

CLAYS and CLAY MINERALS

at a glance

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APPEARANCE AND STABILITY OF HYDROLYZED $\text{Fe}(\text{ClO}_4)_3$ SOLUTIONS

Pa Ho Hsu

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$\text{Fe}(\text{ClO}_4)_3$ solutions of different concentration and acidity were studied to search for the factors governing their appearance and stability during aging and to elucidate the mechanisms for the formation of amorphous and crystalline iron(III) hydroxides from slow hydrolysis. It was found that dilute solutions (0.001M or lower) rapidly hydrolyzed to clear sols after a brief induction period. With an increase in iron(III) concentration, one could notice gradual increases in the induction period, turbidity and particle size. Thus, solutions 0.006M to 0.01M in iron(III) developed into dense, cloudy, yellow suspensions impervious to light. The polymeric iron(III) species in the aged 0.02M solution were primarily large particles that settled under gravity, resulting in a suspension of low turbidity. It was also observed that in dilute solutions, the initial polymerization product was amorphous iron(III) hydroxide which yielded X-ray diffraction peaks for FeOOH only after prolonged aging or not at all. In 0.01M and 0.02M solutions, however, crystalline FeOOH was the major product from the very beginning of polymerization. The results suggest that the initial degree of supersaturation with respect to amorphous iron(III) hydroxide is the key factor governing particle size distribution, which in turn governs the appearance, stability and crystallinity of the hydrolysed product during aging.

The addition of HClO_4 to dilute $\text{Fe}(\text{ClO}_4)_3$ solutions decreased, whereas the addition of NaOH to concentrated solutions increased, the degree of supersaturation and, thus, induced changes in induction period, appearance, stability and crystallinity of the hydrolyzed product accordingly.

ADSORPTION AND OXIDATION OF BENZIDINE AND ANILINE BY MONTMORILLONITE AND HECTORITE

T. Furukawa and G. W. Brindley

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Quantitative measurements are made of the adsorption of benzidine and aniline from aqueous hydrochloride solu-

tions by Na-, Li-, and Ca-montmorillonite and of the displaced inorganic cations. From these data, the ionic states of the adsorbed organic species are determined. Under conditions of controlled pH, the adsorption of benzidine increases as the pH increases, and involves mainly divalent species at $\text{pH} < 3.2$, and increasing proportions of monovalent and neutral species at $\text{pH} > 3.2$. With aniline, monovalent and neutral species are adsorbed, and hydrogen ions also appear to participate in the reactions.

Color developments of benzidine and aniline complexes of montmorillonite and hectorite are considered qualitatively in relation to the adsorption data, to various experimental conditions including the nature of the inorganic exchangeable cations, the pH, and the presence or absence of oxygen in the system, and to relevant previous work. It is hypothesized that the blue color of the benzidine complex is due to semiquinone formation by oxidation on montmorillonite by the clay itself, and on hectorite by dissolved oxygen or H_2O_2 , and that the yellow color under acid conditions arises from reversible formation of quinoidal cations from semiquinones. The color developments of the aniline complex are due probably to oxidation of aniline by atmospheric oxygen.

OCCURRENCE OF COLLAPSED AND EXPANDED CRYSTALS IN MONTMORILLONITE-DEXTRAN COMPLEXES

Alan Olness and C. E. Clapp

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X-ray diffraction patterns obtained from montmorillonite-dextran complexes prepared with either B-512F or Polyantran dextran showed maximum oven-dry crystal expansions of about 5.3 Å. X-ray diffraction patterns of individual complex preparations containing < 20 per cent dextran showed evidence of both expanded and collapsed crystals. The observation of expanded and collapsed crystals in individual preparations has not been previously reported and was apparently related to clay preparation. An estimate of the quantity of dextran which could be interacting with the silicate surface was obtained using polymer adsorption weights and volumes. At maxi-

mum adsorption almost all adsorbed B-512F could be in contact with the mineral surface, but only two-thirds of the adsorbed Polytran could be in contact with the mineral surface.

THE EFFECT OF ALUMINUM ON THE SURFACE PROPERTIES OF KAOLINITE

Wayne M. Bundy and Haydn H. Murray

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Aluminum ions as well as hydroxide precipitates promote improved extraction of iron from kaolinites during leaching. Selective aggregation of ultrafine particles in kaolinites, seemingly induced by precipitation of aluminum hydroxide, gives brightness improvement in excess of that which can be ascribed to iron extraction. Aggregation of anatase, a primary discolorant confined mostly to the fine end of the kaolinite particle size distribution, is the suggested mechanism for complementary brightness improvement.

Precipitation of aluminum hydroxide in kaolinite systems substantially changes flocculation characteristics, surface area (methylene blue), and rheology. Edge-edge and edge-face flocculation are promoted where sulfate retention is high, becoming progressively more face-face with sulfate removal. The character of the flocculation can be interpreted by the combined use of surface area and low shear viscosity data.

The extent to which kaolinites can be dispersed after processing increases with increase in sulfate retention. Stability of suspensions deflocculated with polyphosphates shows an inverse relationship, decreasing with increase in sulfate retention.

THE ALTERATION PRODUCTS OF POTASSIUM DEPLETED OXYBIOTITE

R. J. Gilkes

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Artificial weathering of biotites, which contain various levels of structural ferric iron, by NaCl and NaBPh₄ solutions produces minerals and structures similar to those described for naturally weathered biotites. Oxidation of structural iron leads to K removal from alternate layers and development of hydrobiotite. The growth of order with increasing ferric iron content has been assessed by comparison with theoretical calculations for random and most ordered interstratified structures. There is evidence for the existence of two layer types in biotite prior to oxidation. The depression in rates of K release due to oxidation has been confirmed.

THE CHEMISORPTION OF ANISOLE ON Cu(II)HECTORITE

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and Thomas J. Pinnavaia

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The sorption of anisole and some related aromatic ethers on the interlamellar surfaces of Cu(II) hectorite has been

investigated by i.r. and e.s.r. spectroscopy. In addition to physical adsorption, anisole forms two distinct types of Cu(II) complexes which are analogous to the type I and II species previously reported for benzene-Cu(II) smectite systems. These complexes can be transformed to type I and II complexes of 4,4'-dimethoxybiphenyl. Possible mechanisms are proposed for the oxidation process. Butyl phenyl ether formed a type II complex with Cu(II)-hectorite, but no dimerization reaction was noted in this system. Phenyl ether and benzyl methyl ether form a type I π complex with Cu(II)-hectorite. No type II analog was noted. E.S.R. spectra of each of the type II ether-Cu(II)-hectorite systems showed a single, narrow band with g near the value expected for a "free spinning" electron. The type I phenyl ether and benzyl methyl ether complexes also exhibited this e.s.r. band. Ag(I) hectorite adsorbs anisole by forming exclusively a type I complex. Na(I) and Co(II) hectorite adsorb anisole by physical means only, indicating association with the silicate surface.

SEGREGATION AND EXCHANGE PROPERTIES OF ALKYLAMMONIUM IONS IN A SMECTITE AND VERMICULITE

M. B. McBride and M. M. Mortland

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X-ray diffraction analysis of mixed alkylammonium-exchanged smectite revealed segregation of different ion species into randomly ordered layers. Vermiculite, however, showed segregation into crystallites, a behavior attributed to clay inhomogeneity. Ion segregation is explained by the hydration properties of cations as well as the energy requirements of layer expansion. Quaternary ammonium ions of different size were used to exchange ethylammonium-clays, and the effectiveness, as well as steric hindrance, of cation size in ion exchange was demonstrated. Layer charge density was related to the degree of ease of large cation adsorption. Basal spacing in suspension was found to be important in determining the preference of vermiculite for certain cations, while more freely-expanding, lower layer charge smectite did not demonstrate this phenomenon.

NEW STABILITY DIAGRAMS OF SOME PHYLLOSILICATES IN THE SiO₂-Al₂O₃-K₂O-H₂O SYSTEM

W. H. Hwang and W. D. Keller

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Aluminum is treated as a mobile, reactive component in newly designed stability diagrams for the SiO₂-Al₂O₃-K₂O-H₂O system. The diagrams show that halloysite and K-mica can not coexist at equilibrium, that the stability field of kaolinite is strongly dependent on pH at or below 6.7 but at 6.7 or greater the stability field is independent of pH, and also that in present sea water, K-mica is a stable phase with respect to kaolin minerals.

Natural waters from present-day, kaolin-forming localities in Mexico and Kentucky are consistent with theoretical interpretations from these stability diagrams.

apparently anomalous transmittance (Christiansen peak) of the incident electromagnetic radiations. The peak appears at wavelengths for which the refractive index of the sample and the refractive index of the matrix are equal (Christiansen wavelength: λ_{chr}).

On account of the great variation of the sample refractive index in the immediate neighborhood of the absorption bands (anomalous dispersion curve), one often observes the occurrence of a transmittance peak or of a band deformation in this spectral range. A change in the position of this transmission peak with the value of the matrix refractive index is indicative of the Christiansen effect.

The equality of the refractive indices of the sample and of the matrix for λ_{chr} has been used to determine some points of the anomalous dispersion curve in the neighborhood of the hydroxyl stretching band (3678 cm^{-1}).

Spectral distortions caused by the Christiansen effect can be reduced by preparing the sample in such a manner that the width at half-maximum ($\Delta\nu_{1/2}$) of the Christiansen peak is several times greater than that of the absorption band itself. Clarke's theoretical formula, which gives an estimation of $\Delta\nu_{1/2}$, has been qualitatively verified and thus gives an appropriate guide in the choice of the parameters which one can optimize during the sample preparation. One can reduce the Christiansen effect spectral modifications, without running the risk of modifying the sample itself, particularly by overly severe grinding.

OXIDATIVE POWER OF SMECTITES MEASURED BY HYDROQUINONE

Thomas D. Thompson and William F. Moll, Jr. 337

The oxidative power of a smectite can be measured quantitatively by oxidation of hydroquinone to *p*-benzoquinone in a clay slurry. Oxidation takes place in the presence of O_2 (air) but not N_2 , unless Fe^{3+} or Cu^{2+} are the exchangeable cations. This study examined 26 smectite samples with varying compositions and processing. The oxidative power increases with decreasing Li-fixation and increasing cation exchange capacity. Li-fixation does not depend upon the tetrahedral Al. The cation exchange capacity can decrease markedly by mere storage in water.

The oxidation proceeds principally on the surface by adsorbed oxygen molecules or radicals. A mechanism is proposed. With Fe^{3+} or Cu^{2+} present, even under N_2 , oxidation occurs via electron transfer. With smectites containing Fe^{2+} , both the Fe and the hydroquinone are oxidized in the same reaction.

FIXING CATION INTERACTION WITH BLISTER-LIKE OSMOTIC SWELLING ON VERMICULATE CLEAVAGES

K. Sridhar and M. L. Jackson 369

The shrinkage of osmotically swollen natural and artificial blisters on vermiculite cleavages by exchange saturation with fixing cations such as Cs^+ , Rb^+ , NH_4^+ , and K^+ was investigated by replica electron microscopy. Incomplete collapse of either the natural or artificially produced blisters occurred with Cs^+ , Rb^+ , and NH_4^+ saturation, while K^+ saturation completely collapsed the artificially produced but not the natural blisters. The reason for incomplete collapse with Cs^+ , Rb^+ and NH_4^+ was the incomplete replacement (trapping in the flakes) of interlayer hydrated cations such as Na^+ , shown by electron probe microanalysis. Much less trapping occurred with K^+ saturation. Na^+ entrapment increased with increasing size and decreasing hydration of cations, i.e. $\text{Cs}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{K}^+$.

Semiquantitative determination of Na^+ , by electron probe microanalysis, in vermiculite flakes near the edge revealed that 1 N CsCl entrapped as much as 45.6 per cent while 1 N KCl entrapped only 7.5 per cent. In general, more Na^+ was entrapped by 1 N solutions than by dilute solutions. With 0.01 N KCl solution, the Na^+ entrapment was only 4.4 per cent. The amount of Na^+ entrapment at the center of the macroflakes was less than at the edge, apparently as a result of more CEC at frayed edges and (or) because of incomplete diffusion of Na^+ to the center. Shrinkage of artificial blisters by K^+ could thus be attri-

THE ALTERATION OF SOME AROMATIC AMINO ACIDS AND POLYHYDRIC PHENOLS BY CLAY MINERALS

Thomas D. Thompson and Atsuma Tsunashina 351

These studies concern the catalytic activity of clays on amino acids, particularly tyrosine. Polyhydric phenols were included to help understand the tyrosine reactions.

Below pH 3, tyrosine is adsorbed on clay minerals by cation exchange. Above pH 3, oxidative degradation of tyrosine occurs, the *L*-isomer altering more rapidly. The rate of alteration depends upon the particular clay mineral, surface modifications such as polyphosphate treatment, heating, and the presence of copper, aluminium, and mercury. A free radical mechanism is proposed for the alteration.

THE INFLUENCE OF THE CHRISTIANSEN EFFECT ON I.R. SPECTRA OF POWDERS

R. Prost 363

The Christiansen effect appears in the i.r. spectrum of powders embedded in a solid, liquid or air matrix as an

buted to its more effective removal of the interlayer hydrated cations, whereas the other fixing cations were less effective. Natural blisters on vermiculite from Libby, Montana were not completely collapsed even by K^+ , apparently because the layer charge density was too low in the blister areas.

PROPERTIES OF THE ZEOLITE, FAUJASITE, SUBSTITUTIONAL SERIES: A REVIEW WITH NEW DATA

Dennis N. Stamines

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New information is presented relating to the hydrothermal stability, lattice parameters, and adsorptive, electrical, and catalytic properties of synthetic and natural faujasite. Present concepts concerning the nature and relationship of synthetic and natural faujasite are restated to be consistent with the experimental evidence and the developed physical model. The major structural and physicochemical properties reflect the close similarities and smooth gradations expected of substitutional members of a continuous series. The existing division of the range (2–6) of SiO_2/Al_2O_3 mole ratios (S/A) at 3 into two compositional subranges is shown to be unjustifiable and rather misleading. Individual compositions from these two subranges do not represent distinctly different zeolite species; instead, it is demonstrated that they are members of a continuous series with smoothly changing properties over the studied range of SiO_2/Al_2O_3 . Some of the properties of the natural mineral faujasite are found to be very similar to those of the synthetic analogs with the same SiO_2/Al_2O_3 mole ratio.

Finally, a plea is made for a uniform nomenclature which will serve to identify specific (single) compositions (instead of ranges of compositions); reflect the continuity, close similarities and inter-relationships in their main structural and physicochemical properties; and also identify the characteristics of the faujasite group.

DISCUSSION OF THE OCCURRENCE AND ORIGIN OF SEDIMENTARY PALYGORSKITE-SEPIOLITE DEPOSITS

Wayne C. Ispording

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Marine and non-marine palygorskite-sepiolite deposits are found throughout the world and occur interbedded with chert, dolomite, limestone, phosphates and other non-detrital sedimentary rocks. The origin of these high-magnesium clays has long been attributed to either alteration of volcanic ash or the structural transformation of smectite clays. More recently, others have argued origin by direct crystallization (neo-formation). Recent laboratory studies support this latter concept, particularly in environments where the concentration of alumina is low, the silica concentration high, and the pH alkaline. Such an origin is proposed for the Georgia-Florida deposits in

southeastern United States, since major obstacles exist against formation by alteration of volcanic ash or by transformation of smectites. Lateritic weathering during the Miocene would have favored direct precipitation of these clays in the shallow, marginal seas. The basinward increase in the $MgO:Al_2O_3$ ratio is further support.

Deep weathering of crystalline rocks in northern British Honduras and Guatemala would have produced similar high silica, low alumina conditions on the adjacent submerged Yucatan Platform during the late Tertiary. The seaward increase in the $MgO:Al_2O_3$ ratio, the lack of associated detrital constituents, and the absence of associated smectites strongly indicate a similar origin by direct crystallization of these Yucatan palygorskite-sepiolite clays.

Some occurrences of palygorskite and sepiolite may well be related to the alteration of smectite clays or volcanic ash. However, many of the large sedimentary deposits are more probably the result of direct crystallization adjacent to areas undergoing tropical or subtropical weathering.

PARTICLE SIZE-SHAPE RELATIONSHIPS IN GEORGIA SEDIMENTARY KAOLINS—II

J. P. Olivier and Paul Sennett

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Crude sedimentary kaolin clay from central Georgia, U.S.A., which had a wide distribution of particle size, was divided into several size fractions by repeated sedimentation in water. The resulting fractions had approximately a 2:1 ratio in dia. between their upper and lower limits. Each fraction was then studied by transmission and scanning electron microscopy and characterized in terms of surface area (both geometric and by gas adsorption), particle shape and impurity analysis.

Particle diameter determined from measurements made on electron micrographs showed considerable deviation from the diameter obtained by Stokes sedimentation. This deviation was especially large for the coarser particles and could be explained by the microscopically observed porosity of the kaolinite booklets. Imperfect stacking of the crystallites within a kaolinite booklet leads to a moderately regular array of slit-like voids. Effective particle densities as low as about 1.6 have been observed. The pore structure was also investigated by use of mercury intrusion porosimetry.

ELEMENTARY LAYERS IN THE INTERSTRATIFIED CLAY MINERALS AS REVEALED BY ELECTRON MICROSCOPY

Tsunoru Yoshida

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Interstratified layer structures were studied by electron microscopy and electron diffraction. In order to distinguish between expansible and non-expansible layers, inter-

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stratified mica-smectite was treated with laurylamine hydrochloride solution. Electron micrographs of the layers at the curled edges of the crystals show expanded basal spacings of 24 Å and unexpanded spacings of 10 Å. It was observed that adjacent pairs of expanded and unexpanded layers in the micrographs form non-expansive units. Ar-

rangements of the expanded and unexpanded layers show that the layers expanded by sorption of laurylammonium ions have expansive and non-expansive surface characteristics on opposite sides of the layer. The relationships between the ratio of component layers and basal spacings in two component systems are discussed.