CLAY MINERAL RESEARCH IN AUSTRALIA

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ABSTRACT

An account of recent progress and current work is given in a summarized form dealing mainly with clay investigations in C. S. I. R. O., an Australian government research organization.

Although some emphasis is laid on the work designed to identify the nature and assess the properties of clays concerned with building-material manufacture, soils, and ceramics, there are several investigations which deal in a fundamental manner with the crystal structure and surface properties of clay minerals. These items of general interest include projects on the structure of vermiculite, the rehydration and surface properties of kaolinites, the nature and occurrence of Australian illites and attapulgites, and a regular exfoliation effect in montmorillonite suspensions.

INTRODUCTION

Australian research in clay mineralogy has developed almost wholly during the past decade. At present several groups of research workers concerned with the structure, occurrence, and properties of clays and allied minerals, are situated mainly in Melbourne and Adelaide, in three Divisions of the Commonwealth Scientific and Industrial Research Organization (C. S. I. R. O.), one of the principal government research establishments in the country. The Divisions concerned are Building Research, Soils, and Industrial Chemistry. The following notes record some of the results and current activities in these laboratories and in certain university departments.

THE DIVISION OF BUILDING RESEARCH, HIGHETT, MELBOURNE

Research here is connected with the heavy clay industry, particularly with respect to surveying works and raw-material resources under the direction of J. S. Hosking (1951, 1955), studying the durability of fired heavy clay products, and investigating the nature and properties of clay minerals of importance in the raw-material deposits. Field surveys and laboratory evaluation of heavy clays by J. A. Ferguson (now at Armour Research Foundation, Chicago) are covered in reports on the clays of the Brisbane area (Ferguson, 1954) and the Sydney area (Ferguson and Hosking, in press). Certain clays from Tasmania have been examined by W. F. Cole and A. R. Carthew (1953), and the general correlation of the mineralogy with the physical properties of these clays has been studied.

The survey work has raised a number of problems with regard to identification and quantitative estimation of clay minerals, in particular by the D.T.A. method (Carthew and Cole, 1952, 1953). The identification of mixtures by D.T. A. is difficult (Carthew, 1955), but some success has been attained in the differentiation of illite-montmorillonite minerals by treating with piperidine before thermal analysis (Carthew, in press). A further note on this topic is about to be published.

Many industrial clays have been found to contain mixed-layer illite-montmorillonite and vermiculite-biotite assemblages. W. F. Cole, investigating this field, claims that there are two main groups, the minerals of which can be altered from one to another, and that the direction of transformation (whether from montmorillonite to illite or vice versa) can be determined from the position, in the D.T.A. curve, of the endotherm due to release of hydroxyl water (Cole, 1955; Cole and Hosking, in press).

Studies on the dehydration of vermiculite by W. F. Cole, in collaboration with G. F. Walker (Division of Industrial Chemistry), have employed thermal and x-ray methods to interpret the mechanism of dehydration in the low-temperature range (Walker and Cole, in press). The desorption-adsorption isotherms of powdered vermiculites saturated with various cations have shown a marked hysteresis effect similar to that found with montmorillonite, occurring between successive phases containing single and double water sheets.

The durability of fired clay products may be affected by their tendency to rehydrate in normal atmospheric conditions, and past work by R. D. Hill (1953a) has shown that products made from the common clay minerals may all rehydrate to some extent even when the firing temperature exceeds 1000° C. This rehydration can cause an expansion of the body which may have serious consequences when it occurs in masonry units, ceramic tiles, and the like. The rehydration has been attributed to zeolite formation in well-burnt clay bodies containing alkali oxides (Hueber and Milne, in press). The connection between the rehydration and expansion, and the amount of alkali and alkaline earth metals in the original clay body is being investigated.

In the course of the foregoing study it was found that bodies formed from well-crystallized kaolinites harden considerably on rehydration after firing at relatively low temperatures (Hill, 1953), and later work has shown that a further increase in compressive strength (up to 20,000 lb./sq. in.), may be obtained when the rehydrated kaolinite is refired. Some understanding of the structural changes that occur has been obtained, in part by a parallel study of fired and rehydrated dickite.

THE DIVISION OF SOILS, WAITE INSTITUTE, ADELAIDE

The work of the Clay Mineralogy Section, headed by K. Norrish, has demonstrated that many agriculturally important soils in Australia contain dominant illite. This mineral is of very small particle size and is not normally interstratified with other clay minerals. Available data suggest a reciprocal relation between exchange capacity and potash content. Further work by Norrish has provided some confirmation of an earlier suggestion (Brown and Norrish, 1952), that H_3O^+ replaces K^+ in hydrous micas.

Projects on montmorillonite have produced items of basic interest, particularly the demonstration that there is no evidence for the formation of the alleged esters and silanes of this mineral (Brown, Greene-Kelly, and Norrish, 1952), and the discovery of novel phenomena related to the swelling of montmorillonite in dilute salt solutions (Norrish and Quirk, 1954; Norrish, 1954, 1955). It was shown in this latter work, that montmorillonite suspended in salt solutions more concentrated than 0.5 N swells in a stepwise "crystalline" fashion, giving limiting spacings between 15 A and 22 A depending of the size and charge of the cations in the solution. In more dilute solutions, an osmotic, macroscopic type of swelling occurs. In this type, the swelling proceeds in a linear manner with respect to water content, up to very large separations.

The transition to macroscopic swelling occurs only with small monovalent cations in the salt solutions, such as Na^+, Li^+ and H_3O^+, where the hydration energy of the cations is sufficient to overcome the potential barrier to further swelling set up by the electrostatic attractive forces acting between the silicate layers in the mineral. Hydration energies of the larger monovalent cations are insufficient to effect the transition, so that swelling is limited to a maximum of two molecular thicknesses of water between the basal planes, even when very dilute solutions are used. With polyvalent cations, the higher hydration energies are offset by other factors, and swelling is limited to two or three molecular steps.

A feature of the swelling process is the sudden "explosion" in spacings from values between 19 A and 22 A for the more concentrated solutions containing small monovalent cations, to a figure near 40 A when the solutions are diluted. A similar effect is shown by certain vermiculites under these conditions. Once the exploded stage has been passed, swelling proceeds steadily as a reciprocal function of the normality of the solution phase, and the small cations used to overcome the potential barrier may be exchanged with larger monovalent cations without affecting subsequent swelling. At extreme dilution, spacings as high as 140 A have been recorded, and they appear to go on beyond this value, though diffraction effects become more diffuse and difficult to record in this range. The measured increase in spacing accounts for all, or almost all, of the volume increase in physical swelling.

In the course of work on clay-mineral occurrences, an interesting deposit of palygorskite was found in Queensland (Rogers, Martin, and Norrish, 1954). The mineral is associated with sepiolite and Tertiary lacustrine dolomite, and in places forms layers as thick as four feet. Since then, palygorskites have been found in other localities in Australia, in deposits formed under similar conditions.

A dolomite, probably lacustrine, near Tintinara, South Australia, contains a mineral which gives an x-ray pattern similar to sepiolite, but the chemical composition is that of palygorskite, so that the substance appears to be an aluminum-sepiolite. The mineral occurs as the clay fraction of local soils, giving these some unusual physical properties which first attracted attention to the area. On a 100 percent clay basis, the soil contained 120 percent water at wilting point. The same conditions for montmorillonite give a figure for water of only 50 percent whilst figures for illite and kaolinite are even less. Studies of palygorskites and sepiolites showed that the fibrous minerals have a higher water content at wilting point than the platy clay minerals, the particularly high value for the Tintinara Al-sepiolite being due to the very small particle size of this fibrous mineral (Rogers, Quirk, and Norrish, in press).

General projects on soils include a comparative study of the clay mineralogy of rendzinas and terra rossas in South Australia (Norrish and Rogers, in press). The two soil groups occur intermingled and over the same parent material. The color and classification of these soils were determined by the amount of free iron oxide in the clay fraction, and this in turn was related to the amount of iron weathered from the parent material. Red terra rossas occur commonly over rocks containing chlorite, but where the parent rocks contain little iron, or only iron in minerals which change little during soil-formation (e.g., illite), the overlying soils are rendzinas.

In the Regional Laboratory of the Division of Soils, at Canberra, work on the occurrence and genesis of clays is in progress. A. D. Haldane is studying the natural weathering of igneous rocks in relation to soil formation. Particular attention is being directed to the type of clay mineral formed from each of the primary component minerals under various weathering conditions. It is hoped that the mechanism of the chemical changes involved may ultimately be established. Other investigations in progress are concerned with the formation of horizons of high clay content in the soil profile.

THE DIVISION OF INDUSTRIAL CHEMISTRY, CEMENT AND CERAMICS SECTION, MELBOURNE

One of the functions of this group is to advance knowledge of clay minerals with special reference to Australian raw materials used in various industries. Some of the topics are of general basic interest, particularly those concerned with the structure of vermiculite, the behavior of clay-water systems, and the surface properties of clay minerals. Survey work on local clays for special purposes (ceramics, paper, rubber, oil decolorizing, etc.) is a feature of the group.

An account of the structure of Mg-vermiculite has been published by G. F. Walker, in collaboration with A. McL. Mathieson (Chemical Physics Section), in which the interlayer water molecules and exchangeable cations were located (Mathieson and Walker, 1954). More recently they have been investigating the structures of partially dehydrated forms of this mineral with results discussed in more detail in a separate communication to this conference.

Walker (1956) has developed an optical technique to measure the rate of diffusion of water molecules into vermiculite crystals. The optical effect is produced when a flake of partially dehydrated vermiculite, in the single water-sheet condition, is allowed to rehydrate, when refractive-index changes show up as moving boundaries representing wave fronts of water molecules diffusing into the crystal. Two lines may be observed, the stronger corresponding to an expansion of the lattice in the *c*-direction from 11.6 A to 13.8 A, and the second to a smaller expansion from 13.8 A to the 14.4 A normal phase. Rate measurements indicate that the lines move in accordance with diffusion theory, so that the technique may prove to be convenient for the study of general sorption kinetics.

Research in the field of plastic clay behavior, including clay-water relationships and orientation phenomena, has been due largely to W. O. Williamson, assisted by R. W. Cox and J. H. Weymouth. The current work of W. O. Williamson on the effects of strain on the microstructure of plastic masses has both theoretical implications and industrial significance, particularly with respect to anisotropic effects such as differential drying-shrinkage of ceramic bodies.

In this work, optical and x-ray methods have been employed; a versatile "peel" technique allowed preferred orientation of clay minerals to be deduced (Williamson, 1941, 1955; Weymouth and Williamson, 1953). Early studies on orientation effects in ceramic bodies (Williamson, 1941) have been extended to the behavior of a kaolinite-illite mixture deposited by casting, or plastically deformed. The development of tension fissures and shear joints was related to stresses applied to these plastic materials (Weymouth and Williamson, 1953, 1953a; Williamson, 1947, 1954). During the course of the work, an interesting effect was discovered; i.e., a rotationally rolled sphere of plastic clay became first a cylinder, but then a tube (a comparable effect is exploited in the manufacture of certain metal tubes; Williamson, 1954). Subsequent collaborative work by A. J. Gaskin with K. Weissenberg at Cambridge University showed that the effect is not related to particle shape or size, but is more a reflection of the ratio between the flow characteristics and the elasticity of the mass.

Studies on the orientation of planar elements in clay fabrics showed that greater drying-shrinkage occurred in a direction normal to the planes of alignment of flakes than parallel thereto. As the clay minerals were not of the lattice-expanding type, this was explained by assuming a greater thickness of water films in the directions normal to the planes of alignment of the clay particles (Williamson, 1947, 1948, 1954).

Drying-shrinkage ceased at a critical, though relatively large, water content, in the internally oriented test-pieces studied (Williamson, 1951, 1955b; Cox and Williamson, in press), suggesting that clay particles are separated when the water content of the mass is adequate, and come into virtual contact when sufficient water has been lost (Williamson, 1955). The mechanical properties of certain regions of close aggregation in a plastic clay mass may differ from those of associated less compact regions (Williamson, 1955b). A novel finding concerned the effect of drying on the recovery of a deformed clay mass; i.e., if drying were prevented, recovery was at first spontaneous, ultimately ceased, but could then be renewed by drying.

Studies on linear fabric-elements (prismatic rutile and tourmaline included in plastic clays) showed orientation effects on deformation that could be expressed quantitatively and compared with the lineations found in naturally deformed rocks (Williamson, 1955a).

Survey work on Australian clays for ceramic purposes forms a large part of the work of the section. Information on such clays occurring in South Australia has been published (Gaskin and Samson, 1951), and similar data will soon appear for Western Australian clays. Techniques of identification include methods based on dye adsorption developed by R. W. Cox and A. J. Gaskin, and x-ray and thermal methods. An automatic thermobalance has been designed and used by Gaskin for quantitative estimation of clay-mineral components in mixtures, in which samples are dehydrated at a rate automatically related to the reciprocal of the decomposition rate of the components, through the whole temperature range. Sharply defined isobaric curves are produced on a single record with weight loss and temperature as coordinates.

Recent collaboration with the Soils Division has shown that unusual clay minerals are quite widespread in Australia. Attapulgites from Queensland and South Australia are being examined and compared with American material in regard to bleaching and gelling characteristics. Some work is in progress on local specimens of dickite, sepiolite, halloysite and hydrobiotite.

The work of the late Dr. H. R. Samson was at first connected with the occurrence and properties of ceramic clays (Gaskin and Samson, 1951). A project on the influence of fluoride ions on the surface of kaolinite particles raised interesting points regarding surface charge and phosphate desorption (Samson, 1952). Later he collaborated with R. K. Schofield at Rothamsted in research designed to correlate the behavior of clay minerals dispersed in dilute solutions with the surface structure and charge characteristics of the particles. The link between chloride adsorption and the deflocculation point of kaolinite suspensions proved an important step in the establishment of a theory of "edge-to-face" assemblies in a flocculated clay suspension, in which a stable framework was produced by the electrostatic attraction of negatively charged (basal) faces of clay flakes for the positively charged edges of neighboring flakes (Schofield and Samson, 1953).

Since then a good deal of evidence has been appearing to substantiate the hypothesis of "edge-to-face" flocculation. The remarkable effect produced by the neutralization of positive charges on kaolinite edge-faces when minute amounts of (negatively charged) montmorillonite are added to kaolinite suspensions is an example. Not only is the kaolinite deflocculated under pH conditions normally causing flocculation, but it is no longer able to adsorb chloride ions or complex dyestuff anions (Samson, 1954). This leads to a sensitive method for the detection of small quantities of illite and montmorillonite in kaolinites; i.e., pure kaolinite is stained strongly by an anionic dye such as sodium alizarin sulfonate, but kaolinite mixed with a trace of illite or montmorillonite remains unstained or lightly stained.

The last detailed account of the relations between flocculation effects in kaolinite suspensions and the presence of anionic agents (sodium pyrophosphate, polymetaphosphate, aliginate etc.) was published (Schofield and Samson, 1955) shortly after the untimely termination of the career of this young and promising worker.

THE UNIVERSITY OF MELBOURNE, DEPARTMENTS OF GEOLOGY AND CHEMISTRY

An investigation of the behavior of kaolinite suspensions, by N. Street, has shown that correlation may be established between rheological effects and zeta-potential values. The material used was a pure kaolinite from Egerton, Victoria, fractionated and converted to the hydrogen form, with a specific surface of 17.8 sq. m/g. Measurements of surface conductance provided values that agree reasonably well with those calculated from the zeta-potentials.

In general, the rheological picture agrees with that proposed by Samson and Schofield for kaolinites and by van Olphen for montmorillonites; i.e., that clay particles possess negatively charged faces, and, at least at low pH, positively charged edges. From the results of these studies which include data about the region before the equivalence point, it is proposed that the hydrogen clay is flocculated by edge-to-face attraction, and that the gradual neutralization of the clay, causing increased zeta-potential, gives rise to increased face-to-face repulsion, with unravelling of "coils" of particles, as with polymers. Increased hydration associated with a particular ion will have the same effect. Both these effects give increased anomalous viscosity, and the results have been correlated with yield value measurements. Above a certain pH, the edges of flakes also become negatively charged, and a low viscosity system develops as the "coils" break up to give a dispersed suspension.

At present, streaming-birefringence measurements are being made to gain more information about the shapes and sizes of the particles in suspension, as electron microscopy has so far not given a sufficiently comprehensive picture of these factors. In addition, some precise conductivity studies are being made, both for the purpose of axial-ratio determination, and for surface conductance measurements at high electrolyte concentrations.

An examination of the conditions under which strong colorations are produced in clays such as montmorillonites, by the action of amines such as benzidine, has given G. Leeper evidence to suggest that the implied oxidation may be connected with the presence of iron ions in the minerals concerned. The matter may be resolved more definitely by current work in which it is hoped to produce the color reaction in an environment under controlled redox-potential conditions.

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