CLAYS and CLAY MINERALS

at a glance

EFFECT OF PARTICLE THICKNESS ON POTASSIUM EXCHANGE FROM PHLOGOPITE

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Rates of exchange of K with Ca for fine (0·2–2 μm) and coarse (54–75 μm) and for thin and thick (37–45 μm) phlogopite particles were determined using a repeated batch technique, which gave a measure of K selectivity.

Potassium selectivity of the fine fraction was higher than that of the coarse one throughout the exchange process in which 93 per cent of the total K was exchanged from the fine fraction and 100 per cent from the coarse one. Potassium selectivity of the thin 37–45 μm particles was higher initially than that of the thick 37–45 μm particles but the difference disappeared subsequently and practically 100 per cent of the total K was exchanged from both the thin and thick particles.

The results are interpreted as tentatively confirming the hypothesis that bending and deformation of elementary layers during K exchange increase with particle thickness, which in turn increase K exchange and decrease K selectivity.

The K exchange curves for the fine and coarse phlogopite fractions suggest that in natural conditions, as in soils, where K is not continuously removed from solution, vermiculization of coarse mica particles may be not only more complete but also more rapid than vermiculization of fine mica particles.

EFFECT OF PARTICLE SIZE ON POTASSIUM SORPTION BY POTASSIUM-DEPLETED PHLOGOPITE

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Sorption of K from mixed KCl and CaCl$_2$ solutions by K-depleted, Ca-saturated phlogopite was studied to determine the effect of particle size. The experiments were done at room temperature with 25 mg of K-depleted phlogopite samples in 50 ml solutions which were 0·002 N with respect to KCl and 0·02 N with respect to CaCl$_2$.

Sorption of K increased sharply with increase in particle size. The 54–75 μm fraction sorbed nearly all, whereas the 0·2–2 μm fraction sorbed less than half, of its depleted K. The 5–20 μm fraction sorbed an intermediate amount. This relationship is explained by the same hypothesis which accounts for the increase of K release with increase in particle size. That is, bending of unit mica layers due to peripheral expansion is greater in large and thick particles than in small and thin ones. This increased bending induces the greater K release from large particles. Similarly, bending due to peripheral collapse of hydrated layers is greater in large particles than in small ones. Thus, more energy is needed to initiate layer collapse and restrict further K uptake in the large particles which results in their greater K sorption capacity.

These results imply that in natural conditions, as in soils, the coarse vermiculite and weathered mica fractions may be more effective in sorbing K from solution than their fine counterparts.

A NATURAL 17 Å MONTMORILLONITE–ORGANIC COMPLEX FROM ALLEPPEY, KERALA STATE, INDIA

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A black organic-rich alluvial clay from Alleppey, Kerala State, India, gave a well defined 17 Å reflection in the natural untreated state. Ethylene glycol and heat treatments showed it to be essentially a smectite. Treatments with H$_2$O$_2$ and 0·1 NaOH contracted the spacing to about 14 Å indicating that sorbed organic matter was responsible for the original enhanced spacing.

In the natural state, the clay was chiefly divalent with respect to the ions on its exchange sites and was at a pH of 6·2. Subsequent attempts to resorb the organic matter (which had been extracted from the clay by repeated NaOH treatments, converted to the H-form, concentrated and freeze-dried) into the interlamellar space of H$_2$O$_2$-treated clay proved successful only after the pH was brought down to 3·2 and the clay converted to an essentially monovalent state through repeated 1 N NaCl treatments.

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THE TRANSFERENCE NUMBERS OF THE COUNTER IONS IN MONTMORILLONITE PASTE AS A FUNCTION OF WATER FILM THICKNESS AND ELECTROLYTE CONCENTRATION

The transference numbers of the counter ions in montmorillonite paste are determined as a function of the thickness of the water film (h) and of the diffuse double layer ($1/\kappa$).

From measured E.M.F. values of a cell with two liquid junction potentials (C'_{KCL} solution-paste-C''_{KCL} solution) and by applying the Henderson equation, the transference numbers t_+ were calculated. It is shown that the transference numbers of the counter-ions $t_+ \rightarrow 1$ if $h\kappa \rightarrow 0$.

THE CRYSTAL STRUCTURE OF TALC

The crystal structure of a sample of talc from Harford Country, Maryland, has been determined by least squares refinement from X-ray diffraction photographs. A triclinic cell with $a = 5\cdot293$, $b = 9\cdot179$, $c = 9\cdot496$ Å, $\alpha = 90\cdot57°$, $\beta = 98\cdot91°$, $\gamma = 90\cdot03°$, space group $C1$ is adopted. The layers of the structure have almost monoclinic symmetry but the nearly hexagonal rings of oxygen atoms on the surface of the layers, formed by the bases of the silica tetrahedra, are not held in register by the interlayer ions as they are in micas but are partly displaced so that the stack of layers forms a triclinic crystal. The hexagons of surface oxygens are distorted by a $3\cdot4°$ twist of the tetrahedra so that the b axis is $0\cdot2$ per cent shorter than in a structure with regular hexagons, and the twist brings the oxygen ions a little closer to the octahedral magnesium ions.

INFRARED STUDY OF ATTAPULGITE AND HCl TREATED ATTAPULGITE

Infrared absorption spectra show important changes in the positions and form of the absorption bands of a film of attapulgite after it has been pumped out. An attempt to differentiate among some of the multiple frequencies due to OH groups is based on the information obtained from dehydration and deuteration experiments. The $1198\,cm^{-1}$ shoulder, characteristic of attapulgite, is assigned to a Si–O vibration. When attapulgite is refluxed with 5N HCl for 5 hr the octahedral layer is dissolved. The acid attack causes the disappearance of the Si–O–Si absorption bands from attapulgite giving rise to a characteristic vibration at $1090\,cm^{-1}$, as well as another absorption at $960\,cm^{-1}$. The latter indicates the presence of silanol groups.

EVALUATION OF CRYSTALLINITY IN HYDRATED FERRIC OXIDES

The nature of freshly-precipitated and aged hydrated ferric oxides prepared by the addition of ferric chloride to KOH was investigated by the use of scanning and transmission electron microscopy, X-ray diffraction, infrared absorption, and pH $3\cdot0$ ammonium oxalate extraction. The results show the fresh material to be essentially non-crystalline hydrated ferric oxide, which when aged at $60°C$ and high pH rapidly crystallizes as goethite, without any indication of coexisting hematite. The various methods were evaluated as indices of crystallinity for aging materials. The acid ammonium oxalate method was shown to extract selectively only the non-crystalline portion of such mixtures. The use of X-ray diffraction analysis for estimating aging stage requires elimination of the preferred orientation of the goethite crystals. While both the oxalate and X-ray methods can detect as little as 2 per cent crystallinity, the oxalate method is probably superior for quantitative determinations as it depends directly on an inherent difference in the solubility of the crystalline and non-crystalline materials, rather than on a technique dependent intensity measurement. The use of the intensity of the O–H bending vibrations of the infrared absorption spectra can also potentially detect as little as 2 per cent crystallinity, but the procedure is probably less useful for quantitative determinations than the oxalate or X-ray methods because of the problem of evaluating the area under the peaks.

EXCHANGEABLE CATION DISTRIBUTION IN Ni AND Mg VERMICULITES

Abnormal scatterings of X-rays take place between Bragg spots. Their study in hydrated Mg and Ni vermiculites shows that they appear in reciprocal space in the form of modulated lines, elongated along the Z^* axis. These scatterings demonstrate a two-dimensional organization of the compensating cations and of the water molecules in the interlamellar layer. In such ordered domains, the cations are situated at the nodes of a biperiodic centered lattice with parameters $3a,b$.

The distribution of compensating cations must conform with the charge distribution which they neutralize; it can therefore be concluded that the distribution of effective negative charges (tetrahedral negative charges less positive octahedral charges) is also at least partially ordered.