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CLAYS and CLAY MINERALS at a glance

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THE NATURE OF KENYA VERMICULITE AND ITS ALUMINUM HYDROXIDE COMPLEXES

J. E. Brydon and R. C. Turner 1

A specimen of Kenya vermiculite contained no mica or chlorite layers either as separate phases or as components of an interstratified structure. Dehydroxylation occurred in two stages, at 550° and 850°C, with approximately equal amounts of hydroxyl liberated in each stage. Al-saturated Kenya vermiculite showed low temperature dehydration characteristics similar to those of the natural Mg-saturated specimen, but the DTA, TGA and oscillating-heating X-ray diffraction patterns showed that the three stage dehydration process was not as clear-cut with the Al-saturated specimen.

As with montmorillonite, when small amounts of aluminum were precipitated by the addition of $Ca(OH)_2$ in the presence of vermiculite, the $Al(OH)_x$ was taken up and held indefinitely by the clay, the ion product $(Al)(OH)^3$ in solution was maintained at $10^{-33.0}$ and no gibbsite was formed with time. With large amounts, 800 and 1600 me $Al(OH)_x$ per 100g vermiculite, the hydroxide was held initially in the interlayer space, but gibbsite was eventually formed as $(Al)(OH)^3$ approached the solubility product of gibbsite. Unlike montmorillonite, the vermiculite specimens retained an appreciable amount of the interlayer hydroxide and did not regain the original C.E.C. values as gibbsite was formed.

Al–vermiculite which was repeatedly suspended in $AlCl_3$ with $(Al)(OH)^3$ maintained at a value less than $10^{-33.6}$ liberated 435 me Mg, took up 208 me Al as an interlayer hydroxide and caused a reduction in C.E.C. from 130 to 28 me per 100g clay. With vermiculite an appreciable amount of the interlayer $Al(OH)_x$ was stable with respect to gibbsite whereas with montmorillonite it was not.

SWELLING CHARACTERISTICS OF HYDROXY-ALUMINUM INTERLAYERED CLAYS

Gerald Kidder and Lester W. Reed 13

The hypothesis tested was that macroscopic swelling of montmorillonitic clays is reduced by the presence of interlayer minerals. Fine and coarse clay fractions of Camargo and Panther Creek bentonite samples were artificially interlayered by reaction of $Al_2(SO_4)_3$ and NaOH in 0·5% suspensions of the clays. All four clay fractions reacted similarly to artificial interlayering. At an Al:clay ratio of 16 meq Al/g clay the CEC was completely lost, surface area was reduced and X-ray basal spacings were altered. No macroscopic swelling occurred in samples treated with 16 meq of Al/g of clay. At smaller concentrations of hydroxy-aluminum 8 and 2 meq Al/g clay, the clay properties were less drastically altered. Extraction of interlayered clays with Na citrate restored the original C.E.C., surface area, and basal spacings of all samples and resulted in some slight enhancement of C.E.C. and surface areas of the course fractions. Treatment with hot Na citrate resulted in an increase in swelling ability but only slight increases in C.E.C. and surface area. Evidence presented supports the hypothesis that macroscopic swelling of montmorillonitic clays is greatly reduced by interlayer materials. Reduced swelling due to interlayering occurs even when other clay properties may be slightly different from those of nontreated samples. Indications are that interlayer material occurs naturally in the clays studied and this may apply to other bentonite deposits.

ALKYLAMMONIUM DECOMPOSITION ON MONTMORILLONITE SURFACES IN AN INERT ATMOSPHERE

B. Durand, J. J. Fripiat and R. Pelet 21

A study of the thermal transformation of alkylammonium cations adsorbed on the surface of a montmorillonite in various conditions of hydration has been carried out. The experimental conditions were: inert atmosphere, temperatures below 250°C and time periods up to 270 days. The reactions observed are mainly transalkylations, for which a mechanism of acid catalysis is proposed. A high degree of dissociation of the water remaining on the surface of the clay is required and is attained for an optimal, and rather low, water content of the clay.

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CALCIUM–MAGNESIUM EXCHANGE IN MONTMORILLONITE AND VERMICULITE

Rachel Levy and I. Shainberg 37

An experimentally determined Ca–Mg exchange isotherm of montmorillonite is reported. The selectivity coefficient of this exchange over a wide range of Mg saturation was calculated and found constant.

Standard free energies of exchange, thermodynamic equilibrium constants and activity coefficients of the exchangeable Ca and Mg ions in vermiculite and montmorillonite, were predicted from knowledge of the microstructure of these two clays, assuming that coulombic forces are the main ones playing a role in the interaction between the counterions and the charged clay surface. The standard free enrgies of exchange ($\Delta G°_{Ca} = 238$ cal/mole) predicted a preference for Ca in montmorillonite and a preference for Mg in vermiculite ($\Delta G°_{Ca} = -1665$ cal/mole). The predicted thermodynamic equilibrium constants were compatible with the experimentally determined selectivity coefficients $K^{Mg}_{Ca} = 0{\cdot}67$ as compared with $K^{Mg}_{sCa} = 0{\cdot}68$ in montmorillonite, which remains constant over all the range of Mg saturation, and $K^{Mg}_{Ca} = 16{\cdot}7$ as compared with $K^{Mg}_{sCa} = 13{\cdot}9$ in vermiculite at 95% M saturation. The activity coefficients of Ca and Mg counterions in montmorillonite were found to be $\overline{fCa} = 2{\cdot}0 \times 10^{-3}$ and $\overline{fMg} = 2{\cdot}2 \times 10^{-3}$, respectively, and to remain constant. The activity coefficient of exchangeable Ca and Mg in vermiculite were found to be $\overline{fCa} = 7{\cdot}1 \times 10^{-5}$ and $\overline{fMg} = 3{\cdot}5 \times 10^{-5}$, respectively, at an equivalent fraction of unity. The activity coefficient of exchangeable Mg increased as the saturation with Mg decreased, and was found to be $1{\cdot}7 \times 10^{-3}$ in the range of the low Mg saturation.

The microstructure, the isomorphic substitution and the surface charge density provided an understanding of the changes taking place in the activity coefficients of the counterions.

THERMODYNAMICS OF THE EXCHANGE OF *n*-ALKYLAMMONIUM IONS ON Na–MONTMORILLONITE

E. F. Vansant and J. B. Uytterhoeven 47

A thermodynamic study has been made of the ion exchange equilibria of the *n*-alkylammonium ions in sodium montmorillonite. Exchange isotherms of ammonium, methyl-ammonium, ethylammonium, propylammonium and butylammonium with sodium montmorillonite were determined at 4°, 25° and 55°C. From these data the changes in free energy, enthalpy and entropy for the exchange reactions were calculated. In the temperature region used in this work, no enthalpy change was observed. Thus the exchange was only controlled by entropy effects. The thermodynamic excess functions were calculated from the surface activity coefficients. The affinity of the organic ions for the clay increases with chain length. It is shown that this increase can not be ascribed to van der Waals forces, but must be due to the combined effect of variations in electrostatic interactions with the clay lattice and of the hydration state.

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