety of structural and pottery clay products
	unconsolidated clays	contains each of the clay minerals in substantially pure form	alluvial, colluvial, windborne or glacial	windborne (loess) - varies from coarse silty to finely divided plastic clay. High shrinkage glacial - mixture of unassorted boulders, sand, gravel and clay	used only to a small extent for red burning structural ware.
	mudstones	- ? ditto - (no data available)	slightly indurated sediments (mud)	fine-grained, non-laminated, slightly indurated sediments; can be easily worked	
b. SEDIMENTARY CLAYS	bedded clays	contains each of the clay minerals in substantially pure form.	compaction of clays	intermediate in compaction between mudstone and shale. Distinct lamination	various types of structural ware.
	shales	dominant clay mineral is illite chloritic mica common, also kaolinite montmorillonite in Mesozoic or younger shales	deposition of sedimentary clays on sinking sea-bed and subsequent consolidation by pressure	Feebly plastic on first mining	pressed bricks; tile and pipe making as a shortening admixture for plastic clays.
	metamorphosed sediments (slates, phyllites and mica schists)	illites, chlorites, micas and mixed layer minerals. Montmorillonite, attapulgite-sepiolite or halloysite clay minerals not reported in slates	dynamo-thermal metamorphism of argillaceous sediments	almost complete absence of plasticity in native state	brickmaking by the semi-dry press methods, Paving bricks, acid-resistant ware and as admixture for stoneware
	arenaceous sediments (grits, sandstones, greywackes, siltstones arkoses)		compaction of arenaceous sediments in differing environments	can be utilised if sufficiently argillaceous	bricks by semi-dry press method or for admixtures for tiles, pipes and other structural clay products.