treating with e.g. K$^+$ ions for a limited time some of the original 14 Å material remains at 14 Å while the remainder of the 14 Å material collapses to 10 Å and reinforces the original 10 Å line. Whether they are different minerals or not is a matter of definition.

*Dr Brindley.*—If the collapsed spacings are interstratified with the original ones, then an intermediate reflexion between 14 and 10 Å would be expected, and this would provide clear evidence of an interstratified sequence, but if only 10 and 14 Å lines are observed, then the inference is that two separate minerals are present.

*Mr W. A. Mitchell.*—Scottish soil clays on basic igneous rocks frequently have in the lower layers a trioctahedral illite with a 10 Å line. This line decreases in intensity on going up the profile, while a 14 Å vermiculite line which appears in the lower layers becomes much more intense in the top. This may indicate the development of vermiculite at the expense of trioctahedral illite.

*Dr G. Nagelschmidt.*—Does the mineral described make up the bulk of the clay fraction? How many minerals are present in the clay?

*Mr Brown.*—In the surface soil the 14 Å mineral which collapses on heating to 300°C or on prolonged treatment with NH$_4^+$ or K$^+$ ions forms a large part of the clay fraction. At greater depths the proportion of this mineral decreases.

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**THIXOTROPY AND INTRACRYSTALLINE SWELLING**

*BY U. HOFMANN, R. FAHN AND ARMIN WEISS.*

*Read 8th November, 1952*

The phenomenon of thixotropy has often been explained by postulating the formation of a lattice structure from the solid particles of the gel. Such a structure is assumed to arise on standing, and to be destroyed on shaking.

Electrical conductivity measurements by Dowell and Usher (1934) and by Peter (1949) support the existence of such lattice structures, as do also our electron microscope observations (1952) and investigations on the volume change accompanying centrifugation (Fahn, Weiss and Hofmann, 1953).

By subliming off the liquid from set thixotropic gels of kaolin, bentonite and halloysite, which had been frozen, it has been possible to isolate the liquid-free lattice-structures (Weiss, Fahn and Hofmann, 1952).

*This is a brief summary. For full details of this work, consult the papers by Fahn, Weiss and Hofmann, in the list of references.*
In the case of bentonite and kaolin, these liquid-free structures isolated from aqueous gels occupied the same volume as the original gel. With bentonite it was possible to isolate such structures having a specific weight of only 0.055 gm./cm.³ The liquid-free structures possessed a measurable compressive strength, and in the case of bentonite, a considerable degree of elasticity.

The volume of kaolin gels having a given time of setting varies in the opposite direction to the interlayer distance of montmorillonite, if variations are made in the exchangeable cations, and in the concentration of the electrolyte solution. Probably the attachment of the kaolinite platelets to form a lattice-structure is influenced in the same way by the cations and the electrolyte solution as is the linkage of the silicate layers in montmorillonite. The bigger the interlayer distance, the weaker is this linkage. The weaker the force of attachment between the kaolinite platelets the smaller will be the volume of the thixotropic lattice-structure for a given resistivity, or a given setting-time.

In non-polar liquids, the volume of kaolin gels having a given time of setting is larger than in water. Probably the kaolinite platelets become attached to one another by direct contact, in such liquids, and this attachment is the more effective, the less is the tendency of the kaolinite platelets to be wetted by the liquid.

References.

Discussion.
Dr Nagelschmidt.—One of your slides showed an arrangement of spheres. Is it generally recognised that you can get thixotropic systems with spheres?
Prof. Hofmann.—Usher¹ has investigated thixotropic systems which were built up from spherical particles of soot. Correns² has also obtained thixotropic systems with the isometric particles of quartz, but these systems were not very voluminous.

Dr Howard.—I would like to ask Dr Hofmann whether he gets thixotropy in systems which are almost flocculated?

Prof. Hofmann.—The only thing of relevance that can be obtained from our investigations is that the volume of the thixotropic kaolin gels often shows a small diminution at very high salt concentrations, e.g., 3 N and higher.

Dr Howard.—I was wondering whether Prof. Hofmann had observed thixotropy at the iso-electric point, that is in a condition neither flocculated nor deflocculated.

Prof. Hofmann.—We have not so far got measurements which would enable us to say anything definite about this.

Mr Samson.—First of all I would like to mention some work done by Schofield and Dakshinamuriti on the ionic conductivity of montmorillonite gels. It was found that the conductivity of N/10 KBr solution was reduced 16% by adding 1% montmorillonite, which under these conditions formed a thixotropic gel. No reduction in conductivity was observed when the same clay mineral was dispersed in N/40 KBr, and in this case a deflocculated (i.e., fluid) suspension was produced. This was interpreted as indicating that the montmorillonite platelets in the thixotropic gel were drawn together in such a way as to impede the movement of the bromide ions.

In kaolinite suspensions, I have observed that some degree of thixotropy is inhibited when the amount of deflocculant added (say, NaOH) is just half of that required for complete deflocculation. Evidently some of the edge-faces still retain sufficient positive charge to attract the negative surfaces of adjacent particles and cause flocculation. The structure so produced is weak enough to be broken down mechanically, and re-forms with time.

I should like to ask Prof. Hofmann if he had any difficulty in dispersing kaolinite in the non-polar liquids. The process may perhaps be facilitated by saturating the kaolinite with organic cations.

Prof. Hofmann.—We did not use organic cations but only, as you have seen, sodium or calcium. As I said at the beginning of my paper, dispersion in the non-polar liquids was effected by prolonged shaking.

Dr Nagelschmidt.—Is it generally agreed that in the solid state of the thixotropic system, all the particles are combined in just one framework?

Prof. Hofmann.—In the networks illustrated in our pictures* there can be no doubt that the linking of the particles is coherent over the entire region of the network. It is possible however that the network contains regions of varying degrees of solidity, and it is also possible—as the ultramicroscope shows—for a few freely moving particles to exist in spaces in the network.

*Not shown here. See the papers by Hofmann and collaborators quoted in the list of references.
Dr Clark.—From the simple electrical point of view, there have always been two possible explanations of flocculation and deflocculation: either you can imagine that deflocculation is due to a charge which holds the particles apart and a discharge when they are flocculating—or the other point of view, which is obviously very much supported by Samson and Schofield’s information given to-day, that you have a discharge when the material is deflocculating, and a form of dipole when it is flocculating.

Mr Jones.—I think some work on the dielectric constant of water in thixotropic systems and its variation with the state of flocculation of the suspension was done in Germany.

Prof. Hofmann.—I don’t at present know of any investigations which have been carried out in Germany on the dielectric behaviour of water in thixotropic systems. Investigations of this sort could perhaps give some information on how far the water dipoles can still orient themselves freely. They are made difficult by the fact that the water content in our gels is rather high. For instance, in the kaolin gels it is 2-3 cm.$^3$, and in the bentonite gels over 10 cm.$^3$ of water per gram of solid substance.

Dr Clark.—There is an interesting technique for removing water from a system like this in which you take the material up above the critical point and then remove the water as vapour. By this means you effectively remove water without changing the phase. It might then be possible to make electron-micrographs of the substance.

Prof. Hofmann.—This may be a still better method to get an undisturbed structure.

Dr MacEwan.—I think that fairly long-range forces can exist between montmorillonite layers. This idea is mainly based on observations which Norrish made in our laboratories (confirmed, I believe, by certain work in other laboratories—all, so far, unpublished). Norrish took X-ray photographs, with monochromatic radiation, of montmorillonite suspensions, and observed, with Na systems, and, in certain circumstances, with H systems, spacings of up to about 100 Å which might have gone even higher could they have been followed. Two observations must be made regarding these spacings. Firstly, they did not indicate an absolutely uniform distance between layers; fourier transforms performed from the X-ray data show that they represented a mean spacing, with large variations on either side of the mean. However, the layers were probably almost parallel, and not appreciably curved, indicating that some fairly long-range forces were effective. The system was deflocculated in the range of electrolyte concentrations corresponding to the highest spacings.

(Added later). I am none the less convinced that the mechanism postulated by Prof. Hofmann, of linkage of surfaces of like charge through intervening ions, must occur in certain colloidal systems, and that its possible importance has been unduly neglected in
theoretical discussions of the interaction of charged particles (see, for instance, Verwey and Overbeek’s book\(^1\) on this topic).

This idea has quite a long history behind it. Something of the sort was suggested as long ago as 1934 by E. W. Russell\(^2\). I suggested it myself as a mechanism for flocculation in 1948\(^3\), using the known complexes of montmorillonite as an analogy.

![Graph showing electrostatic attractive potential vs. distance](image)

It is interesting in this connexion to speculate on the distances at which this mechanism can be effective. The figure herewith shows the results of calculations (unpublished) on the variation of electrostatic attractive potential with distance, for surfaces, the density of charge of which is the same as that of montmorillonite \((\sigma = \sigma_0)\), 10 times this value \((\sigma = 10\sigma_0)\) and \(\frac{1}{10}\) of this value \((\sigma = \frac{1}{10}\sigma_0)\). It will be


\(^3\)Nature **162**, 935.
seen that the charge density of montmorillonite constitutes something of an optimum value for the operation of this force. With a much lower charge, the potential is everywhere too low to be effective; with a much higher charge, the attractive potential dies out very rapidly with distance, so that the attractive force may in fact never become effective if the surfaces are covered by tightly held films of adsorbed molecules. In illustration of this, the dotted line shows a possible variation of the potential energy of adsorption with distance. This will in general start at a value intermediate between the peaks of curves (1) and (2), and will fall to zero rather steeply. It will be seen that, on combining this curve with curve (1), no stable minimum is obtained, though a stable minimum may be obtained on combining with curve (2). Thus surfaces with a very high charge will probably have no tendency to link in this way at all.

From the paper by Schofield and Samson presented at this meeting, we have seen that serious consideration must be given to the possibility that edge surfaces of positive charge are present on kaolinite crystallites. It should be noted that, from the above arguments we should expect that not only will surfaces of unlike charge attract each other, but also surfaces of like charge (provided the charge density is within certain limits). Uncharged surfaces can also attract each other by van der Waals force, although the presence of adsorbed layers may prevent this force from becoming effective. Bearing in mind these considerations, the interaction between kaolinite particles might be expected to be a complex one, depending on pH, somewhat as follows:

1. pH low or neutral. Faces -ve, edges +ve. Face-to-face, edge-to-edge and edge-to-face agglomeration all possible, the latter probably predominating.

2. pH near to isoelectric point for edge. Faces -ve, edges uncharged. Face-to-face agglomeration most likely. Thixotropy unlikely in this region.

3. pH high. Faces and edges -ve. Face-to-face, edge-to-edge and edge-to-face agglomeration all possible. Which predominates will depend on the extent of each type of surface, and its charge density. It is in this region that the analogy with interlamellar swelling of montmorillonite would be expected to show itself.

Dr Hofmann (communicated).—I am convinced that all the points which have been brought up in the discussion, and in the subsequent communication by Dr MacEwan, are of great interest. I regret only that our experimental material is not adequate to answer these questions in a way which is reliable, and free from speculations. To solve the numerous mysteries, which are still bound up with the phenomenon of thixotropy, many experiments will be required. These should as far as possible be carried out in such a way that only a few parameters are altered at a time. We have made an attempt to
operate on this principle by using kaolin instead of bentonite in order to exclude intracrystalline swelling, and by using electrolyte solutions containing the same cation as that with which the clay was saturated, in studying the influence of electrolyte concentration.

ORIENTED-AGGREGATE SPECIMENS OF CLAY FOR X-RAY ANALYSIS MADE BY PRESSURE

BY W. A. MITCHELL.

Read 10th April, 1953.

The use of preferentially oriented aggregate specimens of clay for X-ray diffraction has been widely adopted since its origination by Bradley, Grim and Clark (1937). It is an extremely useful technique giving greatly enhanced intensity of diffraction from the basal planes of platey minerals relative to that from the general planes; the amount of one particular clay mineral which can be identified in a mixture is very much less than by the normal powder method.

The usual method of preparing oriented aggregate specimens of clay is by the evaporation of suspensions. To get good orientation in this way certain conditions should be fulfilled. The specimen should contain no material larger than clay-size; this can be ensured by separating the required size-fraction by sedimentation methods. Also the sample should contain a minimum of non-platy minerals such as quartz or felspar. It may sometimes be necessary to remove oxides and hydroxides of iron and aluminium, which frequently occur either as coatings on the surface of the individual clay particles or as a cement binding the particles into irregularly shaped aggregates. Various chemical methods have been used for their removal, for example, Tamm (1922), Dion (1944) and Mackenzie (1953). It is then necessary to get as complete a dispersion as possible of a two or three per cent suspension of the clay in water. Clay saturated with Na⁺ or NH₄⁺ is readily dispersed, and it is often advantageous to replace the exchangeable ions with one of those. A small quantity (about 1 cm. deep) of the suspension is evaporated slowly on a glass plate in a vacuum desiccator. The flat clay particles tend to settle horizontally and the film of clay so formed can be cut into specimens of suitable size.

Making oriented specimens in this way may involve the expenditure of a considerable amount of time, but a new technique (Brown 1953) employing centrifuge sedimentation instead of evaporation is much quicker.

The new method now to be described has been very useful in the routine examination of a large number of clay samples. It is very simple and rapid, the specimens being made directly from the dry clay. The apparatus (fig. 1) is made of steel, and consists of a plate with a half-inch diameter button projecting about one-eighth inch