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Industrial Applications Of Clay Mineralogy

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ABSTRACT

In the field of clay mineralogy attention has mainly been directed to the identification and estimation of clay mineral components of various clays by techniques like X-ray diffraction, electron microscopy, staining, differential thermal, thermogravimetric and infrared analysis. Only recently has the practical utility of basic research in clay mineralogy been realised.

Since the physical and chemical properties of clay materials are mainly dependent on the structure, composition and properties of clay minerals, a knowledge of clay mineralogy is essential in industrial practice where clays are involved.

A few of the applications of clay mineralogy include ceramics, catalysis, constructional engineering, petroleum industry, foundry, paper manufacture, lubricant and plastic industry and agriculture.

Clay mineralogy may find application in unexpected fields. For example, the type and content of the clay mineral will indicate its usefulness for disposing of hot undesirable isotopes from nuclear reactors. The mineralogical composition of a clay would be an important factor for assessing its suitability for the manufacture of clay lightweight aggregates. A quantitative determination of the clay minerals in brick clays will provide an accurate estimation of the thermal efficiency of kilns.

The paper presents briefly some of the basic concepts of clay mineralogy and stresses by way of suitable examples the wide applicability of clay mineralogy in building technology, petroleum industry, foundry, paper manufacture, lubricant and plastic industry and agriculture.

BASIC CONCEPTS OF CLAY MINERALOGY

Clay Mineral Classification :

A clay mineral is a hydrated silicate with layer or

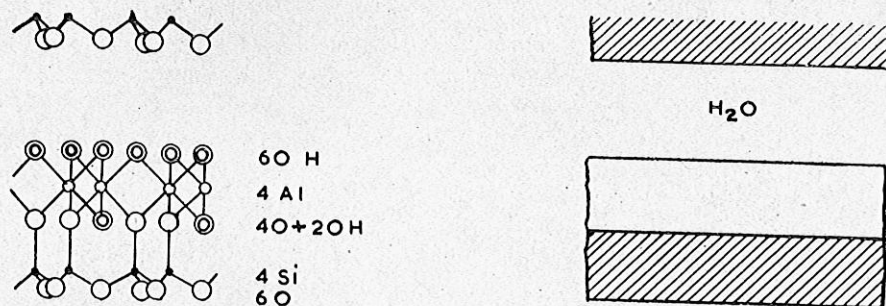
chain lattice consisting of sheets of silica tetrahedra, arranged in hexagonal form, condensed with octahedral layers. It usually consists of particles of spherical diameter less than 2 microns.

The classification of clay minerals has been a subject of much controversy. Various classification systems have recently been proposed.¹ According to Grim,² the clay minerals may broadly be divided into two groups, amorphous and crystalline. Allophanes form the amorphous group. The crystalline group consists of two layer sheet structures like kaolinite, halloysite, nacrite and dickite, and three layer type sheet structures such as montmorillonite, saunonite, vermiculite, nontronite, saponite, hectorite and illite. Regular mixed layer type is represented by chlorite group. Attapulgitite, sepiolite and palygorskite are placed under a separate group as they have a chain structure.

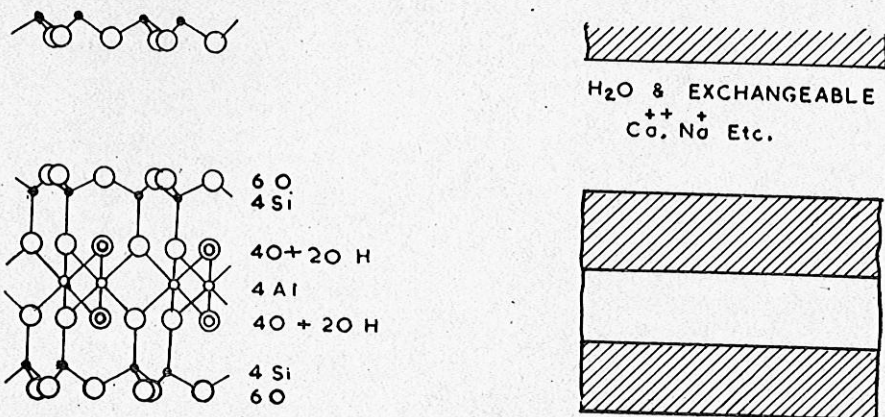
Structure of Clay Minerals :

All the soils contain kaolinite, montmorillonite and illite as the dominant clay minerals. In Fig. 1 are given the simplified and schematic representations of these clay minerals.

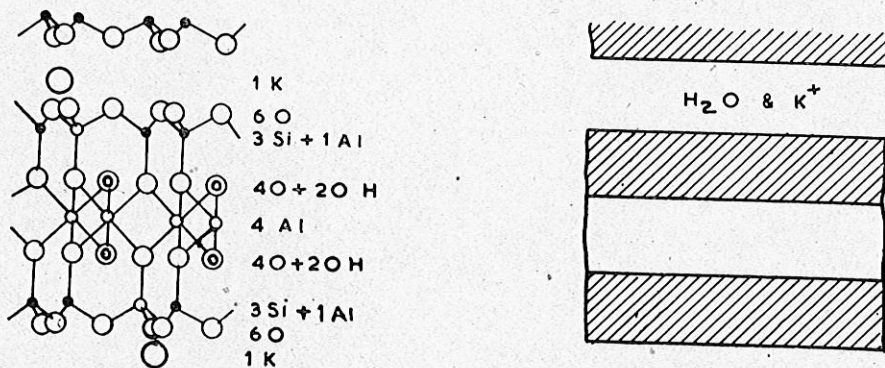
The kaolinite comprises of a single silica tetrahedral sheet fused with an octahedral sheet of alumina. Since there is little replacement of Si^{+4} or Al^{+3} by other ions, the structure is balanced. Montmorillonite consists of an aluminate layer sandwiched between two silicate layers. Part of the Al^{+3} is substituted by divalent ions like Mg^{+2} and Fe^{+2} and to a smaller extent, Si^{+4} is replaced by Al^{+3} . The resultant negative charge is balanced by cations occupying the interlayer spacing. Montmorillonite swells considerably in an aqueous medium. The structure of illite is similar to that of montmorillonite except that Si^{+4} is substituted by Al^{+3} mainly in the tetrahedral layer. The resulting charge deficiency is balanced largely by K^{+} . In illite the interlayer forces are much stronger and swelling occurs to a limited extent.



KAOLINITE



MONTMORILLONITE



ILLITE



(a)

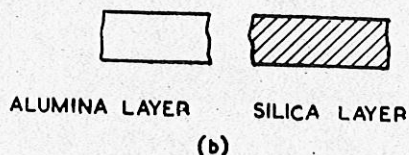


FIG. 1(a) SCHEMATIC REPRESENTATION OF CLAY MINERALS.

FIG. 1.(b) SIMPLIFIED REPRESENTATION OF CLAY MINERALS.

Physico-chemical Properties :

The clay minerals have the property of sorbing cations and anions and these ions are exchangeable with other cations, usually in an aqueous environment. The common exchangeable ions present in clay materials are Ca^{+2} , Mg^{+2} , H^+ and Na^+ . The ion exchange property of a clay mineral finds many applications in industry. The cation exchange capacities of a few clays and clay minerals reported by Grim² and Grimshaw³ are given in Table I.

TABLE I. Cation Exchange Capacities of a Few Clays and Clay Minerals.

CLAYS :	Cation exchange capacity (m. e./100 g.)
Ball clay (Dorset)	14.45
Bond clay	21.50
Fire clay (Weathered)	10.65
Fire clay (Unweathered)	11.32
Brick clay (Jurassic)	7.32
Bentonite	56.80
CLAY MINERALS :	
Kaolinite	3-15
Halloysite, $2H_2O$	5-10
Halloysite, $4H_2O$	40-50
Montmorillonite	80-150
Illite	10-40
Vermiculite	100-150
Chlorite	10-40
Sepiolite, attapulgite and palygorskite	20-30

The cation exchange capacity, swelling property, plasticity, permeability, refractoriness and vitrification behaviour of a clay are mainly dependent on the clay mineral constituents of clays.

INDUSTRIAL APPLICATIONS

Constructional Engineering:

Economy in foundations is best achieved by a proper understanding of the bearing capacity, settlement and permeability of the soils. These properties depend basically on the clay mineral constituent of the soil. Montmorillonites consisting of minute particles and great surface activity exhibit low permeability. Of all montmorillonites the sodium montmorillonite shows the least permeability. The surface activity being low, the kaolinite soils show high permeability. The rod-like structure of halloysite hinders dense packing and makes the halloysitic soils very permeable.

Montmorillonitic clay being very plastic and least permeable will exhibit greatest settlement. Kaolinitic clays have least settlement characteristics. The settlement of the illitic clays is intermediate and lies over a wide range.

In presence of water molecules montmorillonite shows swelling, shrinkage and plasticity to a greater

extent than kaolinite or illite. If the soil is predominantly montmorillonitic, the constructional engineer should guard against excessive swelling when wet and high shrinkage when dry. In kaolinitic soils precaution is needed against excessive seepage and ill effects resulting from the low cohesiveness of the particles.

Structural Clay Products :

In the manufacture of structural clay products certain generalizations can be made based on the knowledge of clay mineralogy.

Illitic clays are quite suitable in structural clay industry. They burn to a satisfactory product at a relatively low temperature ($900^\circ - 1000^\circ C$). The Oxford clay used for the manufacture of Fletton bricks consists of illitic clay mineral.⁴ Kaolinitic clays are suitable provided they contain fluxes to bring down the vitrification temperature. Clays containing halloysite, montmorillonite, chlorite and hydrobiotite predominantly do not produce structural clay products of good quality.

Prediction of the firing behaviour of clays can be done by a knowledge of the nature and content of the clay minerals, and the accessory minerals present along with the clay mineral.⁵

Safe Rate of Firing :

In the production of structural clay products the ceramist is mainly interested in obtaining a good strength and colour, with the least fuel consumption in the shortest possible time. An example is shown below to indicate how a knowledge of clay mineralogy is applied in formulating an optimum firing schedule for the manufacture of structural clay products.

Clay minerals loose the chemically bound water in the range, $400^\circ - 600^\circ C$. In some clays this reaction takes place quite abruptly even if the firing schedule is slow. It is a common practice to fire clays at a very slow rate in this temperature range which leads to waste of time and fuel.⁶

Grim and Johns⁷ used full size bricks for investigating the mineralogical inversions in clays and their results permitted proper planning of firing schedules

Kiln Efficiency :

The heat of dehydration of clays caused by the loss of combined water between $500^\circ - 750^\circ C$ accounts for nearly ten per cent of the total heat input in estimating the thermal efficiency of kilns used for the production of structural clay products. The heat of dehydration is measured by determining the residual ignition loss based on certain assumptions.⁸ From a quantitative estimation of clay minerals the heats of dehydration can directly be obtained.⁹

Lightweight Aggregates from Clays :

The importance of the mineralogical composition as a factor in producing suitable clay lightweight aggregates was stressed by Everhardt.¹⁰ Of the hundred clays tested by him seventy-eight showed good bloating characteristics. Of the clays that bloated, the ratio of illite to kaolinite contents was 2.7 and

in non-bloating clays the ratio was 1.6. Accordingly it was shown that the mineralogical composition was a deciding factor. Illites are known to fuse between 1830°-2370°F and kaolinite between 3000°-3230°F. Thus with increasing amounts of illite larger portion of the material would melt in the range, 1830°-2370°F. Montmorillonitic clays fuse at low temperature with very short vitrification range so that in practice it will be very difficult to control the firing temperature.¹¹ Hence montmorillonite clays do not produce aggregates of good quality.

Refractories:

Kaolinites are known to be very refractory. Montmorillonites and illites are less refractory as they contain alkali and alkaline earths in the structural frame work and as adsorbed ions.

In the manufacture of refractories the raw material is fired to get the maximum amount of mullite. Mullite is formed above 1250°C very rapidly.¹² Hence a slow rate of heating in the range 950°-1250°C is unnecessary and a waste of time and fuel. Wahl¹³ found that traces of various elements enhance or retard the formation of mullite not below 1250°C.

The mineralogical estimations are often used to investigate the properties of the refractories. For glass tank blocks using silliminite, and containing kaolinites it was found that on heating these tend to shatter at 600°C if over 12 per cent kaolinite is present.¹⁴

Soil Stabilization :

For a stabilization of soil for the construction of roads and air port runways, a clay is usually treated with an organic agent.¹⁵ The stabilizing behaviour is usually found by trial and error. A better understanding and control can be attained if the mineralogical nature and content of the soil is known.

Organic-Clay Complexes :

Research on clay mineral-organic reactions was mainly confined to the nature of adsorption of polar and cationic organic ions on various clay minerals. Such results have resulted in the discovery of new products known as organic clad clay materials.⁶ Organic clad montmorillonites and kaolinites are now commercially produced and are applied in gelling agents, manufacture of lubricants, as fillers and strengthening agents in paints. Organic clad clay minerals are tailor-made to fit a particular organic molecule with which it is to be used.

Agriculture :

In agriculture clay mineralogy provides an understanding of how the plant nutrient is retained in the soil. The retention capacities mainly depend on the cation exchange capacities of the clay minerals.¹⁶ Table II gives the dissociation behaviour of cations for three types of clay minerals quoted by Chatterjee.¹⁷

TABLE II. Cationic activity of homoionic clays
Fraction of cation active at the saturation point

Clay Minerals	Na	K	NH ₄	Mg	Ba	Ca
Montmorillonite	0.21	0.25	0.18	0.011	0.020	0.050
Illite	0.10	0.13	0.12	0.020	0.014	0.040
Kaolinite	0.34	0.33	0.25	0.030	0.050	0.030

Table II shows that though kaolinite adsorbs only a small amount of plant nutrients, it parts with the nutrients much more readily than montmorillonite or illite. For a proper economy of fertilizers it is expedient that kaolinitic soils should be treated with fertilizers in small quantities frequently. For montmorillonitic soils a larger quantity of fertilizer should be added, all at one time. Acid clays release Al and Fe ions on treatment with fertilizers. These ions fix the phosphate nutrients making them unavailable to the plants. This action depends on the clay mineralogy of the soil.

Petroleum Industry :

Montmorillonitic clays are used for preparing drilling muds in petroleum industry because of their favourable rheological properties. Activated bentonites are used for separating undesirable chemical constituents from petroleum.

Clays are used as catalysts in the manufacture of gasoline from crude oil. For a catalyst to be useful in petroleum industry, it should produce mainly high octane gasoline and should not break down the hydrocarbon to a gas and carbon. These conditions have been achieved and catalysts are being produced from clays composed of montmorillonite, halloysite and kaolinite. Processes have been developed to modify the structures of clay minerals without destroying them.¹⁸

Foundry :

A mixture of clay and sand is used in foundry practice for casting metals. The dry and green strength values are important factors for assessing the suitability of a clay. These values depend on the clay mineralogy and cation exchange capacity. Sodium montmorillonite has high dry and green strength i.e., before drying to remove the tempering water.^{19,20} Calcium and hydrogen montmorillonites produce very high green strength and moderately low dry strength. The fire clays have lower green strengths than bentonites.⁶

By a mineralogical study Grim and Bradley²¹ could suggest the potentiality of an illitic clay for use in foundry, which was earlier discarded as worthless by a refractory manufacturer.

Paper Manufacture :

Kaolinites are used as coating agents in paper manufacture to make the paper opaque, white and printable. Some of the qualities which the kaolinites should possess are, absence of quartz and other impurities, closely controlled particle size, and shape and crystal perfection.²² The kaolinite mineral should be well crystallized with distinct hexagonal outlines in book-like units.

Disposal of Atomic Waste :

Clay mineralogy has found a prominent application in the disposal of undesirable isotopes from nuclear reactors. These isotopes are adsorbed on the clay minerals and heated to high temperatures to get an insoluble compound. The resulting product being insoluble, does not contaminate the ground water when buried. The adsorptive capacities of clay minerals for isotopes depend on the cationic properties.²³ Barrer and coworkers²⁴ have suggested that the clay minerals can be used as atomic sieves to separate some of the more useful isotopes which are usually disposed off with other undesirable isotopes.

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REFERENCES

1. Mackenzie, R.C. Clay Min. Bull., 4, 52, 1959.
2. Grim, R.E., 'Clay Mineralogy', McGraw Hill Book Co., New York 1953, pp. 384.
3. Searle A. B., and Grimshaw, R. W., 'The Chemistry and Physics of Clays and Other Ceramic Materials', Ernest Benn Ltd., London, 1959, pp. 942.
4. Freeman, I. L., Clay Min. Bull., 3, 50, 1956.
5. Everhart, J. O., and Van der Beck, R. R., Bull. Amer. Ceram. Soc., 32, 239, 1953.
6. Grim, R. E., Amer. Mineral, 45, 259, 1960.
7. Grim, R. E., and Johns W. D., J. Amer. Ceram. Soc., 34, 71, 1951.
8. Noble, W. 'Filing of Common Brick', Natl. Brick Advisory Council Paper, No. 4, London, 1950, pp. 123.
9. Ramachandran, V. S., and Majumdar, N. C., J. Amer. Ceram. Soc., 44, 96, 1961.
10. Everhart, J. O., Brick and Clay Record, 134, 58, 1959.
11. Ramachandran, V. S., Majumdar, N. C., and Patwardhan, N. K., Ind. Conc. J., 34, 380, 1960.
12. Grim, R. E., and Kulbick, G., Bull. Soc. franc. Ceramique, 36, 21, 1957.
13. Wahl, F. M., Ph.D. Thesis, Univ. of Illinois, 1958 (cf. reference, 6).
14. Wilburn, F. W., J. Soc. Glass Tech., 38, 271, 1954.
15. Wintercorn, H. F., Colloid. Chem., 6, 450, 1946. Chem., 54, 671, 1950.
16. Chatterjee, B., and Marshall, C. E., J. Phys. Colloid
17. Chatterjee, B., Sci. & Culture, 27, 272, 1961.
18. Milliken, T. H., Oblad, A. G., and Mills, G. A., Bull. 169, Div. of Mines, Calif., 314, 1955.
19. Grim, R. E., and Cuthbert, F. L., Rept. Inv. 110. 111, Geol. Surv., 1946.
20. Grim, R. E., and Cuthbert, F. L., Rept. Inv. 102, 111, Geol. Surv., 1945.
21. Grim, R. E., and Bradley, W. F., J. Amer. Ceram. Soc., 22, 157, 1939.
22. Murray, H. H., and Lyons, S. C., Pub. 456, Natl. Acad. Sci., U. S., 31, 1956.
23. Kerr, J. M., Bul. Amer. Ceram. Soc., 38, 374, 1959.
24. Barrer, R. M., Mackenzie, N., and McLeod, D. M., J. Phys. Chem. 58, 568, 1954.