

EFFECT OF KAOLINITE AND SULFATE ON THE FORMATION OF HYDROXY-ALUMINUM COMPOUNDS

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Abstract—OH-Al solutions were prepared by adding appropriate amounts of NaOH to $AlCl_3$ to obtain OH/Al mole ratios of 2.0, 2.5, 2.7, 3.0, and 3.3 in the final suspension. Solid Na_2SO_4 and Georgia kaolinite (KGa-2) were added individually and jointly to the OH-Al solutions. All samples were aged for 30, 70, and 180 d. X-ray diffraction, infrared spectroscopy, scanning electron microscopy, and energy dispersive X-ray spectrometry were used to characterize precipitates. Bayerite, gibbsite, and nordstrandite crystallized at mole ratios of 3.0 and 3.3, with bayerite being the most abundant. A morphology of clusters of triangular pyramids is described for bayerite. Despite the aging duration, only noncrystalline Al compounds were obtained in mole ratios of 2.0, 2.5, or 2.7. The addition of sulfate to OH-Al solutions in mole ratios of 2.0 and 2.5 produced crystalline basic aluminum sulfates of variable morphology, but with similar chemical compositions. These phases lost crystallinity with aging. The product from a 2.7 OH-Al solution was X-ray amorphous hydroxysulfate. In contrast, products obtained at mole ratios of 3.0 and 3.3 contained no sulfate ion, which restricted the formation of gibbsite, bayerite, and nordstrandite. The addition of kaolinite to the solutions in OH/Al mole ratios of 3.0 and 3.3 favored the formation of nordstrandite. The simultaneous addition of sulfate and kaolinite to the OH-Al solutions in mole ratios of 2.0 and 2.5 produced prevalent sulfate over kaolinite, whereas the opposite occurred at mole ratios 3.0 and 3.3.

Key Words—Bayerite, CMS Clay KGa-2, Gibbsite, Hydroxysulfate, Noncrystalline Compounds, Nordstrandite.

INTRODUCTION

When an Al salt is dissolved in water, the initial hydrolysis reaction yields a series of monomeric species that reach a rapid steady state. With addition of a base, an OH^- attaches to an Al^{3+} , and the OH-Al complex tends to link to another Al^{3+} . This mechanism may be the principal process for developing positively charged OH-Al polymers in solutions. Because Al^{3+} has a higher net positive charge per Al atom than OH-Al polymers, the addition of more NaOH will probably cause further reaction of OH with Al^{3+} to produce additional OH-Al polymers. OH-Al polymers are limited to narrow ranges of size and charge during early stages of neutralization (~2.1–2.5 NaOH/Al mole ratio). Positively charged OH-Al polymers repel one another, which prevents precipitation. At a NaOH/Al mole ratio of 3, all Al ions in solution are neutralized, and crystalline $Al(OH)_3$ develops rapidly. In partially neutralized solutions (pH 4–5), however, the hydroxide forms slowly or not at all, even after years of aging (Tsai and Hsu, 1984, 1985; Hsu, 1989).

Studies on the formation mechanisms of Al-OH compounds (Hsu and Bates, 1964; Schoen and Roberson, 1970; Elderfield and Hem, 1973; Hsu, 1966, 1988, 1989; Tsai and Hsu, 1985; Violante and Huang, 1993) were largely confined to crystalline Al-hydroxide polymorphs. However, noncrystalline and crystalline Al hydroxides show essentially the same chemical properties, but differ only in particle size, crystallinity,

and reactive surface. Because of the extremely small particle sizes and highly reactive surfaces, the noncrystalline compounds probably govern chemical reactions in soils (Hsu, 1989).

Many anions can delay or inhibit $Al(OH)_3$ crystallization; the effect is governed by the ionic size, structure, and concentration of the anion, as well as by the solution pH. Sulfate, which has a strong affinity for Al^{3+} (Hsu, 1973; Serna *et al.*, 1977), can displace the H_2O or OH^- ligand in the first coordination sphere of Al^{3+} , thereby inhibiting the crystallization of $Al(OH)_3$. Johansson (1960, 1963) obtained well-crystallized basic Al sulfates by adding Na_2SO_4 to partially neutralized Al solutions of 2.5 NaOH/Al mole ratio. However, the nature of the resulting basic Al sulfate varied with the OH/Al mole ratio used and the solution aging time (Bersillon *et al.*, 1980; Tsai and Hsu, 1984, 1985; Wang and Hsu, 1994).

Soils and clay minerals with variable charge on external faces and edges (such as kaolinite) modify their original surface and colloidal properties when hydroxides and polycations of aluminum precipitate on them (El-Swaify and Emerson, 1975; Oades, 1984; Robert *et al.*, 1987; Arias *et al.*, 1995). Little is known about the influence of kaolinite on the formation of hydroxy-Al compounds (Barnhisel and Rich, 1965). In this work, the interaction between OH-Al solutions, kaolinite, and the sulfate ion was studied to determine the effects on the formation of hydroxy-Al compounds.

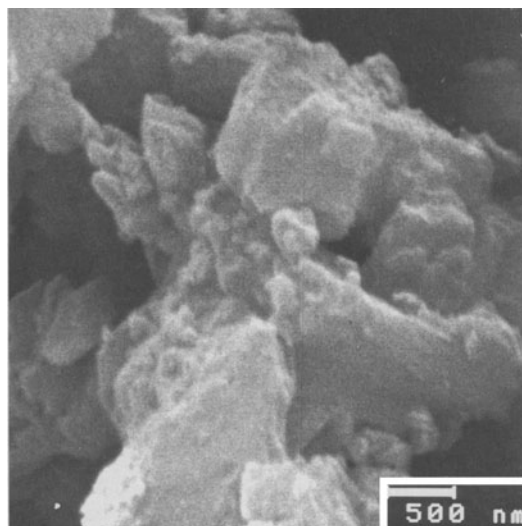


Figure 1. SEM micrographs for sample 2.0 aged for 30 d, amorphous $\text{Al}(\text{OH})_x$ which forms microparticles.

MATERIALS AND METHODS

OH-Al solutions were prepared by adding appropriate volumes of a 0.1 M NaOH solution dropwise, at a rate of 1 mL min^{-1} , to 200 mL of a freshly prepared 0.1 M AlCl_3 solution under vigorous stirring. The volume of NaOH added was that required to obtain an OH/Al mole ratio of 2.0, 2.5, 2.7, 3.0, or 3.3 in the final suspension, equivalent to a final Al concentration of 0.033, 0.029, 0.027, 0.025, and 0.023 M, respectively. Aliquots of the freshly formed suspensions were: a) used as controls (samples 2.0, 2.5, 2.7, 3.0, and 3.3); b) added to solid Na_2SO_4 to form an Al/ SO_4 mole ratio of 1.5 (samples 2.0s, 2.5s, 2.7s, 3.0s, and 3.3s) to obtain a SO_4^{2-} concentration of 0.022, 0.019, 0.018, 0.017, and 0.016 M, respectively; c) added to high-defect Georgia kaolinite (KGa-2) in a ratio of 10 meq Al/g clay (samples 2.0k, 2.5k, 2.7k, 3.0k, and 3.3k); and d) added to solid Na_2SO_4 and Georgia kaolinite at the same concentrations as in b) and c) (samples 2.0sk, 2.5sk, 2.7sk, 3.0sk, and 3.3sk).

The resulting suspensions were aged in pyrex-glass reaction vessels at 22°C for 30, 70, and 180 d without shaking. Then, each suspension was placed in a dialysis tube (Medicell International Ltd., pore size 20 Å) that was, in turn, suspended in deionized water. The water was changed twice daily, and the samples were allowed to stand until the external water was free of Cl^- (based on the AgNO_3 test). Finally, the samples were air-dried.

The high-defect kaolinite KGa-2 used here was obtained from the Source Clays Repository (The Clay Minerals Society). KGa-2 has a cation-exchange capacity (CEC) of 3.3 meq/100 g of clay, and a specific surface (as measured by BET, N_2) of $23.50 \pm 0.06 \text{ m}^2/\text{g}$ (van Olphen and Fripiat, 1979). The isoelectric point

of charge (IEP) was determined by measuring the electrophoretic mobility with a Coulter Delsa 440 instrument. Experiments were performed at 25°C , using a solid concentration of 200 mg/L KNO_3 as electrolyte, and KNO_3 and KOH to adjust the suspension pH over the range 2.5–9. The IEP was 4.2. Particle-size distribution was determined with Mastersizer equipment (Malvern Instruments), using sodium hexametaphosphate and ultrasound as dispersants. Sample KGa-2 contains 80% of particles $<14.25 \mu\text{m}$, 50% of particles $<4.48 \mu\text{m}$, and 10% of particles $<0.71 \mu\text{m}$.

X-ray diffraction (XRD) patterns were obtained on a Philips X'Pert diffractometer (graphite monochromator and $\text{CuK}\alpha$ radiation). Operating conditions of 40 kV and 50 mA were used. Oriented mineral aggregates were obtained by drying washed suspensions on glass slides. Infrared spectra (IR) were obtained from KBr discs containing air-dried samples (3 mg/200 mg KBr). Spectra were recorded over the $250\text{--}4000 \text{ cm}^{-1}$ range on a Perkin Elmer 683 IR spectrophotometer. Morphological studies used a DSM 960 Zeiss scanning electron microscope (SEM) operating in the secondary electron (SE) emission mode; air-dried samples were mounted on aluminum stubs and coated with gold. Semi-quantitative elemental analyses, using point analyses, were done by energy dispersive spectrometry (EDS), with an Oxford Link 5118 microanalytical system at a 35° take-off angle, an accelerating voltage of 15 kV, a working distance of 25 mm, a specimen current of 1–5 nA, and employing ZAF-correction procedures; samples were mounted on carbon stubs and coated also with carbon. Analysis conditions were standardized by using gypsum as a reference. Estimates of standard error were calculated from ten replicate analyses.

RESULTS

Samples with OH/Al mole ratio of 2.0

A freshly prepared solution has a pH of 4.14, and becomes a colloidal suspension after a few days of aging. The pH remained nearly unchanged during aging (30 d, 4.20; 70 d, 4.22; 180 d, 4.29). Based on XRD data, sample 2.0 contained no crystalline compounds. The corresponding IR spectra showed characteristic bands for AlOH vibrations (3486 , 1630 , 971 , 714 , 578 , and 371 cm^{-1}). SEM revealed irregular, sharp-cornered plates of variable size accompanied by microparticles of ill-defined shape (Figure 1). Aging did not affect these results.

The XRD patterns for sample 2.0s (Figure 2) contained sharp peaks at 1.20, 0.98, and 0.402 nm. After 70 d of aging, the product showed strong peaks at 1.20 and 0.98 nm, the intensity of the 0.96-nm peak being slightly increased. After 180 d, the compound showed a sharp peak at 1.12 nm, in addition to two small peaks at 0.98 and 0.96 nm. These products could not be iden-

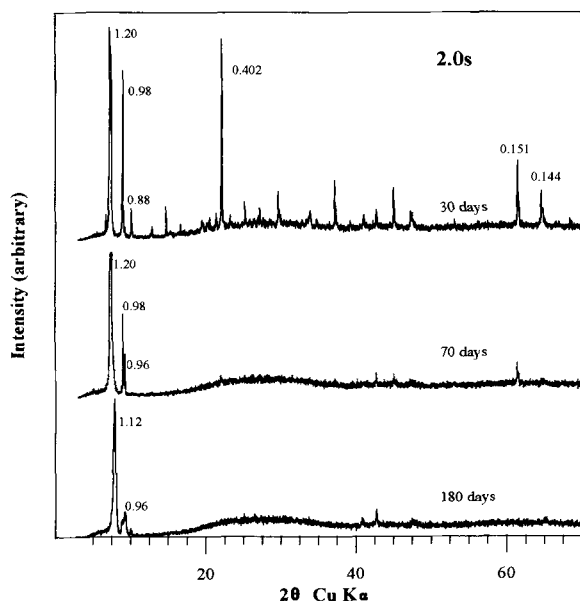


Figure 2. XRD patterns of oriented aggregate particles for sample 2.0s aged for 30, 70, and 180 d (*d*-values in nm).

tified. The IR spectra (Figure 3) showed characteristic vibrations of SO_4^{2-} (1127 and 605 cm^{-1}) and those of AlOH; the latter were similar to sample 2.0. SEM results (Figure 4) suggested that compounds occurred as: globules, sheaves of fibers, and bipyramidal tabular crystals (size 20×3 to $110 \times 47 \mu\text{m}$). Based on EDS analysis, chemical compositions were similar (globules: Al 37.0(4), S 11.6(4), and O 51.4(1) wt. %; sheaves of fibers: Al 37.5(8), S 11.0(6), and O 51.5(2) wt. %; and tabular crystals: Al 38.0(8), S 10.6(5), and O 51.4(4) wt. %). Aging did not affect shape or chemical composition (not shown).

The XRD, IR, and SEM study of sample 2.0k revealed the presence of irregular, sharp-cornered plates

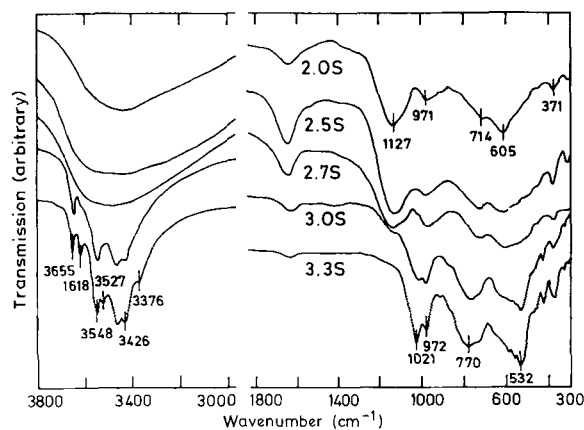


Figure 3. IR spectra for samples obtained by adding sulfate to OH-Al solutions in different mole ratios and aged for 180 d.

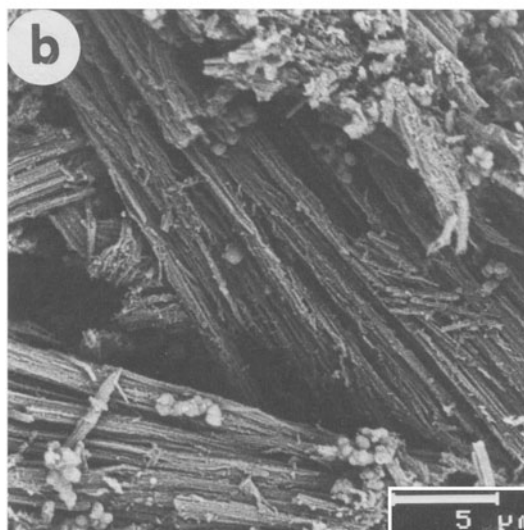
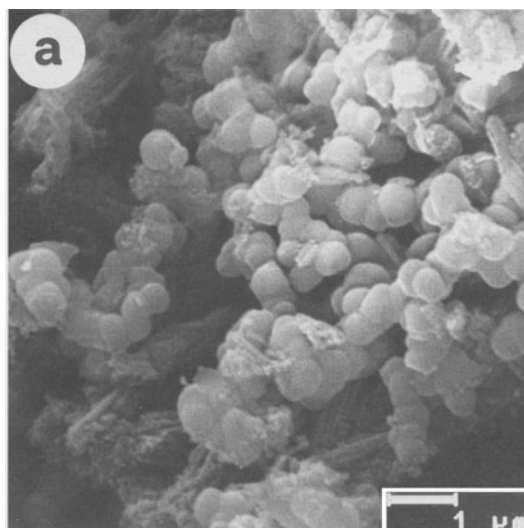


Figure 4. SEM micrographs for sample 2.0s a) aged for 30 d, Al hydroxysulfates forming globules; and b) aged for 180 d, Al hydroxysulfates forming sheaves of fibers.

of X-ray amorphous Al(OH)_x and kaolinite. With aging (180 d), Al(OH)_x plates became microparticles of ill-defined shape similar to those observed in sample 2.0.

The XRD patterns for sample 2.0sk (Figure 5) showed sharp peaks at 1.22, 1.20, and 0.98 nm. The 1.22-nm peak was not observed after 70 d of aging. After 180 d, the pattern showed a broad peak at 1.18 nm. SEM photographs showed similar morphologies to Al hydroxysulfate for sample 2.0s. After 180 d of aging, kaolinite particles were observed on the surfaces of the tabular Al-hydroxysulfate crystals (Figure 6), which underwent a loss of crystallinity with aging as judged by the XRD results.

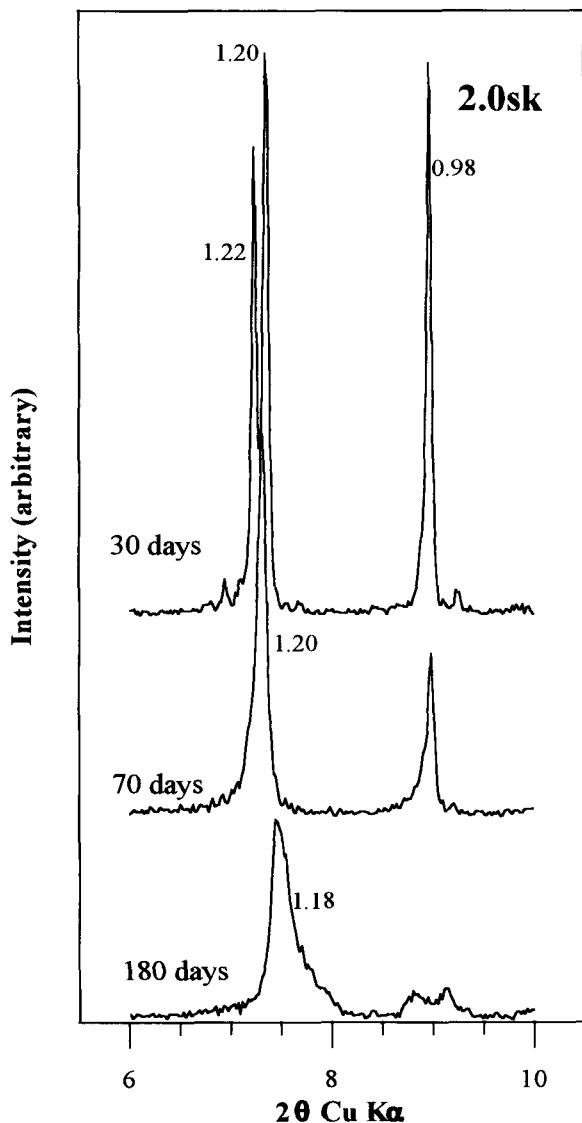


Figure 5. XRD patterns of oriented aggregate particles for sample 2.0sk aged for 30, 70, and 180 d (d -values in nm).

Samples with OH/Al mole ratio of 2.5

The pH of the fresh colloidal suspension was 5.40 and decreased slightly with aging (30 d, 5.32; 70 d, 5.17; 180 d, 5.13). Results were similar to sample 2.0 except for the thickness of the hydroxide plates, which was greater for sample 2.5.

Sample 2.5s aged for 30 d (Figure 7) showed an XRD pattern with a sharp peak at 1.20 nm and a smaller peak at 0.98 nm. After 70 d, the product showed peaks at 1.20, 1.14, and 0.98 nm; after 180 d, crystallinity was diminished and two small peaks (1.20 and 1.04 nm) were observed. The SEM study revealed two different particle shapes (Figure 8), microparticles (Al 39.1(5), S 9.8(4), and O 51.1(1) wt. %) and tabular crystals (Al 39.1(5), S 10.1(4), and O 50.6(1) wt. %)

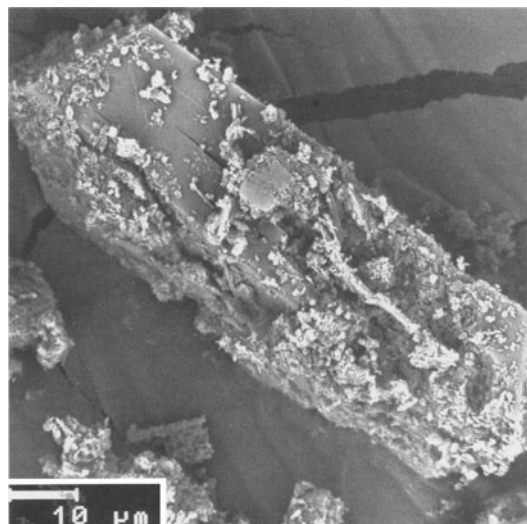


Figure 6. SEM micrographs for sample 2.0sk aged for 180 d showing kaolinite on the surface of a bipyramidal tabular Al-hydroxysulfate crystal.

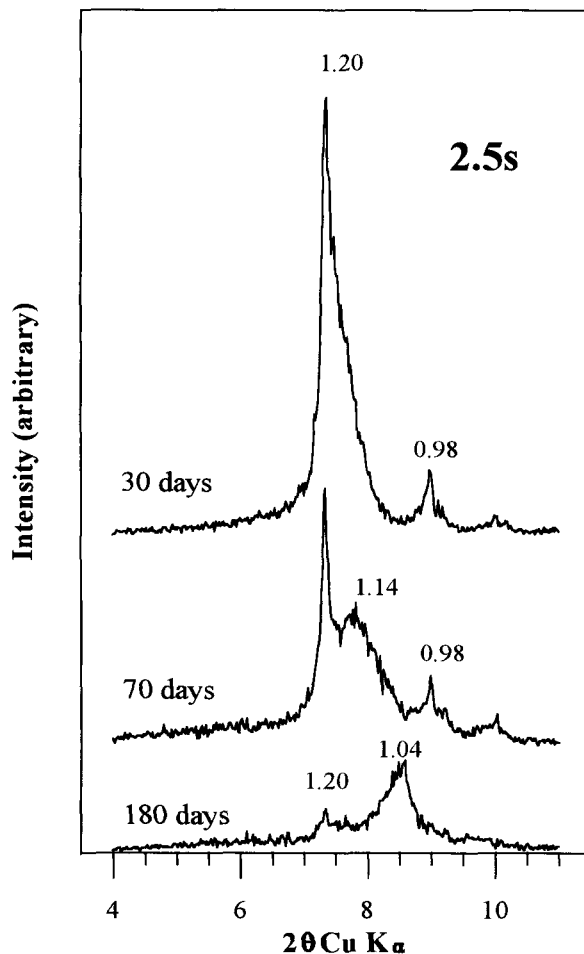


Figure 7. XRD patterns of oriented aggregate particles for sample 2.5s aged for 30, 70, and 180 d (d -values in nm).

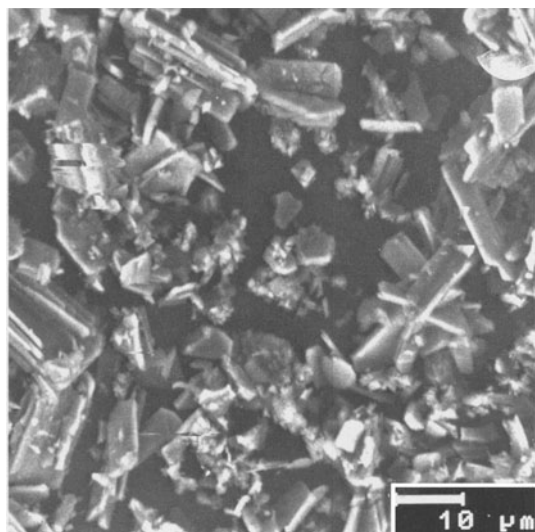


Figure 8. SEM micrographs for sample 2.5s aged for 30 d showing tabular crystals grouped as sterns or books.

forming sterns or books. Aging had no effect on shape or chemical composition of the compounds (not shown).

The XRD, IR, and SEM results for sample 2.5k aged for 30 d, revealed two components, X-ray amorphous Al(OH)_x, similar to sample 2.5, and kaolinite. In the sample aged for 70 d, kaolinite was seemingly adhered to the Al(OH)_x plates. This was also observed for samples aged for 180 d, and in addition, Al(OH)_x plates had transformed into microparticles, as in sample 2.0k.

The XRD pattern for sample 2.5sk aged for 30 d (Figure 9) showed two peaks at 1.20 and 0.98 nm that remained after 70 d. However, only a small peak at 1.04 nm was observed after 180 d. SEM revealed tabular crystals that were either isolated or forming books. After 30 d of aging, kaolinite was found to be adhering to Al-hydroxysulfate crystals, similar to sample 2.0sk, which was aged for 180 d.

Samples with OH/Al mole ratio of 2.7

The pH of the fresh colloidal suspension was 5.84 and decreased slightly with aging (30 d, 5.87; 70 d, 5.70; 180 d, 5.77). The XRD and IR results for sample 2.7 were similar to those for samples 2.0 and 2.5; there was only a small difference in the SEM results, which revealed microparticles as incipient clusters of triangular pyramids (Figure 10a); 180 d of aging increased the number of microparticles, some showing a conical habit (Figure 10b). XRD patterns showed all particles to be noncrystalline.

SEM examination of sample 2.7s revealed irregular plates of large size accompanied by microparticles of ill-defined shape; both compounds have similar compositions (Al 43.8(3), S 6.9(2), O 49.3(1) wt. %). XRD

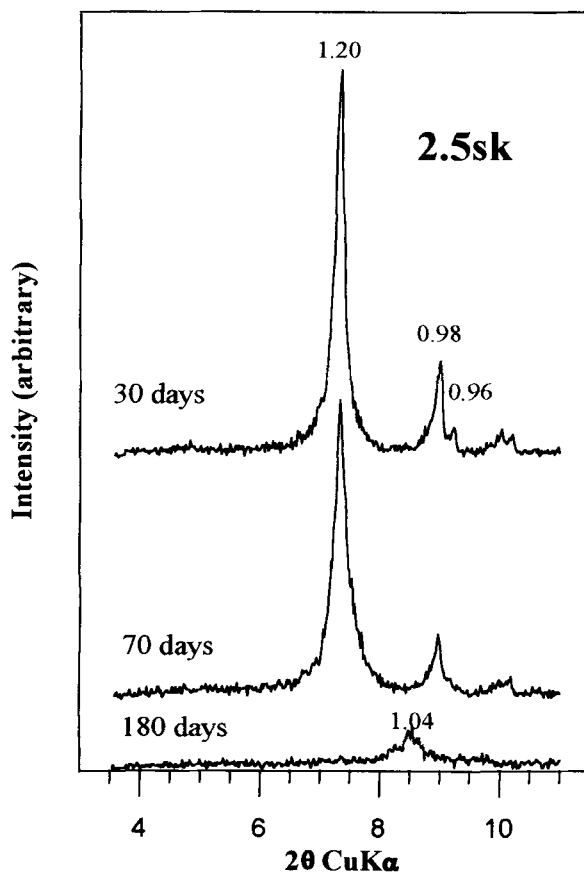


Figure 9. XRD patterns of oriented aggregate particles for sample 2.5sk aged for 30, 70, and 180 d (*d*-values in nm).

patterns showed the absence of crystalline compounds, and the IR spectra showed characteristic vibrations of SO₄²⁻ and AlOH. Aging did not alter the results. SEM study of sample 2.7k aged for 30 d showed kaolinite particles deposited on one surface of the hydroxide plates, which are curved (Figure 10c). In the sample aged for 180 d, inclusion of kaolinite in the hydroxide plates was observed (not shown). This sample contained hydroxide microparticles with a conical habit similar to that for sample 2.7 also aged for 180 d. The XRD patterns and IR spectra only showed the characteristic patterns of kaolinite. SEM study of sample 2.7sk showed irregular hydroxide plates with adhered kaolinite after only 30 d of aging (not shown).

Samples with OH/Al mole ratio of 3.0

The pH of the fresh colloidal suspension was 9.85 and reached a steady state at 8.30 after 30 d of aging. The XRD patterns for sample 3.0 (Figure 11) were consistent with three polymorphs of Al hydroxide, gibbsite (0.486 nm), nordstrandite (0.478 nm), and bayerite (0.472 nm), with bayerite the most abundant. Aging did not alter the XRD results. IR spectra showed characteristic bands for the O-H stretching vi-

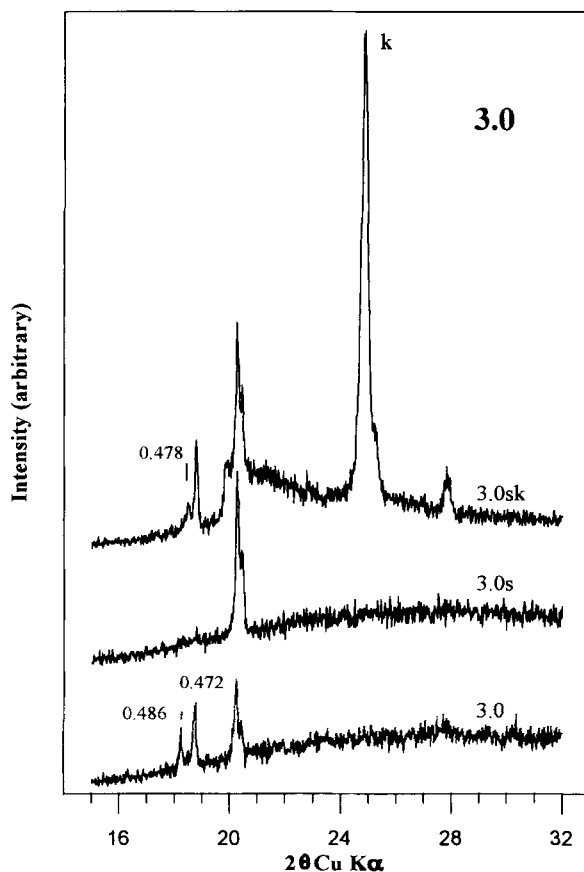
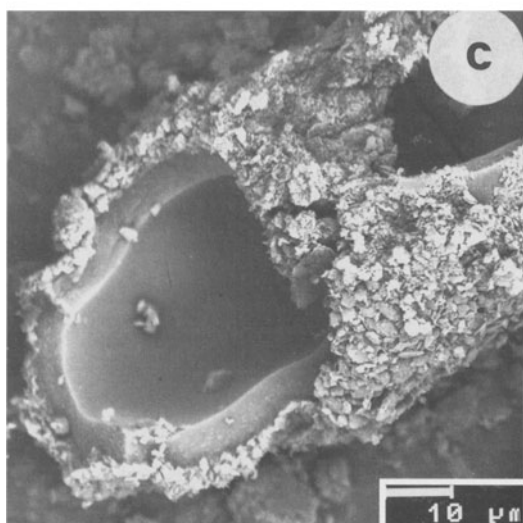
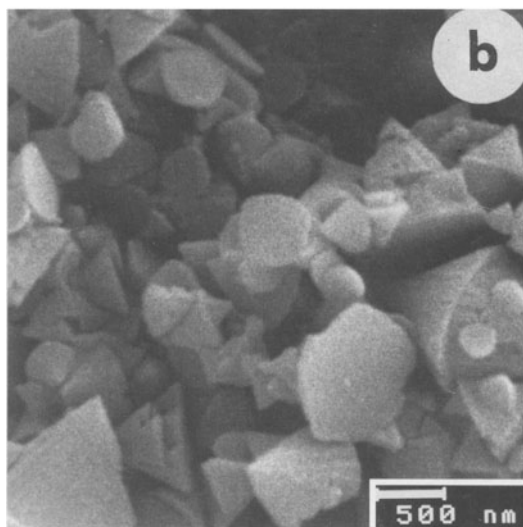
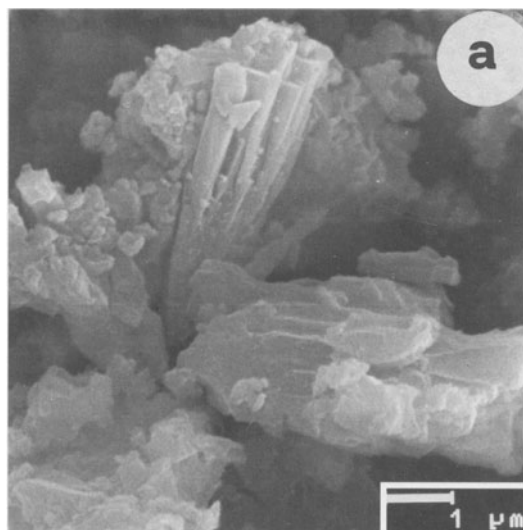


Figure 11. XRD patterns of oriented aggregate particles for samples 3.0, 3.0s, and 3.0sk aged for 70 d (d -values in nm).

brations of the three polymorphs (Figure 12). Bayerite (Figure 13) was identified also by SEM as clusters of triangular pyramids and isolated crystals. Identification of bayerite by this morphology is consistent with the TEM results of Schoen and Roberson (1970) and the SEM and TEM results of Tait *et al.* (1983). Bayerite occurred in these studies as well-developed prism faces and less well-developed pyramidal faces, and as isolated cone-shaped crystals with serrated edges (occasionally, two crystals joined at their apices produced hour-glass shaped particles of bayerite similar to Figure 13). Elongated parallelograms of nordstrandite and plates of gibbsite (Figure 13) were also observed in smaller amounts. Aging did not affect the morphology.

A comparison of the XRD results for sample 3.0s (Figure 11) with those for sample 3.0 suggested that

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Figure 10. SEM micrographs for: a) sample 2.7 aged for 30 d, incipient clusters of triangular pyramids (size 0.1–4 μm), b) sample 2.7 aged for 180 d, microparticles with a conical or biconical habit, c) sample 2.7k aged for 30 d, kaolinite deposited on one surface of an amorphous hydroxide plate.

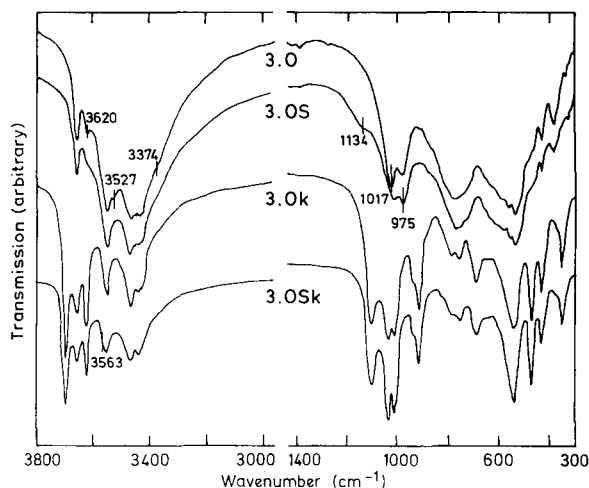


Figure 12. IR spectra for samples 3.0, 3.0s, 3.0k, and 3.0sk aged for 180 d.

sulfate decreased the amounts of each of the three polymorphs. The IR spectra were consistent with the XRD results: the bands corresponding to O-H stretching vibrations, 3620 cm⁻¹ (gibbsite + bayerite + nordstrandite) and 3527 cm⁻¹ (gibbsite + bayerite), were less intense in relation to sample 3.0 (Figure 12); and the characteristic bands for sulfate were weak (Figure 3). SEM showed bayerite crystals of the same shape as in sample 3.0 as the main Al-hydroxide species. EDS determinations only detected sulfate in morphologically ill-defined zones.

Sample 3.0k contained a high proportion of bayerite, little nordstrandite, and an even less gibbsite. A comparison of this sample with sample 3.0 suggests that kaolinite inhibits the formation of gibbsite (as indicated by the decrease in intensity of the 3374-cm⁻¹ band) and increases nordstrandite content (increase intensity of the 3563-cm⁻¹ band) (Figure 12). In the 3.0k sample, bayerite occurs as triangular pyramids, but not clusters as observed in sample 3.0. Sample 3.0sk consists largely of bayerite, in addition to some nordstrandite. Bayerite is present as triangular pyramids (size 1 μm).

Samples with OH/Al mole ratio of 3.3

The pH of the fresh colloidal suspension was 10.98 and decreased with aging (30 d, 9.23; 70 d, 8.94; 180 d, 8.95). The study of sample 3.3 provided results similar to those for sample 3.0. However, the shape of bayerite crystals was longer and there were fewer clusters (not shown). The presence of sulfate (sample 3.3s) inhibited the formation of crystalline Al hydroxides relative to sample 3.3. IR spectra showed none of the characteristic vibrations of the SO₄²⁻ group (Figure 3). The presence of kaolinite (sample 3.3k) increased the proportion of nordstrandite (0.478 nm) relative to sam-

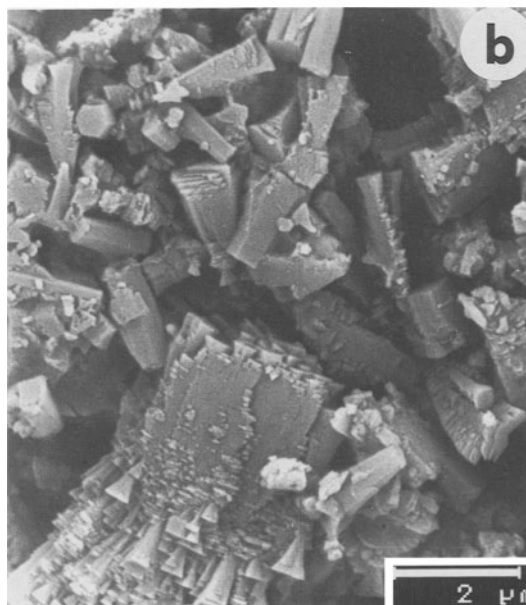
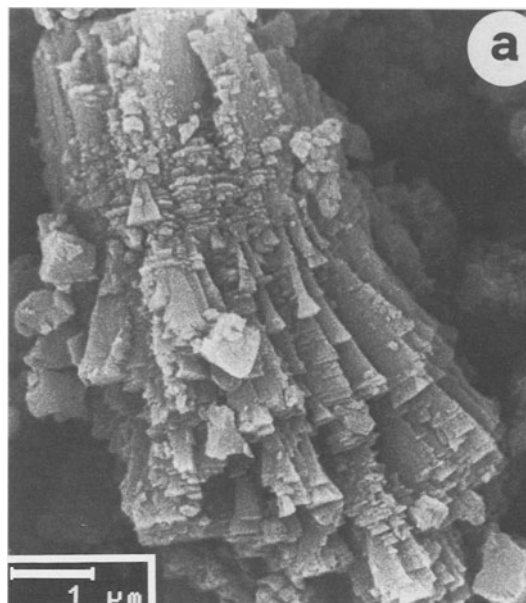


Figure 13. SEM micrographs for sample 3.0 aged for 30 d showing bayerite as: a) clusters of triangular pyramids, and b) isolated crystals (size 1.7 × 0.6 μm) and clusters of triangular pyramids.

ple 3.3 (Figure 14). Bayerite formed isolated crystals. Sample 3.3sk was similar to 3.3k.

DISCUSSION

The presence of a visible colloidal suspension a few days after preparation of the OH-Al solutions in 2.0, 2.5, and 2.7 NaOH/AlCl₃ mole ratios (concentrations of Al 0.033, 0.029, and 0.027 M, and of Cl 0.099, 0.087, and 0.081 M, respectively) is not in agreement

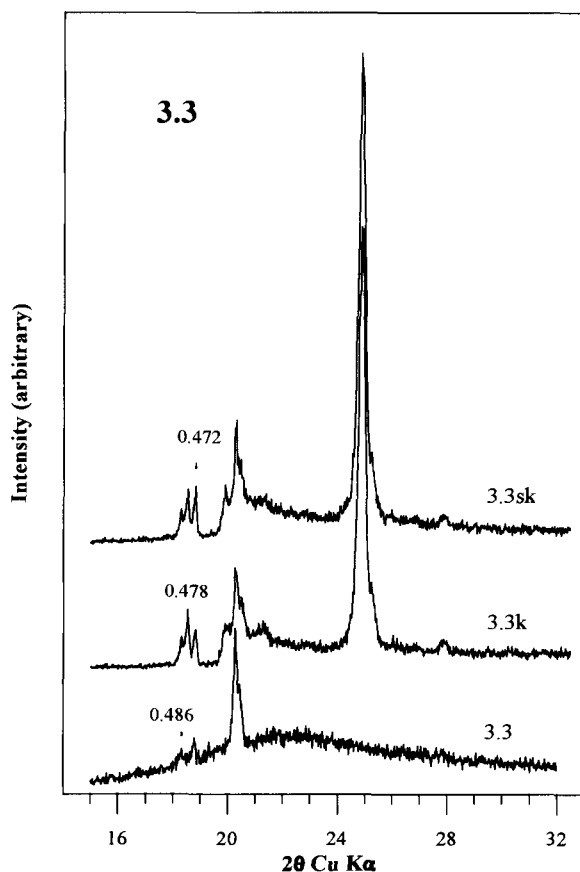


Figure 14. XRD patterns of oriented aggregate particles for samples 3.3, 3.3k, 3.3sk aged for 70 d (*d*-values in nm).

with the results of Hsu (1966). Hsu found solutions with 1.8–2.7 NaOH/AlCl₃ mole ratios and with final concentrations of Al and Cl of 0.02 and 0.06 M, respectively, to be stable for ~6–12 mo, after which they gradually became turbid and eventually contained gibbsite formed in association with a decrease in pH. This difference in behavior is not understood because Al and Cl concentrations are rather similar. However, when NaCl was used (Hsu, 1966) to adjust the chloride concentration to 0.6 and 1.2 M, amorphous Al precipitates formed immediately and these precipitates remained amorphous even after 2 y. These amorphous Al precipitates may be similar to that obtained in this work, although the Cl concentration in the bulk solution (0.099, 0.087, and 0.081 M) was smaller.

Although the product derived from solution with a mole ratio of 2.7 was an X-ray amorphous compound, the SEM observation revealed, after 30 d of aging, incipient clusters of triangular pyramids of bayerite. These clusters may originate from localized high alkalinity in the OH-Al solution or when sufficient OH⁻ was added to neutralize some of the larger Al polymers present at 2.7 OH/Al mole ratio. However, because we found no increase in the concentration of

clusters or in the gibbsite content with aging, these incipient bayerite clusters did not act as nuclei for further crystal growth as Hsu (1988) reported.

Three Al(OH)₃ polymorphs crystallized at mole ratios of 3.0 and 3.3, with bayerite being the most abundant. According to Barnhisel and Rich (1965) and Hsu (1966), this result suggests rapid precipitation. At a mole ratio of 3.0, bayerite occurred largely as clusters of triangular pyramids (size 5 μm). Increasing the OH/Al mole ratio to 3.3 produced isolated crystals from the bayerite clusters of triangular pyramids, but why this occurs needs further investigation.

The addition of sulfate to the OH-Al solutions in ratios of 2.0 and 2.5 produced crystalline basic aluminum sulfates in various morphologies and with similar chemical compositions. These compounds showed structural changes with aging; after 30 d, they lost crystallinity (XRD study), although no alteration was apparent by SEM. Except for preferential-orientation artifacts from sample preparation, the product formed from sample 2.0s showed a pattern resembling that reported by Johansson (1963) and Bersillon *et al.* (1980) for solutions with a NaOH/Al mole ratio near 2.2. Upon addition of Na₂SO₄, Tsai and Hsu (1984) showed that the basic Al sulfates varied with the NaOH/Al mole ratio and with the duration of aging of the parent OH-Al solutions. However, the morphology and chemical composition of the Al hydroxysulfate formed here did not vary with aging. In fact, three types of shapes occurred with the same chemical composition throughout the studied periods (30, 70, and 180 d; solution pH of 4.26, 4.21, and 4.26, respectively). The first observation of sample 2.0s was made after 30 d of aging, which may indicate that various positively charged polynuclear OH-Al species may exist (Bersillon *et al.*, 1980). However, note that the different shapes may have formed prior to the initial observation at 30 d.

Formation of crystalline basic aluminum sulfate in samples with the 2.0 and 2.5 mole ratios and a concentration ratio of 1.34 eq of SO₄²⁻/mol Al is consistent with the results of Hsu (1973) for samples with a 2.6 OH/Al mole ratio where 0.6–2 eq of SO₄²⁻ per mol of Al were added. The product formed upon addition of sulfate to the solution with a 2.7 OH/Al mole ratio (sample 2.7s) was an Al hydroxysulfate that remained X-ray amorphous after 180 d of aging. These results are similar to those reported by Hsu (1973). Hsu found that the addition of small amounts of sulfate to a solution of NaOH/Al in a mole ratio of 2.6 produced basic Al sulfate that showed no tendency to crystallize as Al(OH)₃ for at least 3 y.

Sample 3.0s showed decreasing gibbsite, bayerite, and nordstrandite contents relative to sample 3.0. In contrast, EDS analysis indicated the presence of sulfate in ill-defined zones, consistent with the results of Hsu and Bates (1964), who suggested that the precip-

itate obtained from the Al₂(SO₄)₃ + NaOH system (NaOH/Al = 3.0) was a mixture of Al(OH)₃ and a highly hydrated component containing Al and sulfate. Although Hsu (1989) noted that the presence of sulfate in OH-Al solutions with mole ratios of 3.0 and 3.3 was not sufficient to inhibit Al(OH)₃ crystallization, the formation of the three polymorphs (gibbsite, bayerite, and nordstrandite) was partially inhibited in our experiments.

The addition of kaolinite to the OH-Al solution with a mole ratio of 2.0 (sample 2.0k) did not produce any association between X-ray amorphous Al hydroxydes and kaolinite. However, in samples 2.5k and 2.7k, kaolinite had adhered to Al hydroxydes after 70 and 30 d of aging, respectively. Furthermore, the kaolinite was included in the hydroxide plates in sample 2.7k aged for 180 d. The Georgia kaolinite (KGa-2) has an isoelectric point of 4.2 and the pH of the solutions containing samples 2.5k and 2.7k was 5.38 and 5.64, respectively. Therefore, the kaolinite may be considered an "anion" in this case. In the structures of the polymerized hydroxy-Al species, the Al ions at the edge sites are only partially neutralized by OH⁻ (Hsu and Bates, 1964), and it could be of course, a source of the positive charge here. This may explain why kaolinite had adhered to the hydroxide plates in samples 2.5k and 2.7k. A comparison of the IR spectra for samples 2.5 and 2.5k on the one hand, and 2.7 and 2.7k on the other, showed no changes in the position of the OH bands, suggesting that an electrostatic interaction may exist between both components. In samples 3.0k and 3.3k (solution pH of 8.20 and 11.74, respectively), the presence of kaolinite favored the formation of nordstrandite, relative to samples 3.0 and 3.3.

The simultaneous addition of sulfate and kaolinite to the control samples revealed that, at the lower mole ratios (samples 2.0sk, 2.5sk, and 2.7sk), the effect of sulfate prevailed over that of kaolinite and resulted in compounds similar to those obtained from samples containing sulfate only. In sample 2.7sk, in a similar way to sample 2.7k, the kaolinite, which acts as an "anion" over this pH range, is electrostatically bonded to Al-hydroxysulfate plates, after the first month of aging. In samples with higher mole ratios (3.0sk and 3.3sk), the effect of kaolinite prevailed over that of the sulfate and produced an increased nordstrandite content.

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