

CLAY.

LECTURE BY

MR. R. H. WORTH, M.INST.C.E., F.G.S.

(Read 16th November, 1911.)

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FROM the dictionaries and textbooks immediately at hand the writer has compiled the following description :—

**CLAY.**—“A common earth of various colours, compact and brittle when dry, but plastic and tenacious when wet. It differs from mud mainly in being more or less tough and plastic. Dry clay gives forth an argillaceous odour when breathed upon; and when it is moistened with water it is rendered plastic, and can be moulded without subsequently losing its shape. The plastic nature of clays when freshly collected, and their easy sectility when dry, the cut surface appearing polished, are characters known to every one. In many respects it varies so much that no general description can be applied to it.”

*Plasticity* and *tenacity* when wet, *sectility* and *brittleness* when dry, are to be regarded as essential to the definition of this substance; less obvious properties are, the power of forming with large quantities of water a mixture from which the finer particles will not separate except after long standing, and the ability, when in a dry compact state, to resist tensile stress.

None of these properties are ever absent from any clay, but all may vary in the degree to which they are developed in particular samples.

Just as all clays have certain qualities in common, more or less marked, so they all have one and the same essential constituent in greater or less proportion. This essential is *hydrated silicate of alumina* ( $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$ ), a substance familiar in a relatively pure state as “China Clay” or “Kaolin.” This we may take as the true clay substance, although later it will be seen that more highly aluminous silicates, and even hydrates of alumina devoid of silica, have a claim to be included as constituents of pure clay.

Varying with its origin and the amount of foreign matter present, the particles of a mass of clay may vary greatly in size. For many purposes, such as brick and tile making, foreign matter, silica sand and the like, is treated as part of the clay. There may thus be present a fair percentage of particles of over 1 mm. in diameter.

Segar's definitions for grading are as follows:—

|                                        |                           |
|----------------------------------------|---------------------------|
| Coarse sand—over 0.33 mm. in diameter. |                           |
| Fine sand                              | „ 0.04 mm. under 0.33 mm. |
| Dust sand                              | „ 0.025 mm. „ 0.04 mm.    |
| Silt                                   | „ 0.01 mm. „ 0.025 mm.    |
| Clay                                   | „ 0.01 mm.                |

In point of fact it may generally be assumed that very little true clay substance will be in particles of over .003 mm. (.00012 inch) in diameter, and certainly none will be in particles of over .01 mm. (.0004 inch) in diameter.

The following mechanical analysis of an American brick clay of loamy nature may be taken as a fair example of one class of impure commercial clays.<sup>1</sup>

|             |              |                |                 |             |                    |
|-------------|--------------|----------------|-----------------|-------------|--------------------|
| Above 1 mm. | 1 to .05 mm. | .05 to .01 mm. | .01 to .003 mm. | Below .003. | Hygroscopic water. |
| 5.19        | 22.44        | 32.06          | 14.15           | 23.55       | 2.59%              |

This clay unburnt has a porosity of 22.43 %, and burnt 25.27 % by volume. Although not very plastic it is, when dry, a strong clay. To all intents it consists of 76 % of sand bonded by 24 % of clay. It is quite satisfactory as a brick material, moulding, drying, and burning to a good shape.

It is surprising how small a proportion of true clay is necessary to give strength to a mixture with sand and gravel, when once thoroughly incorporated and allowed to dry. The “cob walls” of Devonshire, formed as they are of mere clay soil, are sufficient proof of this.

**Plasticity** may be defined as the property of yielding and flowing readily under moderate degrees of pressure and stress, and of presenting absolute resistance to lesser pressures and stresses. Thus a plastic clay may be moulded to a definite shape, which, if properly proportioned, will not deform under its own weight. To develop to the full its plastic character the clay must

<sup>1</sup> Beyer and Williams, *Technology of Clays*.

have incorporated with it an appropriate proportion of water. With too much water the impressed shape will not be retained, with too little water the clay will break rather than flow.

There is no satisfactory measure for plasticity, none which will give numerical results correctly comparable with varying samples of clay. Plasticity in clay, like hardness in other minerals, is a quality the variations of which are readily recognised in practice, but for which no reliable physical unit has yet been devised.

**Strength** is best measured in the dried plastic mass. The ordinary test is for tensile strength, and is made in the same manner as is adopted for the testing of Portland cement. A briquette is prepared, the cross section at the centre of which is square and may be accurately measured, the ends expand in such manner as to afford a grip for the jaws of the testing machine. One of these jaws is fixed, the other is movable. The briquette, gripped by both, holds them together, the movable jaw is drawn away from its fixed companion by a constantly growing load, the amount of which can at any moment be accurately ascertained. A point is reached at which the strain upon the briquette becomes too great for its cohesion and it breaks. The area of cross section of the briquette and the precise pull at the moment of fracture being known, the ultimate strength in tension per square inch, or other unit, of the particular sample of dried clay is a matter of simple calculation. With due precaution reliable and comparable results are obtained.

As is frequently the case with brittle substances, dried clay presents a quite considerable resistance to tensile strain; strengths up to 300 lbs. per square inch may be met with. Clays tested while still damp from moulding, but the shrinkage of which has nearly reached their limit, are much weaker, and 50 lbs. per square inch or a little over is near the extreme.

Beyond doubt there is a general correspondence between strength and plasticity, but particular instances are not infrequent which prove that the one is no constant function of the other. More especially the dry tests may be misleading. At the other extreme, tests with clay which contains exactly the proportion of water required to develop its greatest plasticity yield concordant results, and strength is then the measure of plasticity. But clay in this condition imposes mechanical difficulties in the test, and the best compromise for practical purposes is to use briquettes

which are still moist but have nearly shrunk to the dimensions they would have when dry.

There is no one quality in which clays differ so widely as in plasticity, while still retaining similarity in chemical composition. And there are few points on which experts so thoroughly disagree as on the determining factors which make toward this quality.

At the extremes very pure clays, such as kaolins, and very impure clays, such as loams, may both be deficient in plasticity; while intermediate grades, but little less or little more pure, may leave nothing to be desired.

Wheeler experimented with Calcite and Gypsum, and found that by finely grinding these materials a plastic mass could be formed on the addition of water; the substances thoroughly dried after kneading and moulding bore tensile strains of 100 lbs. and 350 lbs. per square inch respectively. Slate also can be so ground as to form a plastic mass. Physically the feature common to these mineral substances and to clay is the form of the constituent particles, which in each case is tabular or lamellar.

Other substances, such as glass, which do not yield lamellar forms on grinding are practically non-plastic, no matter how extreme the fineness of such grinding; yet yield some increase in plasticity in proportion to their fineness. Clays already plastic become more eminently so on grinding.

It would appear, therefore, that the form of the clay particles is the origin of the plasticity of the mass; this form would be most characteristically developed in the smallest particles, the proportion of surface to cubic content in which would also be greatest.

As usual, however, in seeking the explanation it is necessary to recognise that the most potent is rarely also the only influence at work. The presence of a colloid substance in clay may, and in fact almost certainly does, increase its plasticity. Thus a two per cent solution of tannin has been found to exercise material influence in this direction; it is evident, therefore, that impurities may in some cases bring with them an increase in this valuable property.

It is necessary for the development of plasticity that the particles shall come within a certain minimum distance from each other. Probably one of the principal reasons for the low plasticity of china clay is that the process of manufacture tends to separate

the particles. Certainly clay taken direct from the decomposed felspar crystals in the pit is much more plastic than clay from the "dry" after manufacture. Long standing undisturbed in a moist state increases the plasticity of china clay, probably by allowing the particles to approach each other more closely.

Coincident with plasticity is the property of forming a "puddle" resistant to the passage of water, and hence of value in engineering work where waterproof surfaces or dams are required. In each and every clay there is a certain proportion of admixed water which is necessary to the formation of the best puddle. Exceed this fixed proportion and tenacity and impermeability are alike lessened. A total loss of both ensues at the point at which the clay particles are so far separated by intervening water that each has a free range of movement practically uninfluenced by the attraction of the surrounding particles and unrestricted by the surface tension of the water. The tendency to flocculate or gather in groups of constantly increasing closeness and density may almost disappear if very fine particles are once discretely suspended in large proportions of water. This matter will be more fully dealt with later, but since an electrolyte added to water holding clay in suspension will at once initiate flocculation and agglomeration, it would be of interest to ascertain what influence such a substance would have on the puddling properties of various clays. Inasmuch as it tends to a greater freedom of movement of the particles of clay in water and a nearer mutual approach, it would evidently tend also to a closer and denser mass, but one more liable to part with any small excess of water used in its formation, and hence to shrink. The ultimate effect on the value of the material as puddle might readily be argued to be either useful or detrimental, and only careful experiment could decide the point.

**Impurities.**—If we take *kaolinite*,  $\text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2 \cdot 2 \text{H}_2\text{O}$ , as true clay substance, there are associated with it, as it usually occurs, various other bodies in greater or less proportion. Some of these are harmless, some injurious, and some for defined uses of the clay are beneficial.

Of the harmless, or even beneficial, is *Pholerite*, a more aluminous silicate than kaolin. No definite determination of this mineral in English clay is known to me. But it has been proved

to occur in some Missouri clays, which in instances reach 43 % of alumina, whereas kaolin carries but 39.2 %.

Equally harmless, probably useful, are the hydrous oxides of aluminium, more especially *gibbsite* ( $\text{Al}_2\text{O}_3\text{H}_3$ ). Some Dartmoor china clays, notwithstanding the free silica which remains as traces after even the most careful washing, show a higher percentage of alumina than does pure *kaolinite*, and obviously either *pholerite*, *gibbsite*, or some similar compound must be present in small quantity.

Whether derived from the decomposed granite, or from the slates bordering it, Alumina as an hydroxide is present in considerable quantity in at least one spring water of Dartmoor. From Mr. Pode I have received samples of a deposit which forms in boilers fed with water rising at Rook, near Cornwood, the analysis of which deposit is as follows :—

|                                   | per cent. |
|-----------------------------------|-----------|
| Vegetable fibre . . . . .         | 1.00      |
| Other organic matter . . . . .    | 0.50      |
| $\text{SiO}_2$ . . . . .          | a trace   |
| $\text{Al}_2\text{O}_3$ . . . . . | 33.00     |
| $\text{Fe}_2\text{O}_3$ . . . . . | 1.00      |
| $\text{CaCO}_3$ . . . . .         | 0.50      |
| $\text{MgCO}_3$ . . . . .         | 14.75     |
| Water and undetermined . . . . .  | 49.25     |

This is a distinctly unusual deposit to be obtained from the evaporation of a spring water.

For nearly all purposes, *iron* in any form may be taken to be a deleterious impurity. In bricks and tiles in which a red colour is desired, or in some bricks which are to be vitrified, iron may be not merely harmless but essential. This metal may occur in a variety of combinations, the most interesting of which is *nontronite*,  $\text{Fe}_2\text{O}_3, 2 \text{SiO}_2, 2 \text{H}_2\text{O}$ , the hydrated ferric silicate which corresponds to the aluminic kaolin. Nontronite is not, however, a very stable substance.

The *Hydroxides* of iron when present in clay are usually fairly uniformly distributed through the mass, but sometimes segregate. In china clay they are more often local, and their presence frequently corresponds to variations in the original granite, sometimes to secondary variations such as occur in veins and joints.

In a clay work near Cornwood, iron oxide occurs in an intensely localised form. The late Mr. H. T. Mundy first drew the writer's attention to this. In the clay rock, along planes which are evidently veins with secondary silica, there occur small hard masses of flattened form, harmless while intact. Once broken, they prove to have a hard outer crust only, the interior being filled, or nearly filled, with a powdery substance consisting of finely divided silica and red iron oxide. The outer case is mainly granular silica in quartz grains, with a little interstitial oxide of iron, the whole thoroughly cemented together. It need hardly be said that, if the presence of such a mineral purse is suspected, every care is taken to avoid breaking it.

In the ball clays, iron occurs, in addition to its possible presence as hydroxides, in two especially harmful forms, in both of which it is a secondary mineral, formed after the deposit of the clay. For it is a feature of the ball clays that they are detrital in origin.

As *pyrites* of the *marcassite* type it is singularly objectionable. It may be present as minute specks that are hardly to be detected with the aid of a hand lens. But each such speck, from its fluxing and staining properties, means a black glassy bleb or blister in the finished ware.

Or the pyrites may be found in a quaint variety of larger forms, the origin of which is not known, although their growth in size can be understood, once granted a nucleus. Even through a plastic clay in its most resistant form there is a constant if extremely slow circulation of water carrying mineral matter in solution; and the growth of any mineral, especially when crystalline, by the addition of like substance is no matter for surprise, granted the presence in solution of the necessary constituents. As regards *iron disulphide* ( $\text{FeS}_2$  pyrites) it is known to be formed by the interaction of organic matter and water charged with iron sulphate; solutions of alkaline sulphides acting on iron oxides are another possible source, and organic matter may supply the necessary sulphides by the reduction of soluble sulphates.

The ball clays are associated with considerable masses of ancient vegetable matter, and mostly contain some in their own substance. Such vegetable matter not only affords a nucleus for the formation and concentration of the *marcassite*, but, since sulphur is widely distributed both in the animal and the vegetable economy,

may also be one source of the supply of this element to the compound.

Clay iron stones also occur in ball clays and in the clays associated with the coal measures; in these the iron is in combination as a carbonate. Provided the carbonate is in fairly considerable masses it may pay to pick it from some clays, but finely disseminated it is a fatal impurity.

*Carbonate of lime* is not infrequent in secondary or redeposited clays; it is harmless in a small quantity and where bricks or wares are not intended to be vitrified, in which latter case its fluxing qualities may lead to disaster unless the amount of the mineral is small. It is allowed to find admission to the body used in the manufacture of porcelain, the Cornish stone which is added to the clays in the preparation of this body being frequently ground in pans floored with chert, and the chert stones, which necessarily wear away in the grinding process, contain appreciable proportions of lime carbonate. As sulphate, lime is wholly injurious.

In china clays derived from granites in which lime feldspars formed part of the original constituents, lime remains mixed with the kaolin, but in reduced quantity, and never in harmful proportions. It may possibly be present as carbonate, but this matter has never been determined.

The *alkalies* are also present in clays, and act as fluxes, reducing the resistance of the material to fusion. In good china clays they should be in merest trace or entirely absent; in seconds china clays, where feldspar only partially decomposed and where mica may be present, the alkalies are rarely wanting. They are always to be found in ball clays, partly from the existence of the same traces of feldspar and mica, partly from the absorptive powers of the clay which retains potash and other soluble salts, and may thus gain in alkalies by robbing the very slowly percolating waters.

Free *silica*, either as wholly impalpable powder or as sand of varying degrees of coarseness, is practically never absent from any clay, but in some washed china clays there is very little free silica.

**Origin.**—All clay is originally derived from the alteration and hydration of feldspathic minerals, a process involving a loss of

alkalies and of silica and the addition of water. Some clays are first-hand, such as china clay which has never been removed from its parent rock, but the separation of which is an artificial process. These first-hand clays are always found mixed with the non-feldspathic minerals of the rock from which they are derived. Relatively unmixed masses of clay, found under natural conditions, have all had a detrital origin and are the product of natural processes of levigation; some such masses may not only be second, but third or fourth hand, or may indeed have had a long and very varied career.

Thus a feldspathic rock may be altered and then removed by denudation, and the products carried by a stream into a lake of sufficient area and depth. Here the delta of the stream will be formed by the sands and gravels, while the minute clay particles will be carried further into the lake and subside on its floor as relatively unmixed clays. Or the same clay particles may be carried to sea and may settle in small quantity where a chalk or limestone formation is in its first stage of growth; as a constituent of the chalk or limestone rock ultimately formed the clay is second-hand. In the course of the earth's changes the chalk or limestone may be subjected to solvent action which will remove the carbonate of lime, but which will be powerless to dissolve the included clay, and from large masses of lime rock much smaller beds of third-hand clay may be derived. From these in turn by heat, by pressure and other agencies new feldspathic minerals or dehydrated porcellaneous rocks may be formed, the ultimate decomposition of which must be taken as the commencement of the history of new clay particles. But on the other hand the clay derived from the lime rock may go through many further stages of existence without chancing upon the conditions requisite to make it the raw material for the constitution of feldspathic minerals, or to dehydrate it.

In this respect clay resembles silica, that the grains of a sandstone may have had long individual existences in geologic time, the minute particles of clay may have similarly retained their individuality.

**China Clay.**—The most interesting source of clay is the feldspar of granite, and the granites yield the most extensive and commercially important masses of kaolin-bearing rock.

The possible metamorphoses of the feldspars of granite are very varied; a few only are of present interest.

1. The feldspar may be entirely removed, leaving a hollow space in the rock in the form of the original crystal.
2. The feldspar may be entirely replaced by tourmaline, with which will usually be associated a little quartz.

This alteration will sometimes occur in rocks which show practically no further trace of tourmalinisation and rarely accompanies any development of kaolin. It is noteworthy that it then takes two forms.

- a. The replacement of the larger order of feldspars only, the smaller feldspars and the felsitic ground mass remaining unaltered.
- b. The replacement of the smaller feldspar and the felspathic materials of the ground mass, the larger feldspars remaining unaltered.

Both 'a' and 'b' are common in parts of Dartmoor. The former appears to have escaped notice hitherto, but, for three or four miles on the southern border, well-marked specimens may readily be obtained.

- c. When all feldspar alike is attacked a quartz schorl rock results, in which the mica also has usually disappeared.
3. The feldspar may be entirely replaced by quartz, having perhaps been first kaolinised, but this last suggestion awaits proof.
4. The feldspar may be altered to kaolin.

Other types, such as the formation of cassiterite pseudomorphs after feldspar, the development of mica, of fluor spar (in exceptional instances), and of epidote may here be neglected.

The kaolinisation of granite is always associated, at least where well developed, with the presence of tourmaline and quartz of secondary origin, but these secondary minerals may largely be confined to veins traversing the rock. Bunches and veins of tinstone frequently occur in china clay, and there are evidences of fluorine-bearing minerals.

On the other hand neither secondary tourmaline, secondary quartz, tinstone, nor fluor spar are invariably or even generally

accompanied by kaolin. A tin lode in granite will not infrequently have a few kaolinised feldspars present in the rock immediately bordering it, but these are sporadic. Tourmaline even where pseudomorphous after large feldspars is often found in association with granite which is otherwise but slightly altered. Veins of secondary quartz traverse the hardest and freshest rocks, and the finest known development of fluor spar on Dartmoor occurs at Meldre in the dyke of Muscovite granite, in which the feldspars have lost none of their alkalies. It is true that in this latter case the feldspar alkali is chiefly soda. But *Trowlesworthite*, and other highly fluoriferous granites of Dartmoor, confirm the evidence. (To avoid possible misunderstanding it may be necessary to note that feldspars entirely free from any and every form of alteration are practically unknown in granite.)

The kaolinisation of feldspar has been attributed to various agencies—to the action of humic acids, of carbonic acid waters, of fluoric and boric emanations. In each case confirmatory evidence can be adduced. But the kaolinisation of feldspar does not necessarily mean the production of a valuable deposit of china clay, and this latter is an especial case which requires individual consideration.

Humic acids derived from the peat and carbonic acid waters from the same source are constantly present over large areas of our Western moorlands, and the granite has long been subjected to their action, but the product is not china clay rock. Locally known as "growan," it is a decomposed granite, stained by peat, occasionally with a clayey texture, sometimes in part resembling a laterite. It may be dismissed very shortly with the statement that it is doubtful whether its resemblance to china clay rock has ever been close enough to deceive a prospector. If it be argued that carbonic acid derived from subterranean sources has in the past accomplished the work which surface agencies now fail to perform, then this argument lacks certain confirmatory evidence; there is a notable absence of carbonates in both the granite and its surrounding metamorphic rocks. On the other hand the marked association of boric and fluoric minerals and the clay rock is at least suggestive that compounds containing boron and fluorine have played their part in its origin. Mr. J. M. Coon believes that the action of fluorine is still continuing, and that water falling on Dartmoor passes through the buried granite rocks and

then rises in the Cornish hills, having acquired fluorine compounds on the way, and being thus enabled to attach the felspars of the Cornish granite and continue in these days the production of china clay. But his suggestion as to the source of the water is founded on an unproven assumption. He states that more water flows off some of the Cornish moors in the rivers than ever falls upon them as rain. Until reliable river gaugings and good rainfall statistics are available, this may well be doubted, and even if it be proved, some other source than Dartmoor must be found for the surplus. Certain Dartmoor watersheds, typical in character, have been utilised for water supply purposes, the rainfall and the flow of the rivers both being accurately ascertained; in the result it is found with certainty that no balance of available rainfall exists over yield of the watersheds, and Dartmoor has no excess for her Cornish neighbours' use. There is also china clay on Dartmoor, and that in its origin could not by Mr. Coon's theory be similar to the Cornish clays, in so far at least that its formation cannot be continuing.

Kaolin is a hydrated silicate, containing 13·7 per cent of water, and any theory which assumes to explain the chemical changes involved in the production of kaolin from felspar must also account for the necessary supply of water of hydration. Granite previous to and after solidification certainly contains some water either as liquid or vapour, but it is not conceivable that it should be capable of self-hydration. Springs, hot or cold, rising through the granite could only be fed by meteoric water, hence, at the time of the formation of the china clay, surface waters must have had access to the rock; they may, however, have penetrated to some considerable depth to reach it. The theory now propounded involves concurrent action of upward gaseous emanations from the cooling granite, and of meteoric water travelling downward through a cap of altered sedimentary rocks to the surface of the granite. Where these met at the junction plane of granite and sedimentary the conditions for kaolinisation existed. The action would be most marked where the water first reached the plutonic rock, and would die out downward, hence as regards the granite boss the formation of china clay would be mainly a surface phenomenon, although by following lines and directions of least resistance it might occasionally result in a horizontal extension from a mass of clay

under unaltered granite. If, as is probable, the whole process was confined to the later stages of cooling of the granite, when its surface was at a temperature below the boiling point of water (allowance being made for the rise of the boiling point due to pressure), then it took place beneath the cap of altered sedimentary rock, and the removal of that cap by denudation must have exposed a much larger area of china clay than is now to be found on the moors. At Smallhanger, near Plympton, a patch of altered slate, now a tourmaline schist, is still to be seen in place above the clay.

Once exposed, the clay rock would fall an easy prey to further denudation, and its removal would not only uncover unaltered granite, but would supply the material necessary to form the ball clay deposits of Bovey and Newton in the south of Devon and of Peters Marland in the north.

The clay beds still left on Dartmoor are either in positions protected by rims of granite and held by these as in basins or are in places where the granite has suffered little or no denudation and where the sedimentaries are not even now completely removed. Indeed there is evidence everywhere on Dartmoor where clay is known to exist that the present surface is not far below, but is practically at the original surface of the buried granite mass, and fragmentary patches of sedimentary rocks still persist associated with the clay. The relatively large proportion of clay area to unaltered granite area in some parts of Cornwall is partly explained by the lower level of these Cornish moors as compared to Dartmoor, and the consequence that the former have lost much less of their original bulk than has the latter. In Cornwall also the observation holds good, that wherever china clay is found there is evidence of the depth of the present surface beneath the plane of contact of the granite and the sedimentaries being but slight. A valuable item of this evidence is the occasional occurrence of a contact felsite which cannot be distinguished from the red contact felsite from Dartmoor, described by the writer in his papers on the petrography of Dartmoor, published in the Transactions of the Devonshire Association.

Inasmuch as the cap of altered rocks would at some places be much more pervious than at others to meteoric water, partly from fissuring and faulting, and since the gaseous emanations from the

granite would also be a quantity varying from point to point, any action dependent upon the joint operation of the two would tend to be localised, and kaolinisation would be by no means universal over the surface.

Bearing in mind the observation by Barus that felspar in the Comstock rock is not affected by the continued action of steam at 100°C., and experimental evidence pointing in the same direction, we may probably conclude with safety that water and not steam was responsible for the hydration of kaolin. Such water, in consequence of being under pressure, may have been at a higher temperature than 100°C. No downward limit of the temperature at which the change from felspar to kaolin took place can be assigned, beyond the fact that it obviously would not be less than the temperature of the surrounding ground. An upward limit is hinted at by the experimental research of Messrs. Mellor and Holdcraft, who conclude<sup>1</sup>—"The circumstantial evidence, therefore, all points one way. Kaolinite at temperatures near 500° (C.) decomposes into free silica, free alumina, and water." Below this temperature of disassociation the temperature of formation must be assumed to have lain.

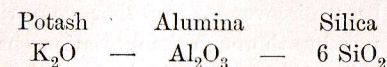
If meteoric water descending to the rock, and gaseous emanations ascending through the rock, conjointly effected the change in the felspar, then the surface of the granite, and the higher levels of the resultant clay, would be subjected to the action of water charged with mineral matters in solution, derived from the rocks above, and iron stains and other impurities might result, but by filtration and chemical action the water would in this sense become purer as it penetrated into the granite, and the lower levels of the clay would be less contaminated; and if we take the gaseous emanations as being the principal cause and the water a secondary necessity for the alteration, it would be in the lower levels to which the water penetrated that the gaseous influences would be most concentrated and there the alteration of the felspars would be most complete. Which meets, but in different manner from his suggestions, some of Mr. Coon's requirements. While another is met, if instead of assuming that the physiographical features of the clay districts had assumed their present condition when the kaolinisation was commenced, we remember the evidence that the present surface where

<sup>1</sup> "Constitution of the kaolinite molecule," *Transactions of the English Ceramic Society*, Vol. X, Session 1910-11, Part 1.

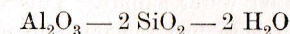
clay exists is practically the original upper surface of the granite where it met the sedimentaries.

It is interesting to discuss the change in volume involved in the conversion of granite into clay rock; for this purpose it is convenient to arrange the chemical formulæ involved as though the molecules were built up of associated oxides, disregarding their probable true constitution.

Their orthoclase felspar would be represented by



From which must be removed  $\text{K}_2\text{O}$  and  $4 \text{SiO}_2$ , and to which must be added  $2 \text{H}_2\text{O}$ , to form kaolinite of composition



The weight of the original orthoclase being 554.78, that of the derived kaolinite would be 257.12.

Now the specific gravity of orthoclase is 2.56, and that of kaolin is 2.61, so that the original volume of  $\frac{554.78}{2.56}$  has been reduced to  $\frac{257.12}{2.61}$  or in the proportion say of 217 to 99, a loss of 56 per cent, nearly.

Hence if there were no interstitial spaces the reduction in volume of the altered rock would be considerable, always assuming the silica not required to form kaolin to be removed, as also the alkali.

A normal granite may well contain 60 per cent of felspars, which may be completely kaolinised, thus losing 56 per cent of their original volume; the loss to the rock as a whole would be 56 per cent of 60 per cent or a little over one third. But the rock never shrinks to this extent, there is also free water present, in addition to the water of hydration, and this not infrequently amounts by weight to 12 per cent, whereas granite does not usually contain more than 1 to 2 per cent at the extreme. This added water would bring down the loss of volume to from 7 to 8 per cent or even less. It is certain also that some at least of the silica is redeposited in the body of the clay rock itself, or in veins traversing it, to the further reduction of the loss. None the less, all things being considered, there is probably a reduction of from 4 to 5 per cent in volume consequent upon the conversion of a

mass of granite into a mass of clay rock. From the manner in which all the forms of the original constituents are preserved in the altered rock, and from the absence of any indication of crushing, further proof may be gained of the comparatively small alteration in volume. Nor has there ever been found in Devon or Cornwall any evidence of an increase in volume due to kaolinisation and attendant alterations, although theoretically there might exist conditions which would lead to an increase. Granites have been discovered, in other countries, which by hydration, but not by thorough kaolinisation, have gained in volume. The evidence for such gain is paralleled in Devonshire by the sedimentary rock removed in extending the Bottle Hill adit for the Plympton water supply. This rock had expanded in place, but the particles had remained in close contact under their mutual pressure, hence on excavation it appeared perfectly sound, but when the broken masses were exposed in the open they fell to pieces much as burnt limestone does on air-slaking, but from a different cause.

The proportion of actual fine clay present in and recoverable from the clay rock varies very widely as the following table will show:

|           | A         | B         | C         | D         | E         |
|-----------|-----------|-----------|-----------|-----------|-----------|
|           | per cent. | per cent. | per cent. | per cent. | per cent. |
| Fine clay | 24.4      | 28.0      | 37.0      | 26.8      | 13.7      |
| Mica clay | 9.7       | 6.8       | 17.0      | 10.7      | 13.0      |
| Sand      | 65.9      | 65.2      | 46.0      | 62.5      | 73.3      |

- A. Actual commercial results at Lee Moor, Devon. B C D E laboratory results from small samples of Cornish clay not strictly comparable with A; another laboratory analysis of a Devonshire sample gave 44 per cent of fine clay, but no clay pit as a whole maintains such a yield.

**Composition of Clays.**—The working process of recovery of china clay, which is one of disintegration by water, suspension in water, and subsequent levigation, yields a very pure product, and can be imitated on a small scale by hand washing. The following are analyses:

|                                          | A     | B      | C      |
|------------------------------------------|-------|--------|--------|
| Silica ( $\text{SiO}_2$ )                | 47.10 | 46.81  | 46.30  |
| Titanic oxide ( $\text{TiO}_2$ )         | 0.13  | 0.07   |        |
| Alumina ( $\text{Al}_2\text{O}_3$ )      | 39.42 | 38.24  | 39.80  |
| Ferric oxide ( $\text{Fe}_2\text{O}_3$ ) | 0.23  | 0.27   |        |
| Magnesia ( $\text{MgO}$ )                | 0.24  | 0.07   |        |
| Lime ( $\text{CaO}$ )                    | 0.31  | 0.12   |        |
| Potash ( $\text{K}_2\text{O}$ )          | 0.16  | 0.21   |        |
| Soda ( $\text{Na}_2\text{O}$ )           | 0.08  | 0.07   |        |
| Loss on ignition                         | 12.24 | 14.28  | 13.90  |
|                                          | 99.91 | 100.14 | 100.00 |

All samples dried at  $109^\circ\text{C}$ . prior to analysis.

- A. Best Lee Moor clay, Devon, commercial sample. Analysis quoted by Messrs. Mellor and Holdcraft.  
 B. Hand-washed sample of clay from Redlake, Devon. Analysis by Mr. Bernard Moore.  
 C. Composition of pure kaolinite, for comparison.

The naturally levigated and redeposited secondary clays never accomplish an equal approach to chemical purity. The "ball clays" essential to the potter approach nearest to china clay in this respect, and the following are two typical analyses, but they are not as thorough and to that extent not as accurate as those given above for the china clay:

|                                          | A     | B     | C     |
|------------------------------------------|-------|-------|-------|
| Silica ( $\text{SiO}_2$ )                | 55.30 | 52.06 | 46.30 |
| Alumina ( $\text{Al}_2\text{O}_3$ )      | 30.20 | 29.38 | 39.80 |
| Ferric oxide ( $\text{Fe}_2\text{O}_3$ ) | 3.30  | 2.37  |       |
| Magnesia ( $\text{MgO}$ )                | 0.82  | 0.02  |       |
| Lime ( $\text{CaO}$ )                    |       | 0.43  |       |
| Potash ( $\text{K}_2\text{O}$ )          |       | 2.29  |       |
| Soda ( $\text{Na}_2\text{O}$ )           |       |       |       |
| Loss above $109^\circ$                   | 8.30  | 12.83 | 13.90 |
| Loss below $109^\circ$                   | 2.08  |       |       |

- A. Blue ball clay from Marland, N. Devon.  
 B. Ball clay, shipped at Teignmouth.  
 C. Kaolinite for comparison.

These two samples of ball clay show an average of 19 per cent of free silica, if we assume the whole of the alumina present to be in combination as kaolinite. Ball clay is placed on the market in the same condition as it is dug from the pit or raised from the mine, and is not subjected to any process of washing or levigation. In Devon the ball clays, stoneware clays and pipe clays are always associated with sands and gravels recognisably derived from Dartmoor, and their origin from the lost clay rock of the Moor seems fairly certain.

Glacial clays are possibly represented in Devonshire by the deposits on the rock bed of the Tamar and Tavy and at Gawton, but no analyses are available. Similarly as to the residual clays associated with the Plymouth limestone, and left as the residue of the solution of previously existing rocks, including probably the limestone itself and possibly liassic and cretaceous strata, of which only detrital traces remain.

**Clay Suspensions in Water.**—It is a property of many substances when in extremely small particles to form mixtures with relatively pure water which remain in almost indefinite suspension, presenting in this respect a strong resemblance to the colloids; clay shares this property.

In the actual working of china clay the material is present at one stage of the process as a suspension of three parts or thereabouts by weight of clay in a hundred parts of water. If the water contains little or no salts in solution the suspension, with many grades of clay, refuses to precipitate, and since the concentration and recovery of the clay depend upon precipitation a practical difficulty ensues. Some river waters, such as those derived from a granite watershed, and all rain water are deficient in the necessary salts; most spring waters, even those from the granite, contain enough to materially accelerate precipitation. When clay is being worked with spring water from the granite a heavy shower of rain will frequently prove sufficient to so dilute the natural solution of salts that precipitation is greatly checked and much clay is liable to escape with the overflow water from the settling pits. The remedy for this latter trouble, and a means of using river water for clay washing, are found in adding small quantities of an electrolyte to the clay suspension. For this purpose alum, or alum cake the crude sulphate of alumina, or sulphuric acid are the

most efficient electrolytes that are commercially available at a reasonable cost. Alum presents no advantages over sulphate of alumina, but on the contrary is less effective weight for weight; sulphuric acid has the highest efficiency.

The result of the addition to some clay suspensions of very small quantities of an appropriate electrolyte, a few grains per gallon at the most, is to accomplish in hours precipitations which would not otherwise take place in weeks. If appropriate means of observation are used, the clay particles from being uniformly distributed, in each horizontal layer at least, are seen to close in about more widely spaced centres, leaving lanes of clear water between; these lanes are simply the sections in the plane of observation of the clear water spaces intervening on all sides between each aggregation of clay particles and its neighbours. The first stage therefore is an immediate concentration of the clay and the separation from it of clay free water, but the bulk distribution of the clay in the water is not thereby directly varied. The aggregates of particles, however, present less surface in proportion to their mass than did the individual particles, for even without actual contact the mutual attraction under the changed circumstances makes of each group and of the water still lying between its members a mass which moves as a whole. In undisturbed conditions the second stage of concentration thus begins, and the little aggregations fall through the water under the influence of gravity, growing in size at the same time. There soon appears a separation into a surface layer of clear water and a bottom layer of concentrated clay suspension. When the concentration, at first rapid and then slower, has reached a certain density there is a check in its rate of progress, and the ultimate possible density is only slowly attained. These facts have to be taken into account in the practical recovery of clay from its suspensions. The first stage of concentration may be in a tank with one inlet for the clay suspension, and two outlets, one at the bottom for the concentrate, and one over a weir at the top for the clear water; such a tank may act continuously when once the inlet and the bottom outlet are properly adjusted in their relative flow and to the amount entering the tank; and in such a tank the greater part of the water may be speedily removed, leaving, however, a much larger proportion of water and clay than is desired as a final result. The concentrate from this first tank may then either be sent to the final settling pit, or may undergo an inter-

mediate further concentration. In the latter purpose it is advisable to provide a tank in which the weir overflows, for the separated water can be raised as the tank fills, thus allowing a little water to be skimmed off, and then when the tank is quite full a period of rest is given, after which the weir overflow is quietly lowered, skimming off the water which is separated during the period of quiescence, and not until this has been done is the bottom outlet opened and the concentrate allowed to escape; the second process is therefore discontinuous. In the final settling pits the overflow is slowly raised as the tank fills and the concentrate is allowed to become a pasty substance, either only just capable of flowing, or stiff enough to require excavation. Although the two or three stage concentration economises tank space as proportionate to the output, there are very many works where the whole settlement of the clay is carried out in one stage only.

Starting with three parts by weight of clay in each hundred parts of mixed clay and water, the following are suitable proportions for the various tanks: For the first or continuous concentrators a capacity equal to four hours' incoming flow of the 3 per cent mixture; the concentrate leaves this tank as a mixture containing 9 to 10 per cent by weight of clay, the balance of the water escaping over the weir; the reduction in volume is about 70 per cent. The second concentrators should have a capacity equal to twenty-seven hours' flow off the first concentrator, and the mixture leaves these containing 23 to 25 per cent of clay by weight, the original volume being now reduced by 88 per cent in all, the balance of water having been skimmed off by the adjustable weir. The final tanks may have a capacity equal to 175 hours' flow of the second concentrate, and the deposit left in them is a mixture containing 50 per cent, by weight, of clay or thereabouts, the total bulk of water removed from the start being  $95\frac{3}{4}$  per cent of the total original volume of 3 per cent mixture. But in the final tanks the whole capacity is never fully in use at one time for concentration purposes, since the tanks are progressively diminished in effective depth by the collection of clay in practically its final state (prior to actual drying). It must be allowed, however, that, even in the bottom layers of such clay, further concentration no doubt continues up to the moment of the emptying of the pits. On the other hand the tank room is not solely determined by requirements of concentration, but questions of storage largely influence it.

The above tank capacities, while suitable to actual practice, allow large factors of safety. The first process of reducing the total volume by 70 per cent can be effected in the laboratory under conditions which can be paralleled in large works in a period of  $1\frac{1}{4}$  hours in place of the four hours allowed above, while using methods unsuitable in practice the same work can be done in eight minutes or less. This first process, as involving continuous adjustment of overflow and bottom outlet, is very apt to be upset by irregularities in the original mixture of clay and water and in its rate of flow, hence the large margin. The second stage, at which a total of 88 per cent reduction in volume is reached, can be accomplished in the laboratory in an additional seven hours, and this also could be accomplished with great care in actual practice, but in emptying these second concentrators a little water always mixes with the concentrate and undoes some of the work. There are other practical considerations, too detailed to set out, which combine to make it desirable to provide at least thrice the minimum experimental capacity.

The final stage in the preparation of china clay consists in drying the deposit from the last settling tanks on heated floors, the temperature being allowed to reach boiling point. The marketable clay so produced should not contain more than 12 to 13 per cent of water, excluding water of hydration.

