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SOME APPLICATIONS OF CLAY MINERALOGY*

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Introduction

Clay materials are the essential components of most soils and therefore, are of great importance in agriculture. The engineer is frequently required to build a structure on, through, or with soil materials. Clays are used as raw materials in many manufactured products, for example, ceramic products, paper, paint, and catalysts. The properties of clay materials are determined largely by their clay mineral composition, or more fundamentally by the structure, composition, and physical attributes of the clay minerals. It follows, therefore, that knowledge of the structure, composition and properties of the clay minerals has great practical value.

This matter of applying knowledge of the clay minerals to practical problems involving the use of clays and soils has fascinated me for a long time. I like to call it "Applied Clay Mineralogy." I wish to present a few examples of the application of clay mineral data mostly from my own experience, but in a few instances from the literature.

There is another reason for selecting this subject for this address. I am convinced that the application of mineralogical knowledge is an excellent way to make known to the general public the importance of our science, and to gain for it, its proper place among the other sciences. It seems to me that too many mineralogists not only have no interest in the application of their findings, but have actually ignored any possible application, to the detriment of the development of mineralogy.

Ceramics

There are many applications of clay mineralogy to ceramics but one example will suffice. In the manufacture of many ceramic products, clays are heated to elevated temperatures to develop strength, perma-

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nence, desired color, etc. The ceramist wishes to fire his product with the least possible cost which involves the use of the least fuel and in the shortest possible time.

Equilibrium phase diagrams have been of great value to the ceramist. However, they do not always provide the data he needs. Thus the ceramist is interested in the events that take place in the clay at low temperatures long before equilibrium is reached and in the rates at which the various changes take place on heating. He is interested in the effect of traces of elements on high temperature reactions. Studies of the changes taking place when the clay minerals are heated from ordinary temperatures up to their fusion point by differential thermal analyses and by continuous *x*-ray diffraction procedures have recently provided data of tremendous importance to the ceramist.

When the clay minerals are heated to temperatures of the order of 400° C. to 600° C. they lose their hydroxyl water. It has long been thought necessary to fire clays through this temperature interval very slowly. Studies of the dehydration characteristics of the clay minerals have shown that for some clay minerals the dehydration reaction is abrupt and that it cannot be slowed down. Further, in many instances the dehydration is accompanied by no complete breakdown of atomic structure or shrinkage. This is not true for all clay minerals, but for many of them there is no reason to go through this temperature interval slowly when clay products are fired. Slow heating in the temperature interval is often a waste of time and fuel (Grim and Johns, 1951).

In the manufacture of many refractory bricks it is desired to burn so as to produce the maximum amount of mullite. It has been shown (Grim and Kulbicki, 1957), that when kaolinite, which is the clay mineral component of clays used in the manufacture of such brick, is heated to about 950° C.–1000° C. some mullite is formed, but it is not until about 1250° C. that the mineral develops rapidly. Heating in the interval 950° C–1250° C. will not develop much mullite when kaolinite is fired, even if the temperature is maintained for very long periods of time. Therefore, slow heating in this interval is useless. It has been shown further by Wahl (1958) that the addition of traces of various elements can enhance or retard the development of mullite at the higher temperature but that such additives have very little if any effect on the formation of mullite at the lower temperature.

In summary then, fundamental studies of the changes taking place when the clay minerals are heated have been of great practical value by showing the ceramist how to arrange his firing schedule for the most economical burning of his products. Indeed, the matter has been carried further in the development of many refractories which are not fired until they are placed in service. Unfired brick or plastic material used to line furnaces or ladles is in effect burned extremely rapidly when first used.

ENGINEERING

The usual procedure in engineering practice when soil materials are involved in construction is to obtain empirical test data on such properties as compaction under load, plasticity, etc., of the soils involved. The design of the structure is based on such test data, evaluated somewhat on the basis of past experience. In the actual construction, the environmental setting of the soil may be changed and with it the properties of the soil so that the test data may need re-evaluation. In essence the engineer frequently must predict the changes in soil properties when he changes the environment. Engineers are coming more and more to appreciate this situation and are becoming interested in the fundamental factors determining the properties of soils realizing that this is important if they are safely to predict the changes that may take place in the soil when they place a load on it, change the water table, place in it a mass of concrete providing a flood of calcium ions for cation exchange reaction, etc. This interest is attested by the symposium of the American Society of Civil Engineers held last year on clay mineralogy in relation to soil mechanics and by the symposium of the Highway Research Board of the National Research Council this year on the properties of soil-water systems.

I would like to present several examples of the relation of clay mineralogy to engineering problems.

The clay mineral halloysite occurs as $2H_2O$ and $4H_2O$ hydrates. The $4H_2O$ form dehydrates to the lower hydration form at ordinary temperatures slowly and irreversibly passing through an intermediate state of hydration. Neither the $2H_2O$ or $4H_2O$ form develops any substantial plasticity when mixed with water as most other clay minerals do. However, the intermediate state is likely to be very plastic and has physical properties quite unlike either the $2H_2O$ or $4H_2O$ forms. A test of properties, therefore, of a soil containing the $4H_2O$ form under conditions such as the engineer generally uses in obtaining his test data which prevent the loss of any water, probably will not give data showing the properties of the soil under conditions of actual use when some moisture may be lost. Failure to appreciate this characteristic of halloysites can lead to serious difficulties for the engineer. Fortunately halloysite is not a very common constituent of soils, but it is very desirable to detect the presence of halloysite in any soil that may be part of a construction program.

There are in some parts of the world soils which have considerable bearing strength in their natural undisturbed state, but very little or no strength in the remolded state, i.e. after their original texture has been destroyed. This is the property called sensitivity by the engineer. Extreme examples are the so-called "Quick" clays well known in many countries but especially in Norway where they have been intensively studied by Rosenquist (1953) and Bjerrum and Rosenquist (1956). These investigators have been able to produce "Quick" clays in the laboratory and have demonstrated the reason for their unusual properties.

It must be emphasized that the explanation offered for these "Quick" clays does not account necessarily for the high sensitivity of other soils. There are other explanations for some other examples.

The clay mineral component in the Norwegian "Quick" clays is largely illite. Some quartz is present also, and much of the material in the crude clay is in a coarse clay or fine silt particle-size range. The material was deposited under marine conditions in a flocculated condition with a loose open texture and with sodium as the dominant adsorbed and exchangeable cation. Later, under present conditions the sodium has been leached being replaced by other cations such as hydrogen, without any change in the natural moisture content of the soils. The water adsorbed directly on the surfaces of the clay minerals is not liquid water but is composed of oriented water molecules and it therefore, serves as a bond, helping to hold the clay mineral particles together and to give strength to the soil. When sodium is present, adsorbed on the surface of the clay mineral particles, the oriented water develops to a very considerable thickness, that is, many molecular layers in thickness. With other adsorbed cation the oriented water does not develop to thicknesses as great as when sodium is present. In these clays the adsorbed water developed initially in equilibrium with sodium. In a sense the sodium ion acted as a kind of prop to maintain the rigid water and to give strength to the soil. The leaching of the sodium ion removed the prop and did not at the same time change the amount of water. There was, therefore, a loss of equilibrium and a condition of great instability. Any slight movement or jarring of such a soil is likely to change the rigid water to fluid water with a complete loss of strength. This is what happens in the sudden development of landslides in "Quick" clay.

An understanding of "Quick" clays, therefore, involves an understanding of the nature of the water adsorbed by the clay minerals and the way adsorbed ions affect this water. This is a matter of very great interest at the moment and much attention is being given to investigations of the nature of the water in clay-water systems. The approach of colloid chemistry to investigations of clay-water systems has paid particular attention to the forces of attraction and repulsion between the particles. The water was thought to have a passive role and to do very little more than provide a medium to separate the particles and to provide for their hydration. Structural attributes have now entered the picture—the structure of the water in its relation to the structure of the clay minerals—particularly in systems where the relative amount of water is not large as is the case in the plastic state.

To pass on to another example in the field of engineering. Some years years ago it was desired to construct a fresh water lake on Treasure Island in the San Francisco Bay area in the preparation for a World's Fair, (Lee, 1940). A depression was made and lined with a plastic clay and fresh water was pumped into it. The fresh water seeped away rapidly. The leakage of the depression could have, of course, been stopped by the placement of an impervious seal such as concrete or asphalt, but a less expensive solution was much desired. An astute engineer knowing something of the composition of the soil and the properties of clay minerals in general suggested that sea water be pumped into the depression and after standing for some time it be removed and replaced with fresh water. This was done and the leakage was stopped. The explanation is that the soil contained some montmorillonite which is a very dispersible clay mineral. The presence of the sea water led to an exhange reaction whereby sodium became the adsorbed cation. The sodium ion caused enhanced dispersion of the clay mineral, that is, it caused it to break down into more and smaller particles. Further the sodium ion led to the development of thick adsorbed layers of oriented water. For both of these reason the sodium clay acted as a seal for the water whereas the clay mineral with another cation did not act as such a seal.

PETROLEUM INDUSTRY

Clay mineral studies are of wide interest to the petroleum industry; in correlation problems, in propsecting, in drilling muds, in secondary recovery operation, in refining processes, etc. I wish to consider here just one of these applications and that in the less generally known field of catalysis in the refining operation.

It has been known for a long time that some of the clay minerals have catalytic properties towards many organic compounds. This property may be desirable or detrimental, in the use of clays in the petroleum industry. It is desirable in the use of clays as catalysts in the manufacture of gasoline from crude oil. It is undesirable when the clay is used to decolorize or purify a product, and it is desired that the product shall not be changed in any way. It is very undesirable when clays are used as carriers for insecticides made from hydrocarbons where the catalytic action may rapidly cause a loss of toxicity of the insecticide.

In recent years there has been much research in many laboratories directed towards finding ways to modify or control the catalytic properties of the clay minerals and this has led to studies of the fundamental factors which give the clay minerals their catalytic properties. Although much remains to be learned on this matter, some generalities appear to be established (for an introduction to this subject, (see Mathieu, 1945; and Milliken, Oblad, and Mills, 1955). Thus, the structure of the clay minerals is important, particularly the structure of the surface of the tetrahedral silica sheet part of the structure. When the silica tetrahedral sheet structure is lost the catalytic activity is lost. The surface of the silica tetrahedral layers must have the property of donating protons and it must be substantially clean of adsorbed alkali earth cations and probably other ions. Further, some aluminum is essential, probably in some particular pattern behind the silica surface.

The problem in preparing a catalyst is to make one that produces the proper products, for example, a large percentage of high octane gasoline from a given feed stock. The catalyst can be too active in that it will break down the hydrocarbon completely to a gas and carbon. Also the catalyst must be hard and resistant to abrasion. It must be durable so that it will withstand regeneration through many cycles of use. These conditions have been met, and now catalysts are produced from clays composed of montmorillonite, halloysite, and kaolinite. Essentially the conditions have been met by processes which modify the structures of the clay minerals but do not destroy them. The character of the catalyst is controlled by controlling the modification of the structure. I would emphasize that success has been obtained by looking at the problem through "structural glasses" rather than simply on the basis of the amount of the elements present.

Bonding Clays

In the casting of metals in foundries, synthetic mixtures of sand and clay are used as a medium for the preparation of the molds into which the molten metal is poured. Various types of clays are used—each giving fairly distinctive properties, depending on the clay mineral composition and the exchangeable cations that are present (Grim and Cuthbert, 1945, 1946). Thus, bentonite from Wyoming, which is composed of montmorillonite carrying sodium as the exchangeable cation provides very high dry strength and moderately high green strength, i.e., strength before drying to remove the tempering water. Bentonite from Mississippi, composed of montmorillonite, which carries calcium and hydrogen as exchangeable cations provides very high green strength and moderately low dry strength. So-called fire-clays which are underclays of Carboniferous age produced extensively in Middle Western states and composed of poorly ordered kaolinite and illite provide good flowability, durability, and good metal surface characteristics. The fireclays have lower green strength than the bentonites, but their geographic location close to foundries makes it economic to use a larger proportion of them in the sand which in turn enhances their desirable properties.

A third type of clay used in foundries is an illite which is very poorly ordered and has a small amount of mixed-layer montmorillonite (Grim and Bradley, 1939). This interesting clay was discarded as worthless overburden by a refractory manufacturer until a clay mineral analysis suggested its potential use as a bonding clay. It has strength characteristics intermediate between those of the sodium and calcium montmorillonites and the flowability and durability of the kaolinite clays. One of the problems sometimes encountered by foundries is the development of many very small pits or depressions in the surface of the cast metal which are known as pin holes. Recently Jones and Grim (1959) found that when illite clay is used such pin holes do not develop. The explanation seems to be that the tempering water and hydroxyl water of this type of clay is gradually driven off when metal is poured into the mold, rather than abruptly as is the case for some other clays. Also the clay is very thoroughly dispersible throughout the sand so that there are no concentrated masses of clay with adsorbed water to suddenly release relatively large amounts of water vapor at given spots to produce the pin holes.

Sometimes it is not possible to translate a laboratory finding that appears to have great practical value into economic usage. For example, some years ago a study of the bonding properties of various types of clay minerals showed that a sample of halloysite had excellent strength characteristics and provided castings with an excellent smooth surface. Halloysite clay had never been used in foundries before, and it appeared to be a discovery of considerable importance. The sample tested had been in the laboratory for some time and was in an intermediate state of hydration between the $2H_2O$ and the $4H_2O$ form. Studies of potential sources of halloysite showed that the material back from exposures was the $4H_2O$ form and that any tonnage production would have to be the $4H_2O$ form which unfortunately has substantially no bonding strength. So far it has been impossible to slightly dehydrate the $4H_2O$ form in the laboratory in any way that could be used commercially to produce the high strength material. Apparently only slow loss of water from the $4H_2O$ form produces the high strength material.

PAPER

The manufacture of paper requires huge tonnages of clay as filling and coating agents to make the paper opaque, white, and printable. For these purposes large tonnages of substantially pure kaolinite clays are used. Actually about two-thirds of all of the kaolin produced goes into the paper industry. Such kaolins are produced extensively from sedimentary beds of Upper Cretaceous age in the southeastern part of the United States and from clays of hydrothermal origin in the Cornwall district of Great Britain.

To obtain the necessary purity and whiteness, the clays are treated chemically to remove various iron compounds. The clays are then washed with wet sedimentation procedures to remove quartz and other non-kaolinite particles. It is well known that the size of the kaolinite particles is important in determining the properties of the coated paper and fractionation is now practiced using centrifuges to produce kaolins of closely controlled particle size in the micron size range. Murray and Lyons (1956) have shown recently that the shape and crystal perfection of the kaolinite particles is important as well as their size in determining coating characteristics. Well crystallized kaolinite particles with distinct hexagonal outlines in book-like units which are not too thin are required.

In the paper coating operation the clay is made into a slurry which is flowed on to the paper stock as it moves through the paper making machine. The paper stock moves at a very rapid speed and consequently clay slurries of the highest possible concentration at the lowest viscosity without any dilatency are required. These specifications pose problems. There are kaolins which give slurries of low viscosity, and other kaolins which produce viscosities several times as great with the same clay concentration, which do not seem in any way to differ from the low viscosity kaolins. *X*-ray diffraction and electron micrographic analyses reveal no differences in the composition of the clay or in the size and shape of the kaolinite particles. The cause of the differences is unknown, but it must reside in some factor of the surface characteristics of the kaolinite particles or in their shape which is not revealed by the electron micrographs. In some cases viscosity differences can be explained by the presence of small amounts of montmorillonite, but in other cases the differences are shown by pure kaolinite kaolins.

ORGANIC-CLAD CLAY MINERALS

One of the areas of most intensive research in clay mineralogy in recent years has been the study of clay mineral-organic reactions (for an introduction to this subject see Grim, 1953). It has been shown that the clay minerals can enter into cation exchange reactions with organic cations in which case the organic molecule is held on the clay mineral surface by a coulombic bond. The clay minerals can also adsorb highly polar organic molecules which are held mainly by hydrogen bonds. VanderWaal's forces also play a role in attaching the organic molecule to the clay mineral surface.

These reactions permit the coating of the clay mineral surfaces with organic molecules producing so-called organic-clad clay mineral particles which in general have been changed from hydrophilic to hydrophobic. Such organic-clad clay minerals become oleophilic in that they can be dispersed in organic liquids and some organic molecules can be polymerized to the organic molecules coating the clay mineral surface. In the case of the exchange reactions, by knowing the surface area per exchange position one can select an organic molecule that completely coats the surface or one that only partially covers the surface. Thus, the clay mineral can be made partially hydrophobic by selecting an organic molecule of the proper size and shape. This is assuming, of course, that one knows the orientation of the organic molecule on the clay mineral surface. Also by selecting the proper coating molecule the clay mineral particles can be made particularly reactable with some types of organic vehicles.

It it interesting that researches in this field started out as a purely fundamental study of clay mineral-organic reactions, and that they have led to completely new clay products which have opened new uses for clays. Organic-clad montmorillonites and kaolinites are now produced commercially. New uses of these products are in the field of gelling agents in the manufacture of lubricants, as fillers and strengthening agents in plastics, as components of printing ink, as flattening agents in paints and many others. In some cases the organic-clad clay mineral is "tailor made" to fit a particular organic material with which it is to be used.

Another area of the application of clay mineral organic reactions is worth notice. That is, in conditioning soils for agricultural use and in stabilizing them for the construction of roads and airport runways (Winterkorn, 1946). In such cases an organic agent is added to the soil and the hoped for effect of the additive must be obtained through a reaction with the clay minerals in the soil. The hoped for results have not always been attained, frequently because the investigators forgot or did not know that various soils contain different clay minerals and that the reaction of organic molecules was not the same for all types of clay minerals.

DISPOSAL OF ATOMIC WASTE

An area of clay mineral research of extreme importance at the moment is the possible use of clays in the disposal of atomic wastes from nuclear reactors. Some procedure for the disposal of hot isotopes with a long half life must be discovered that is safe and economical before there can be widespread development of power from such reactions. One method that seems to have much promise is to adsorb the isotope by clays and then fire the clay to lock up the hot element in an insoluble compound so that the fired material can be buried safely without the risk of the isotope going into solution and contaminating the ground water.

Clay minerals with high cation exchange capacity and low fusion temperatures seem to be desirable and bentonites carrying montmorillonite with cation exchange capacities of about 130 milliequivalents per 100 grams have been suggested (Kerr, 1959). It appears, however, that cation exchange capacity is not the sole determining factor. For example, some of the waste liquors are highly acid and have a high electrolyte content. The property of attapulgite-water systems of being relatively unaffected by large variations in the electrolyte content has indicated that this type of clay may be desirable in some instances.

Before final disposal it may be desirable to separate and isolate some of the isotopes for which there is a possible use. This has led to the investigation of the selective adsorptive properties of various clay minerals with the hope that they could be used as atomic sieves. Barrer and his colleagues in Great Britain (1954) have done much work in this field. It is too early to tell if clay minerals can be used as such atomic sieves. Possibly the clay mineral structures can be altered as in the case of the manufacture of clay catalysts to develop specific adsorptive properties. At the present time the atomic sieves in use are synthetic zeolites. It is worth pointing out that the research that led to the development of such atomic sieves is essentially mineralogic.

REFERENCES

BARRER, R. M., AND D. M. MACLEOD (1954), Intercalation and Sorption by Montmorillonite, *Tran. Faraday Soc.* **50,** 580–585.

BARRER, R. M., N. MACKENZIE AND D. M. MACLEOD (1954), Sorption by Attapulgite, *Jour. Phys. Chem.* **58,** 568–571.

BJERRUM, L., AND I. T. ROSENQUIST (1956), Some Experiments with Artificially Sedimented Clays, *Geotechnique* **6,** 124–136.

GRIM, R. E., AND W. F. BRADLEY (1939), A Unique Clay from the Goose Lake, Illinois Area, *Jour. Am. Ceramic Soc.*, **22,** 157–164.

GRIM, R. E., AND F. L. CUTHBERT (1945), The Bonding Action of Clays, Pt. I, Clays in Green Molding Sands, *Rept. Inv.* **102,** *Ill. Geol. Survey.*

GRIM, R. E., AND F. L. CUTHBERT (1946), The Bonding Action of Clays, Pt. II, Clays in Dry Molding Sands, *Rept. Inv.* **110,** *Ill. Geol. Survey.*

Grim, R. E., and W. D. Johns (1951), The Reaction Accompanying the Firing of Brick, *Jour. Am. Ceramic Soc.* **34,** 71–76.

Grim, R. E. (1953), Clay Mineralogy, McGraw-Hill, New York.

Grim, R. E., and G. Kulbicki (1957), Etude des Réactions de Hautes Températures dans les Minéraux Argileux au Moyen des Rayons X, *Bull. Soc. franç. Céramique* **36,** 21–28.

Jones, D. R., and R. E. Grim (1959), Pin Hole Occurrence in Malleable Castings, *Trans. Am. Foundrymens Soc.*, 397–400.

Kerr, J. M. (1959), Preliminary Tests on Clay Sinters to Retain Reactor Wastes, *Bull. Am. Cer. Soc.* **38,** 374–376.

Lee, C. H. (1940), Sealing the Lagoon Lining at Treasure Island with Salt, *Proc. Amer. Soc. Civil Engineers*, 247–263, February.

Mathieu, M. (1945), Structure et Activite Catalytique, *Bull. Soc. Chem., France*, 14–27.

Milliken, T. H., Oblad, A. G., and G. A. Mills (1955), Use of Clays as Petroleum Cracking Catalysts, *Bull.* **169,** *Div. of Mines, Calif.* 314–326.

Murray, H. H., and S. C. Lyons (1956), Correlation of Paper Coating Quality with Degree of Crystal Perfection of Kaolinite, *Pub.* **456,** *Nat. Acad. Sci., U. S.*, 31–40.

Rosenquist, I. T. (1953), Considerations on the Sensitivity of Norwegian Quickclays, *Geotechnique* **3,** 195–200.

Wahl, F. M. (1958), Reactions in Kaolin-Type Minerals at Elevated Temperatures as Investigated by Continuous *X*-ray Diffraction. Ph.D. Thesis, University of Illinois.

Winterkorn, H. F. (1946), Principles and Practice of Soil Stabilization, *Colloid Chem.* **6,** 459–462.