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CLAYS and CLAY MINERALS at a glance

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ADSORPTION STUDIES ON KAOLINITES—II ADSORPTION OF AMINES

Robert F. Conley and Mary K. Lloyd 273

An investigation of the reaction between amines and hydrogen kaolinites having a broad range of crystallinites and particle sizes has been made. Aqueous and non-aqueous adsorption isotherms, conductivity titrations, rheological measurements and sediment volume studies give strong evidence that edge sites are dominantly involved in the reaction and basal surfaces remain essentially unaltered. The acid–base reaction produces a localized adduct rather than an ionized, protonated amine. The amine-hydrate adduct adsorbs with greatly modified geometry.

PARTICLE GEOMETRY AND OPTICAL DENSITY OF CLAY SUSPENSIONS

N. Lahav 283

Data on montmorillonite and illite collected by A. Kahn were further analyzed to show the relationship between particle geometry and the optical density (OD) of the clay suspensions. A correction was introduced to the calculations of the minor dimension of the montmorillonite particles which took into account the volume of water between unit layers.

The assumption of disc geometry which was used by A. Kahn in the calculations of the clay particle dimension was found to be consistent with his OD measurements, thus showing that optical measurements can be used to find an equivalent radius of montmorillonite and illite when the general geometry of the particles is the same.

THREE TECHNIQUES FOR FABRIC VIEWING AS APPLIED TO SHEAR DISTORTION OF A CLAY

Edward McKyes and Raymond N. Yong 289

A knowledge of the microscopic physical behavior of soils is important and necessary for the correct interpretation of observed macroscopic deformations in soil bodies. This study was designed to determine the particular pattern and distribution of extensive fabric alteration accompanying shear strains in a clay specimen subjected to triaxial stress combinations. The techniques used for observing these microscopic features were polarized light microscopy of thin sections from Carbowax-fixed clay samples, scanning electron microscopy of thinly coated cleavage surfaces in vacuum desiccated specimens, and transmission electron microscopy of metal-shadowed carbon replicas made of similar cleavage surfaces. All three methods showed that the zone of extensive fabric alteration in the triaxially sheared bodies was planar and had an average thickness of about 30 μ.

Most clay particles in the zone were aligned parallel to the zone direction. The results of the study also demonstrated the particular merits of each of the three techniques for fabric viewing.

SURFACE CHARGE CHARACTERIZATION OF LAYER SILICATES BY COMPETITIVE ADSORPTION OF TWO ORGANIC DIVALENT CATIONS

O. D. Philen, Jr., S. B. Weed and J. B. Weber 295

Diquat^{2+} (1,1′-ethylene-2,2′-dipyridinium ion) and paraquat^{2+} (1,1′-dimethyl-4,4′-dipyridinium ion) were competitively adsorbed by Na-saturated kaolinites,

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smectites and expanded and collapsed vermiculites. The relative preference for one or the other cation varied with the surface charge densities of the adsorbents and the location of the adsorption site, i.e. internal or external. Minerals with high surface charge exhibited preference for diquat whereas minerals with low surface charge preferred paraquat. Expanded vermiculites generally showed a preference for paraquat. Smectites and kaolinites preferentially adsorbed paraquat.

Surface charge densities of the layer silicates versus the relative preference for diquat revealed two linear relationships, one for internal adsorption and one for external adsorption. Internal adsorption was characterized by a strong preference for paraquat on low-charged smectites, and a strong preference for diquat on high-charged expanded vermiculites.

Preferential adsorption for paraquat by kaolinite was quite similar to adsorption of paraquat on the external sites of vermiculites. There was no apparent relationship between competitive adsorption and surface charge density of kaolinite.

EFFECTS OF AMORPHOUS CONSTITUENTS ON SOME MINERALOGICAL AND CHEMICAL PROPERTIES OF A PANAMANIAN LATOSOL

F. C. Townsend and L. W. Reed 303

This study was an investigation of the effects of sesquioxide constituents on some mineralogical and physiochemical properties of a Panamanian latosol.

Latosols are soils characterized by high concentrations of iron and aluminum oxides and a general absence of free silica and alkaline earths.

X-ray diffraction studies revealed sesquioxide coatings existed on the surfaces of the clay minerals. Mineralogically, the soil was composed of kaolin, amorphous minerals, hydrated iron and aluminum oxides, free silica, quartz grains and magnetite. The results of DTA data suggested the presence of amorphous colloids in the soil. This suggestion was subsequently confirmed by selective dissolution analysis which revealed the unexpected presence of 17% amorphous silica in the coarse clay size fraction. Grain size analysis and scanning electron microscopy studies showed that the clay minerals are probably agglomerated by the sesquioxides into silt size clusters. CEC values obtained were primarily attributed to the amorphous colloids rather than the crystalline clay minerals because the sesquioxides probably partially blocked the exchange sites of the clays.

Removal of the iron and aluminum oxides by sodium dithionite citrate–bicarbonate procedures (Mehra and Jackson, 1960), (a) sharpened and exposed previously "masked" X-ray diffraction peaks, (b) disaggregated the clay clusters producing greater amounts of clay size particles, and (c) altered the Cation Exchange Capacity (CEC) and water retention characteristics of the soil constituents.

This investigation demonstrated that amorphous silica and iron and aluminum oxides greatly influence the properties of this latosol by coating and aggregating the clay minerals. These sesquioxide coatings suppress the ordinary behavioral characteristics of the indigenous clay minerals and consequently the observed behavior of the soil is dominated by the amorphous constituents.

SODIUM–LITHIUM EXCHANGE EQUILIBRIA ON VERMICULITE AT 25°C AND 50°C

R. G. Gast and W. D. Klobe 311

Sodium–lithium exchange equilibria between dilute aqueous chloride solutions and 0·2 to 62 μ Transvaal, South African vermiculite were studied at 25 and 50°C using a dialysis technique. The K content of the vermiculite was reduced to < 1 per cent of the exchange capacity of 2·14 meq/g by exhaustive extraction using Na–tetraphenylboron. The thermodynamic equilibrium constants and in turn the standard free energies and heats of exchange were evaluated from the equilibrium selectivity coefficients at the two temperatures. The standard entropy of exchange, $\Delta S°$, was calculated according to the relationship $\Delta G° = \Delta H° - T\Delta S°$. Similar results were obtained for Na → Li and Li → Na exchange at 25°C, thus confirming the reversibility of the reaction.

Sodium preference increased with Na saturation of the vermiculite and equilibrium selectivity coefficients ranged from 6·0 to 22·0 at 25°C. In comparison, selectivity coefficients for Na–Li exchange on montmorillonite ranged from 1·0 to 2·0 and became smaller with increasing Na saturation. The standard free energy and heat of exchange on vermiculite at 25°C were −1444 and −5525 cal mole^{-1}, respectively, resulting in a $\Delta S°$ value of −13·7 e.u. This relatively large entropy change is probably due to differences in ion hydration in the solution and surface phases.

REACTIVITY OF CLAY MINERALS WITH ACIDS AND ALKALIES

Dorothy Carroll and Harry C. Starkey 321

One-gram samples of a montmorillonite, a metabentonite, an illite, two kaolinites and three halloysites were treated with 50 ml of hydrochloric acid (6·45 N, 1 : 1), acetic acid (4·5 N, 1 : 3), sodium hydroxide (2·8 N), sodium chloride solution (pH 6·10; Na = 35‰; Cl = 21·5‰) and natural sea water (pH 7·85; Na = 35·5‰; Cl = 21·5‰) for a 10-day period in stoppered plastic vials. The supernatant solutions were removed from the clay minerals and analyzed for SiO_2, Al_2O_3, CaO, MgO, Na_2O and K_2O. All the solutions removed some SiO_2, Al_2O_3 and Fe_2O_3 from the samples, but the quantities were small. Sodium hydroxide attacked the kaolin group minerals more strongly than it did montmorillonite, metabentonite, or illite. Halloysite was more strongly attacked by hydrochloric acid than was any of the other experimental minerals. Hydrochloric acid removed iron oxide coatings from soil clay minerals, but acetic acid did not remove

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them completely. The samples most strongly attacked by HCl and NaOH were examined by X-ray diffraction. Acid treatment did not destroy the structure of the clays, but the halloysite structure was partially destroyed. Sodium hydroxide attacked the halloysite structure, as shown by chemical analysis and X-ray diffraction. These experiments show that treatment in dilute acids has no harmful effect in the preparation of clays for X-ray diffraction. Acetic acid is preferred to hydrochloric acid for this purpose. Hydrochloric acid cleans clay minerals by removing free iron oxide from the surface; acetic acid is less effective.

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