Some difference is also observable between the behaviour of silver as a metal, or oxide, and as an exchange cation. In the former instance, according to Faith and Keyes (1931), it is necessary to work at temperatures between 400 and 650°C, whereas with silver bentonite a temperature of 325°C suffices. Moreover, with metallic silver or silver oxide the use of ozone and hydrogen is necessary, whereas with silver bentonite the more convenient and economic method of an air current suffices.

The other exchange cations used do not increase the activity of bentonite for the oxidation of alcohol, chiefly because they are, by their nature, less active for this reaction than silver and copper. In addition their valency being greater than 1, they may form the complexes similar to those postulated by Méring (1946).

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References.

M. Le Blanc and E. Plaschke, 1911. *Z. Elektrochem.* **17**, 55.

W. L. Faith and D. B. Keyes, 1931. ˙ *Industr. Engng. Chem.* **23**, 1250.

L. F. Marek and D. A. Hahn, 1932. "Catalytic Oxidation of Compounds in the Vapor Phase," New York, p. 72.

J. Méring, 1946. *Trans. Faraday Soc.* **42B**, 205.

A STUDY OF THE SYNTHESIS OF CLAY MINERALS

By S. HENIN and O. ROBICHET.

Read 6th November, 1953.

Previous Attempts at Synthesis.—Up to now no method seems to have been found for carrying out laboratory syntheses of clay minerals in conditions similar to those obtaining in soils. Such a method would be of especial value because it would lead to the possibility of determining the conditions of formation of clay minerals in the natural state.

We have attempted, in a series of previous researches, to elaborate such a method. The aging of co-precipitates of silica and hydroxide, even at a temperature near to 100° and in an aqueous medium, does not produce clay minerals. The hydroxide alone, nevertheless, will crystallize in a few days in these conditions. The association of silica with hydroxides thus hinders, to a considerable degree, the crystallization of the mixture (Caillère and Hénin, 1950).

These silica and hydroxide precipitates showed no detectable alteration after 250 alternations of drying and wetting. At the most, a slight crystallization of the hydroxides is observed in certain pre-

parations where the constituents are less intimately mixed. The formation of flaky minerals as a result of aging processes thus seems improbable.

These negative results led us, in collaboration with Miss Caillère, to make use of electrolytic attack on metal foil. The results obtained have already been published (Caillère, Hénin and Esquevin, 1953). We will merely recall that it is possible in this way to obtain products showing some signs of an antigorite structure, being made up of hydroxide layers separated from each other by water layers; the system is held together by a small quantity of silica. Similar complexes can be obtained with other anions (aluminates and chromates). On the other hand, only magnesium, nickel and cobalt can be used as the metals; aluminium and iron do not give such preparations. The importance of the hydroxide structure is clear, since only metals which readily give brucite-type hydroxides can give these clay-mineral-like substances. Finally, from our most recent work on this subject it appears that the quantity of anions fixed on the brucitic layers cannot be increased, probably because of the high mobility of OH ions compared to other anions. If the pH is lowered, one obtains merely a more or less voluminous deposit of amorphous substances on the electrodes (Caillère, Hénin and Esquevin, 1953).

Method of Work.—These—at least partially—unsuccessful trials, led us to seek other methods. Natural solutions being generally very dilute, especially in silica, we considered that clay mineral synthesis might possibly be realized by working under similar conditions. The difficulty then lay in obtaining the substances in sufficient quantities for study. In order to do this, we used the following method.

The mother solutions, having a concentration of the order of one to some tens of mgm. per 1., trickle into a pyrex glass flask of several liters capacity containing two liters of distilled water. The speed of flow of the solutions is adjusted by capillary inserts until they are both running in at the rate of 1 c.c. per hour. The concentration in the flask thus increases very slowly. In order to maintain a constant level in it, and to give a good mixing of the solutions, the contents are kept boiling lightly, evaporation being controlled by a current of cold air. In this way, after 3 weeks to a month, from 25-125 mgm. of the final product are obtained.

We began with some experiments in which the solutions corresponded to the compositions of the commonest clay minerals. The pH was controlled by adding small quantities of acetic acid or sodium hydroxide to the mother solutions. Also, to avoid excessive pH variations in the flask, we had to add to the distilled water a small quantity of an (acetic acid)-(ammonium acetate) mixture giving the desired pH. Although such mixtures do not always form a buffer for certain pH values, in the conditions of our experiments, they do however attenuate the pH fluctuations which inevitably arise from small differences in the rate of flow of the solutions.

Composition of Synthetic Products.

Nos.	37	33	26	23	24	25	34
pH of medium ...	8·0	8·0	8·0	8·0	8·0	8·0	8·0
SiO_2/MgO molecular ratios of the solutions	0·06	0·15	0·30	0·60	1·00	1·40	2·40
SiO_2/MgO molecular ratios of the product	0·51	1·7	1·8	2·0	1·6	1·9	15

The composition of the products is given in the accompanying table. These results must be treated as orders of magnitude only, since the analyses were carried out on very small quantities of the products, sometimes mixed with organic impurities from the rubber stoppers.

Nature of the Products.—At a pH of 8, the synthesised silicates always show a montmorillonite diagram, whatever is the SiO_2/MgO ratio of the solution up to 2·4. As one approaches this limiting value, the (00*l*) lines become more and more diffuse, but beyond it, *all* the lines of the diagram become diffuse bands.

The weight-loss curves, which resemble that of hectorite for low ratios, differ more and more from it with increasing ratio and finally become quite different, possibly resembling that of sepiolite (Fig. 1).

Finally, electron microscope examination of these synthetic silicates shows them to be formed of large sheets looking rather like crumpled sheets of paper. A similar appearance is presented, by some montmorillonites.

Two other trials were made, one at a markedly higher pH (9·0), the other in the presence of a high concentration of sodium chloride (300 g. per 1.). The concentration of the alkaline mother solutions was 6 mg. $SiO_2/1$. with an SiO_2/MgO ratio of 0·10 in the first trial and 0·06 in the second. In both cases products giving montmorillonite diagrams were obtained with particularly well-defined lines, especially the (00*l*) series. The small quantity of the product did not permit other determinations to be made. In the presence of a high salt concentration, the speed of formation and the quality of the clay products are markedly increased.

Trial synthesis were made at pH's between 6·7 and 7·0, using low and high SiO_2/MgO ratios. We have not been able to identify the synthesised substances unambiguously; some of them were crystalline. However, the results were certainly markedly different from those of the preceding trials.

A pH of 8·0 thus seems, so far as our experiments go, to constitute a lower limit for the formation of magnesian montmorillonite.

It is very remarkable that the SiO_2/MgO ratio of the products we obtained, and which are listed in the table, is approximately constant, in view of the variation of this ratio in the mother solutions. These facts seem to confirm the rule, stated by Sedletskij (1941) and recently
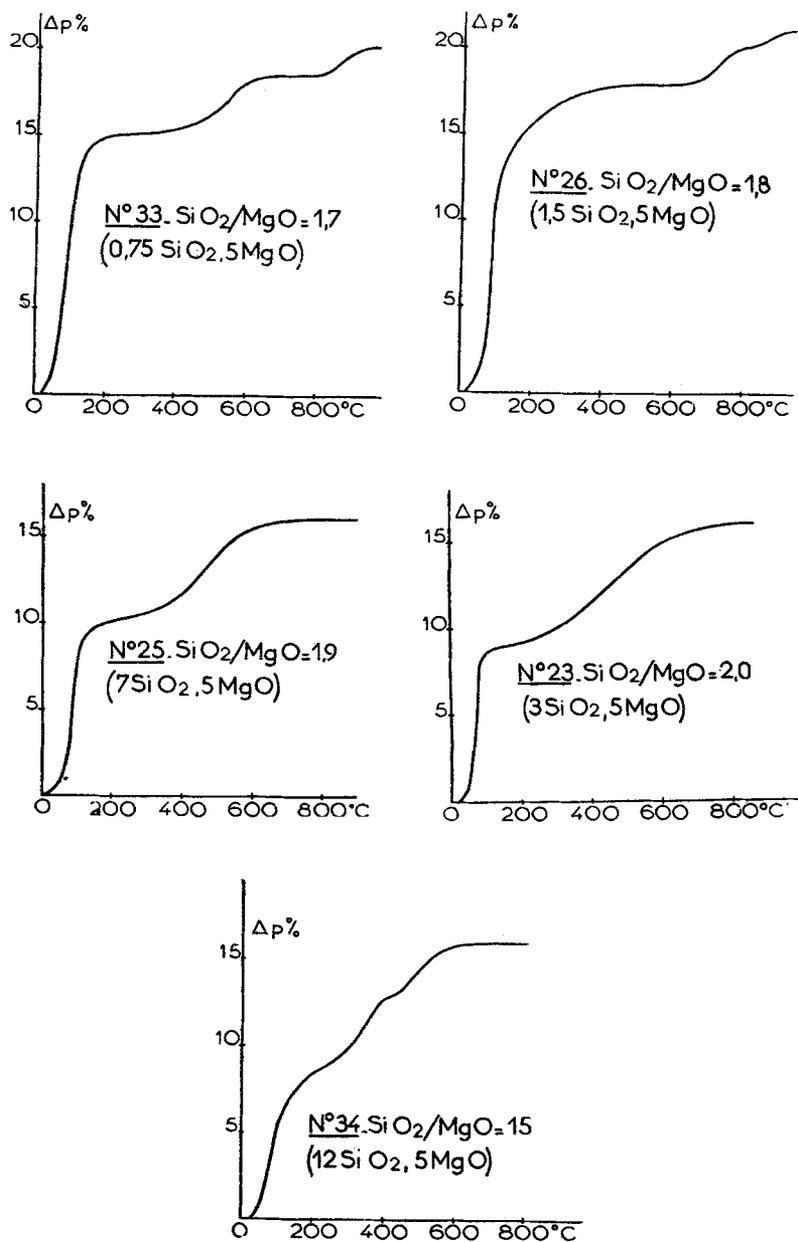
FIG. 1.—Weight-loss curves of the synthesised products.

confirmed by Millot (1950), according to which the formation of clay minerals depends more on the conditions of pH than on the ratio of the constituents in the natural medium.

Using a solution of silicate and aluminate (in the ratio 4:1), and a magnesium acetate solution, and working at a pH near 8·0 in a medium containing 300 g. of potassium chloride per liter a product resembling small flakes was formed, rather similar in appearance to a mica. X-ray and electron-diffraction examination showed that these were not single crystals. On grinding the substance, a powder diagram showed it to resemble a mica; but the (00*l*) lines are very diffuse. This result may be compared with van Keymeulen and Dekeyser's observation (1953) that prolonged boiling of solutions resulting from the decomposition of a mica gives flakes rather similar to ours. Further, Méring and his co-workers (ref.) have noticed membranes, also of similar aspect to our product, in hectorite suspensions.

To sum up, although the only mineral definitely obtained by this technique is magnesian montmorillonite, it is very probable that by using appropriate experimental conditions, it will be possible to prepare a phlogopite-type mica, and antigorites. Further, it is observed that such preparations can only be formed with solutions having a similar concentration to that of the natural medium. The influence of certain factors, such as pH, can be demonstrated. It seems that this factor plays precisely the role that deductions from the study of clay mineral formation *in situ* would lead us to accord it. Although the procedure employed only allows of slow progress, we may hope that it will make possible a complete study of the physicochemical conditions governing the formation of a number of clay minerals.

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References.

S. Caillère and S. Hénin, 1950. Trans. 4th Int. Congr. Soil Sci., Amsterdam. p. 86-88.

S. Caillère, S. Hénin and J. Esquevin, 1953. *Bull. Soc. franç, Minér.* **76**, 300-314.

J. van Keymeulen and W. Dekeyser, 1953. *C.R.* **236**, 1367-9.

J. Méring, A. Mathieu-Sicaud and I. Perrin-Bonnet. Personal communication.

G. Millot, 1950. *Trans. 4th Int. Congr. Soil Sci.*, Amsterdam. p. 37-40.

I. D. Sedletzkij, 1941. *C.R.A.S., U.R.S.S.* **32**, 435-8.

Discussion.

Dr R. Greene-Kelly.—I should like to draw attention to the importance of carrying out syntheses with pure materials and under conditions where undesirable contamination is avoided. For example, Strese and Hofman[1] prepared a synthetic montmorillonoid of high exchange capacity from silica and magnesium chloride.

[1] H. Strese and U. Hofman, 1941. *Z. anorg. Chem.*, **247**, 65-95.

Could not this cation exchange capacity origi.1ate from a small amount of aluminium as impurity?

Dr K. Jasmund.—During the last war, Prof. Correns made similar experiments in synthesis at temperatures of 20° and 80°C. The apparatus used was similar to that of Hénin. Only a few characteristic lines appeared on the X-ray photographs, indicating that clay minerals were in the crystalline state. Perhaps the concentration was too small to allow the formation of sufficiently large crystals in sufficient quantity.

Mr R. H. S. Robertson.—High cation exchange capacity is no criterion of crystallinity in mixed oxide gels, *e.g.*, in Al_2O_3-SiO_2 gel catalysts. The uncrystallized coprecipitated mixed gels often have high exchange capacity, because Al, Mg, etc., proxy for Si in Si-O-Si-O networks in 4-co-ordination. The reactants in this case are, of course, concentrated. (See C. L. Thomas, Chemistry of Cracking Catalysts, *Ind. Engng. Chem.*, (1949), **41**, 2564-2573).

Dr R. Greene-Kelly.—In reply to this suggestion that industrial magnesium-silica gels have high exchange capacities due to replacement of silicon atoms in 4–co-ordination by magnesium, I think it is more likely that the exchange capacity arises from accidental impurities, than from isomorphous replacement between two atoms of widely differing size.

THE REMOVAL OF FREE IRON OXIDE FROM CLAYS*

By B. D. MITCHELL and R. C. MACKENZIE.

Read 10th April. 1953.

The techniques previously employed in this laboratory for removing free iron oxide† from soil clays were the acid ammonium oxalate and the aluminium-ammonium tartrate methods (Tamm, 1922; Dion, 1944). Since both had disadvantages, especially when determining the iron by sodium salicylate (Scott, 1941), the use of sodium hydrosulphite, $Na_2S_2O_4$, (Galabutskaya and Govorova, 1934; Deb, 1950) was fully investigated in the hope that it might lead to the development of a satisfactory, completely inorganic procedure.

Method.—The thoroughly-wetted clay (20-40 mg.) is treated with a *fresh* 4 per cent. solution of sodium hydrosulphite of pH 5·8-6·0 (adjusted by sodium hydroxide solution) at 40-45°C for 15 minutes, the suspension centrifuged, and the supernatant liquid collected. The clay is then treated with 0·05 N hydrochloric acid at 40°C for 3 minutes, recentrifuged, and the supernatant liquid collected in a separate beaker. This complete treatment is repeated, and the clay is finally washed twice with neutral N sodium chloride solution.

*This is a brief summary. For full details consult the papers of Mitchell and Mackenzie (1954) and Mackenzie (1954).

†The term "free iron oxide" includes all iron not present in the crystal lattice of any component mineral, excepting of course the iron oxide minerals themselves.