

THE EFFECT OF ALUMINUM ON THE SURFACE PROPERTIES OF KAOLINITE

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(Received 22 February 1973)

Abstract— 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.

INTRODUCTION

ONE OF the least understood and more frustrating aspects of kaolinite technology is the broad spectrum response to chemicals used in commercial beneficiation. Such variations are also commonly encountered in similar procedures used in laboratory preparation of kaolinites for experimental investigations.

Beneficiation of kaolinite generally consists of deflocculation at the mine face, centrifugal classification of particle size, leaching which entails reduction and acid solution of ferric iron, and filtration and rinsing followed by drying in either the acid or deflocculated form. Although minor variations within each stage of processing can impart significant differences to product character, it is the fate and influence of aluminum dissolved during leaching that is of immediate concern. Because some aluminum may be extracted from kaolinite systems during leaching or may be introduced as the sulfate to facilitate filtration, aluminum ions as well as precipitation products commonly have a major influence on surface chemistry.

Because of a resulting brightness improvement of 2-4 percentage points, leaching is utilized with all paper coating clays. Iron and titanium oxides are the primary non-white components in Georgia kaolins. Titania occurs largely as dark colored colloidal anatase along with minor rutile. Although titanium must be removed by non-solution tech-

niques, acid solution, reduction, and extraction of small percentages of iron provide notable color modification. Kaolin products used in the paper industry contain in the range of 0.2-2.0 per cent Fe_2O_3 , and most coating grades are on the low side, 0.2-0.4 per cent. Iron that is removed by the leaching process ranges up to about 0.2 per cent Fe_2O_3 , averaging about 10 per cent of the total iron present in the clay.

The leaching operation, carried out in the range of pH 2-4, uses sulfuric acid and aluminum sulfate as the most common acidifying agents. Strong reducing agents, sodium or zinc hydrosulfite, are used to reduce ferric iron to the more soluble ferrous form.

Additional brightness improvement of kaolinite may be brought about by the following mechanisms.

1. Reduction of lattice iron from ferric to ferrous

Because most of the iron in kaolinite cannot be removed without complete dissolution, and because Mössbauer measurements indicate the presence of both ferrous and ferric iron in the lattice (Malden and Meads, 1967) it is suggested that some of the iron is an integral part of the kaolinite structure. Additionally, Angel and Hall (1972) have shown by electron spin resonance that iron is a common substituent in kaolinites. Reduction of ferric iron in the lattice to the ferrous form

without extraction could account for some color improvement.

2. Flocculation or inhibition of dispersion of dark colored colloids

Degree of dispersion of colloidal titanium and iron oxides can have a significant effect on pigment brightness. This phenomenon will be elaborated in subsequent discussion.

EXPERIMENTAL

A fine particle kaolinite from the Wrens area of east central Georgia was utilized for all experimental work. Because of high surface area (*ca.* 30 M²/g), it was anticipated that the influence of surface modifications would be maximized. X-ray diffraction indicated a poorly crystallized kaolinite of high purity containing small percentages of anatase and muscovite. Particle size distribution was as follows:

Equivalent spherical dia. (μm)	% Less than
2	100
1	97
0.5	84
0.25	48

A standard processing procedure, designed for convenience but generally simulating commercial conditions, was utilized throughout the study unless otherwise indicated. Percentage of various additions is based on the oven-dry weight of crude clay.

Deflocculation of the crude kaolin was carried out with 0.35 per cent chemical, which consisted of 2 parts sodium polyphosphate and 1 part sodium carbonate. The sodium polyphosphate used is a glass containing polyphosphate chains of varying lengths. The composition is indicated by the general formula (NaPO₃)_x where the value of *x* averages 5. In all experimental data where incremental amounts of polyphosphate are indicated, 0 per cent indicates use of sodium hydroxide as the dispersant. Particle size classification was carried out by sedimentation. The resultant particle size is shown above.

The deflocculated product was leached for 20 min with 0.5 per cent sodium hydrosulfite. The system was maintained at pH 3 with H₂SO₄ and 0.6 per cent alum (Al₂(SO₄)₃ · 18 H₂O). Although not a true alum, this designation is generally used throughout the industry. After final adjustment to pH 3, filtration was followed by rinsing with deion-

ized water to a resistivity of 35,000–45,000 Ω cm. Second stage deflocculation was carried out using 0.35 per cent dispersing chemical. Samples were oven dried at 90°C to less than 0.5 per cent moisture.

Dried samples were pulverized and then redispersed with a Hamilton Beach mixer and blunged with constant energy input for 5 min. Clay solids were adjusted to 71 per cent \pm 0.1. The polyphosphate content was adjusted to give minimum viscosity. Sodium carbonate was added to adjust all systems to pH 7. A low shear, rotational Brookfield viscometer was utilized to determine viscosity at 10 r.p.m. Methylene blue adsorption measurements, conducted by Erika de Mello of this laboratory, were used for surface area determinations following the method of Johnson (1957). Two procedural changes have been incorporated: a buffered solution as described by Bergman and Konski (1963); and a contact solution having a maximum concentration of 7×10^{-6} mole/l.

RESULTS AND DISCUSSION

Although not generally recognized, enhancement of iron extraction, in addition to improvement of filtration, is a potentially useful functionality of alum during leaching. Perhaps the most efficient system for the extraction of iron from kaolinite without lattice attack is afforded by systems containing relatively high concentrations of aluminum in solution. This propitious effect, as well as influence of filtration pH, is shown in Fig. 1. Soluble iron, shown on the ordinate, is that iron which can be removed from kaolinite by standard leaching. It is the amount of iron that can be extracted by soaking 3 g of sample in 25 ml of 6N HCl for 1 hr at 85°C. Soluble iron decreased for

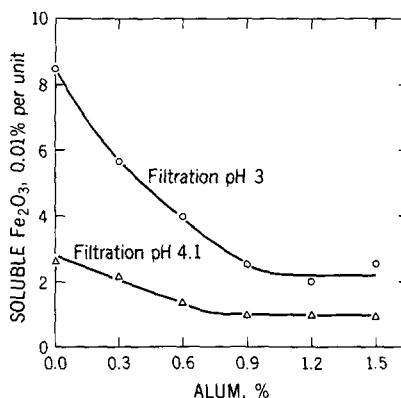


Fig. 1. Effect of alum leach on the extraction of soluble iron from kaolinite.

both pH systems shown in the diagram. More efficient extraction was afforded by filtration at pH 4.1. It is presumed that increasing concentration of aluminum effects replacement of iron at exchange sites, thereby enhancing iron extraction and subsequent removal during filtration. Improved extraction efficiency at pH 4.1 may come about by reduction of exchange capacity due to precipitation of aluminum hydroxide and consequent clogging of exchange sites.

Although no additional iron was extracted beyond alum levels of 1 per cent, Fig. 2 shows that brightness continued to improve with higher concentrations of alum. Clearly, iron extraction did not account for this complementary brightness improvement.

Titanium dioxides, dominantly anatase, contribute notably to the offwhite coloration of Georgia kaolinites. Removal of small amounts gives rise to substantial increase of brightness. Other investigations (Nagelschmidt, 1949; Bundy, Johns and Murray, 1966) have shown that anatase is concentrated in the fine end of the kaolinite particle size distribution.

Selective aggregation of fines seems to be afforded by precipitation of aluminum hydroxide, shown in Fig. 3, and may account for brightness improvement beyond that obtained by iron extraction. Increasing filtration pH not only precipitates aluminum hydroxide, but also provides maximum aggregation of particles near $0.3 \mu\text{m}$ and below. Because such a phenomenon does not occur in leaching systems free of alum, aggregation of fines by precipitation of aluminum hydroxide is the suggested mechanism. Thus, light scatter contributed by anatase would be reduced by virtue of reduction

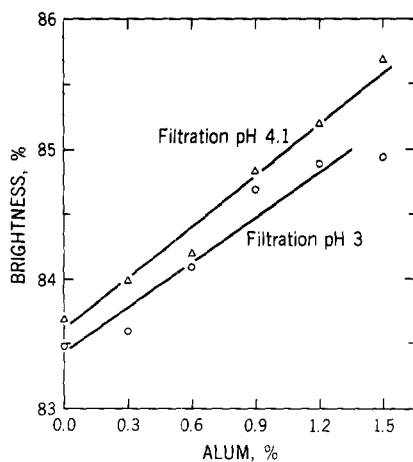


Fig. 2. Effect of alum leach on brightness of kaolinite.

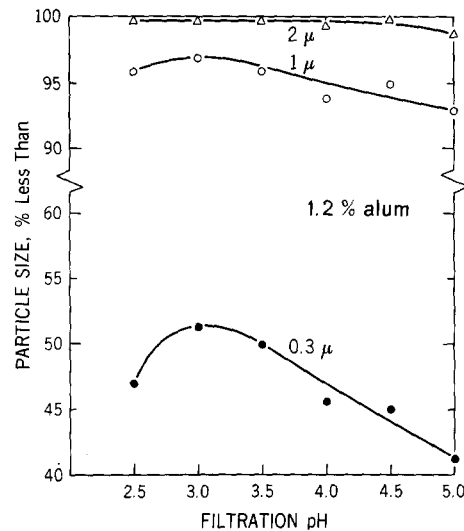


Fig. 3. The effect of hydroxide precipitation of particle size distribution of kaolinite.

in anatase, air, kaolinite interface, and improvement in brightness would be expected.

In addition to change in particle size distribution, such aggregation of kaolinite can effect significant differences in degree and type of floc structures as well as rheological character. Precipitation of aluminum as the hydroxide commonly occurs during leaching and filtration of kaolinite suspensions. Although leaching is carried out near pH 3, it is not unusual for these systems to be in excess of pH 4 at the time of filtration. Inasmuch as aluminum ion begins to precipitate near pH 4, it is not uncommon for products to contain varying amounts of aluminum hydroxide.

Freshly precipitated aluminum hydroxide can have an isoelectric point in excess of pH 8 (Schuylenborough and Sanger, 1949), below which a positive surface charge enables the retention of large amounts of sulfate ion. Such kaolinite systems give inordinately high viscosities, which can be reduced to minimum values by extraction of most of the sulfate. The influence of soluble salts and of aluminum hydroxide is shown in Fig. 4. Resistivity is an approximate measure of soluble salts retained after filtration and rinsing. Viscosity was measured at minimum shear rate to include the contribution of floc structures. The lower curve indicates the effect of resistivity where kaolinite is filtered at pH 3. Except for those ions retained on exchange sites, low pH insures maximum removal of aluminum and iron. Increase in resistivity indicates increased efficiency of extraction, and minimum viscosity is obtained at a relatively high resistivity,

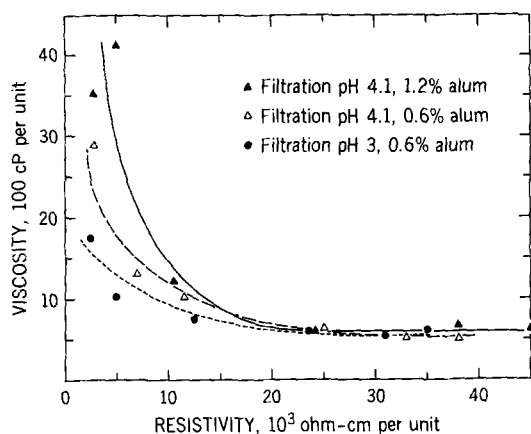


Fig. 4. The effect of resistivity and aluminum hydroxide on the viscosity of clay-water systems.

about 20,000 Ω -cm. Higher filtration pH and consequent precipitation of aluminum hydroxide yields major increases in viscosity.

Analyses indicate that resistivity corresponds closely, but inversely, to sulfate retention. Figure 5 shows that sulfate increases with decrease in resistivity and increase in aluminum hydroxide. Although ions other than sulfate are present, it is presumed that sulfate is the only soluble component influencing flocculation. At pH 4.1 virtually all aluminum ion has been precipitated as the hydroxide. Sodium and polyphosphate ions are present in relatively constant concentrations, and are added in those amounts which maximize dispersion.

High viscosities of low resistivity clays may come about because of compression of the electrical double layer, promoted by high salt concen-

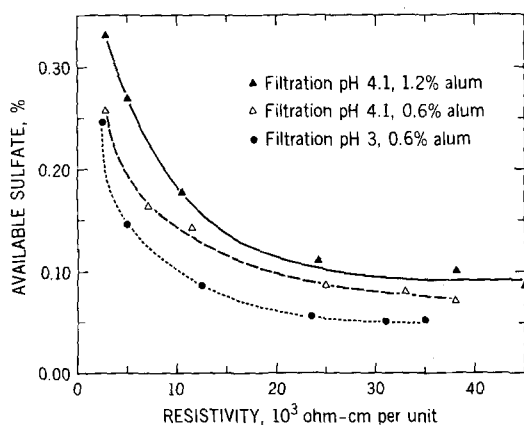


Fig. 5. The relationship of resistivity and aluminum hydroxide to retention of sulfate.

tration, and consequent flocculation by van der Waals attraction. In the present case, however, it is believed that flocculation is influenced predominantly by anion bridging bonds effected by sulfate between positively charged aluminum hydroxide and kaolinite edge surfaces.

Types of flocculation of kaolinite platelets and their relative influence on viscosity have been described by Van Olphen (1963). Edge-edge (*EE*) and edge-face (*EF*) associations, because of increased particle interference, give viscosity increase, whereas face-face (*FF*) associations, because of decreased particle interference give viscosity decrease. In addition to low shear viscosity, determination of methylene blue surface area contributes to additional understanding of floc structure. Because the dominant surface area is comprised of layer surfaces, major changes in surface area imply major changes in *FF* association. As opposed to nitrogen adsorption, methylene blue adsorption is a sensitive measure of *FF* variation. It is more meaningful, therefore, to consider methylene blue adsorption as a measure of degree of dispersion as opposed to total surface area. Concomitant considerations of low shear viscosity measurement and methylene blue surface area makes possible the determination of dominant types of floc structures occurring in kaolinite suspensions.

Figure 6 is an example of how these phenomena can be interrelated. Variables included are filtration pH to show the influence of aluminum hydroxide precipitation, low shear viscosity, and surface area. Soluble salts have been removed to minimize *EE* and *EF* associations. Maximum dispersion seems to have occurred where filtration

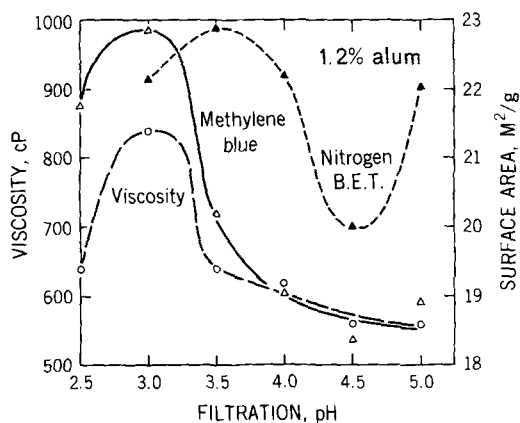


Fig. 6. Effect of filtration pH on viscosity and surface area.

has been carried out at pH 3, as indicated by correspondence with maximum surface area. With increasing filtration pH, the increased amount of aluminum hydroxide precipitated has promoted the formation of *FF* associations as indicated by surface area reduction and a striking correspondence with change in viscosity. This reduction in particle interference has effected significant decrease in viscosity, even below that obtained with well-dispersed systems.

The postulated interaction between kaolinite, aluminum hydroxide, and sulfate ion is depicted in Fig. 7. Where relatively high concentrations of sulfate are retained in kaolinite-aluminum hydroxide systems, *EE* and *EF* structures dominate as indicated by high viscosity and high surface area. It is presumed that the positively charged aluminum hydroxide is bridged to the positively charged edge faces of kaolinite by the sulfate anion. With removal of most of the sulfate, the positively charged aluminum hydroxide would tend to aggregate on the negatively charged layer surfaces and thus promote the formation of *FF* structures. Such a postulate pragmatically accounts for reduction in surface area as well as viscosity.

That *FF* association apparently increases with removal of sulfate (increase in resistivity) for kaolinite-aluminum hydroxide systems is clearly indicated in Fig. 8. Approximately a 35 per cent reduction in surface area was brought about by

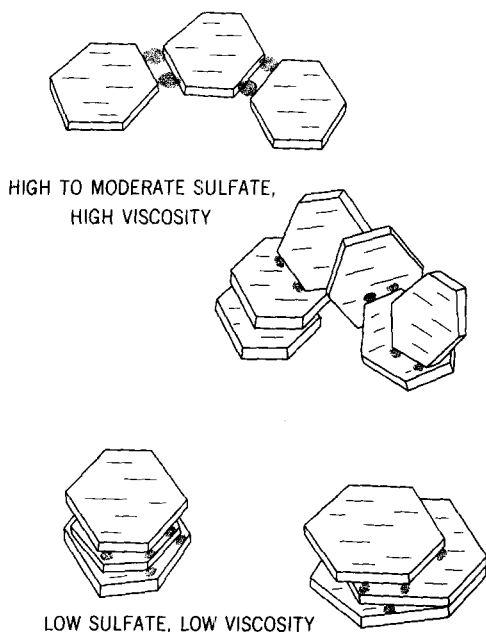


Fig. 7. The postulated effect of colloidal aluminum hydroxide and sulfate ion on flocculation of kaolinite.

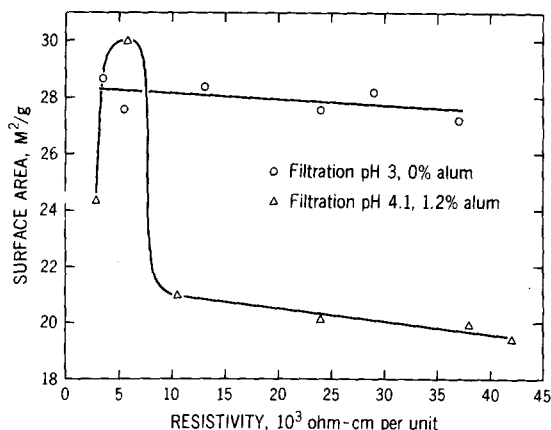


Fig. 8. The effect of resistivity (Ω) and aluminum hydroxide on surface area.

sulfate removal. Removal of sulfate brings about a relatively small decrease in surface area for alum free systems as shown by the upper curve.

The extent to which kaolinites can be redispersed after processing is a complicated function of alum utilization, indicated in Fig. 9. Not surprisingly, least dispersion, as indicated by lowest surface area, is shown by high resistivity systems containing aluminum hydroxide. An abundance of *FF* associations is indicated. Where filtration is carried out at pH3 and clays are rinsed to a high resistivity, regardless of alum utilization, dispersion is similar in character as shown by the two middle curves. The initial low surface area values for the system containing alum is probably due to reaction between aluminum retained at exchange sites and polyphosphate. As shown by the upper curve, maximum dispersion of *FF* structures is obtained for low resistivity kaolinites containing alum. Seemingly *EE* and *EF* structures are so dom-

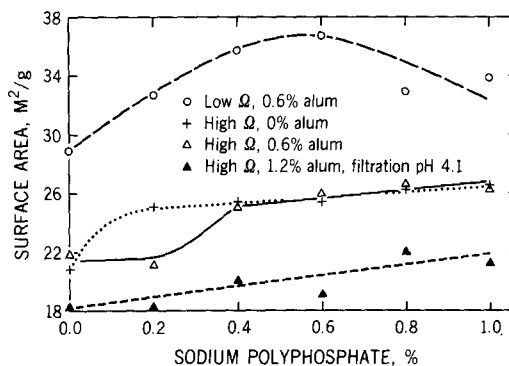


Fig. 9. The effect of alum leach on redispersion characteristics of kaolinite.

inant that *FF* structures are minimized. Those *FF* associations which do form, however, are redispersed readily as indicated by a substantial increase in surface area with increase in polyphosphate.

It is anticipated that some surface area increase may come about by virtue of insoluble reaction products which can form between polyphosphate, aluminum, and iron. Observations under the electron microscope, however, indicate significantly better dispersion of *FF* structures for low resistivity systems. This improved dispersion seems to represent the major contribution to variations in surface area.

Viscosity stability of kaolinite suspensions deflocculated with polyphosphates is also a sensitive function of the amount of aluminum and sulfate retained in the kaolinite system. Suspensions of kaolinite, relatively free of by-products of leaching, show maximum stability as shown in Fig. 10. Initial and aged systems show an insignificant difference in viscosity. Adjusted viscosity is obtained by adding an optimum increment of polyphosphate to the aged slurry. Similar high resistivity systems but with precipitated aluminum hydroxide also show relatively high stability (Fig. 11). The moderate increase in viscosity for the aged system using 0.2 per cent polyphosphate indicates some reaction, however, with aluminum hydroxide. Where high concentrations of polyphosphate are utilized, viscosity decrease with aging becomes significant. Again, *FF* formation is indicated.

In sharp contrast, Fig. 12 shows the extreme viscosity instability for similar low resistivity systems. Colloidal gels and cations which can be sequestered, such as afforded by aluminum, substantially accelerate hydrolytic degradation of polyphosphates (Clesceri and Lee, 1965). The extent to which reaction between aluminum hydroxide

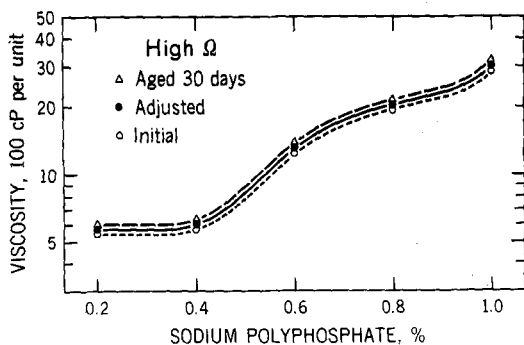


Fig. 10. The effect of high resistivity (Ω) and aging on viscosity of clay-water systems.

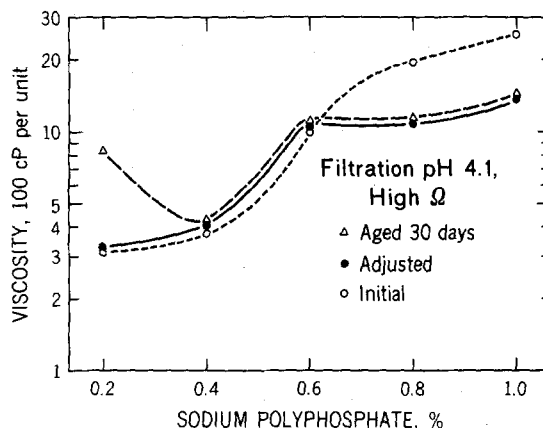


Fig. 11. The effect of high resistivity (Ω) and precipitated aluminum hydroxide on viscosity of clay-water systems.

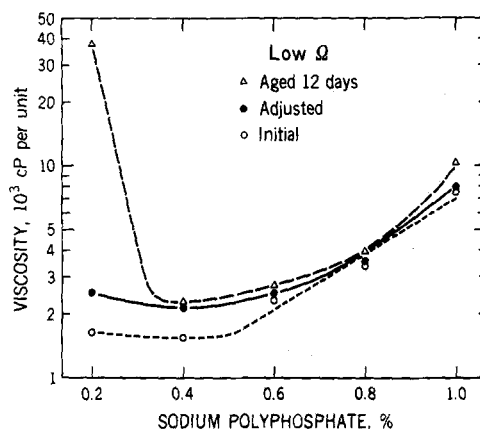


Fig. 12. The effect of low resistivity (Ω) and aging (12 days) on viscosity of clay-water systems.

and polyphosphate takes place, apparently, is related to amount of sulfate retention. A suggested mechanism by which sulfate ion affects accelerated hydrolysis of polyphosphates is the influence that such anions have on crystallization of aluminum hydroxide. Several investigations, summarized by Schoen and Roberson (1970) have shown that crystallization of amorphous aluminum hydroxide is inhibited by retention of anions, and sulfate is one of the more serious offenders. Thus retention of sulfate affects maintenance of aluminum hydroxide in amorphous, more reactive form. In contrast, sulfate removal allows aluminum hydroxide to revert to a more ordered form, thereby reducing reaction with sorbed polyphosphates.

SUMMARY

Maintenance of high concentrations of aluminum ion during leaching of kaolinite facilitates replacement of iron at exchange sites, thus enabling increased extraction in acid solution. Extraction of iron is further enhanced in cases where aluminum hydroxide is precipitated in the final stages of leaching. The mechanism of this improvement is not clear but may be related to clogging of exchange sites and displacement of more iron into the solution phase.

Precipitation of aluminum hydroxide seems to effect selective aggregation of ultra-fines in kaolinites, bringing about brightness increase in excess of that attributable to iron extraction. Because anatase is a primary discolorant and is largely concentrated in the fine end of the kaolinite particle size distribution, selective aggregation of fines would be expected to give improved brightness.

Type and degree of flocculation induced by aluminum hydroxide is a sensitive function of sulfate ion content. With high sulfate, *EE* and *EF* associations dominate as indicated by high viscosity and methylene blue surface area. Removal of sulfate ions results in abundant *FF* arrangements and reduction in viscosity by virtue of reduced particle interference. Such systems show commensurate reduction in surface area.

Dispersion of kaolinite-aluminum hydroxide systems is likewise an important function of sulfate ion content. Maximum dispersion of *FF* structures occurs with systems containing abundant sulfate ion, whereas minimum dispersion occurs with high resistivity kaolinite-aluminum hydroxide systems. Intermediate values of dispersion are obtained for systems free of sulfate and aluminum hydroxide, indicating that considerable *FF* struc-

ture tends to form in all systems relatively free of sulfate.

In a similar fashion, viscosity stability of kaolinite suspensions is a sensitive function of sulfate concentration. Maximum stability is obtained with systems free of sulfate and reactive aluminum. A suggestion is made that the inhibiting effect of sulfate ion on crystallization maintains aluminum hydroxide in amorphous, reactive form. Abundant interaction of aluminum with polyphosphates promotes a large viscosity increase.

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Résumé — Les ions aluminium ou les précipités d'hydroxyde d'aluminium favorisent l'extraction du fer à partir des kaolinites pendant le lessivage. L'agrégation sélective des particules ultrafines dans les kaolinites, induite apparemment par la précipitation d'hydroxyde d'aluminium, contribue à améliorer la brillance en plus de ce qui pourrait être attendu à la suite d'une extraction du fer. L'agrégation de l'anatase, un décolorant primaire trouvé principalement dans la fraction fine de la distribution granulométrique de la kaolinite, est le mécanisme que l'on suggère pour expliquer l'amélioration complémentaire de la brillance.

La précipitation d'hydroxyde d'aluminium dans les systèmes à base de kaolinite en modifie substantiellement les caractéristiques de floculation, la surface spécifique (mesurée au bleu de méthylène) et la rhéologie. La floculation bord à bord et bord à face est favorisée quand la rétention des sulfates est élevée; elle acquiert progressivement un caractère face à face plus marqué lors de l'élimination des sulfates. Les caractéristiques de la floculation peuvent être interprétées par l'utilisation combinée des données sur la surface spécifique et sur la viscosité à faible gradient de cisaillement.

Le domaine dans lequel les kaolinites peuvent être dispersées après traitement augmente avec l'augmentation de la rétention en sulfates. La stabilité des suspensions défloculées avec les polyphosphates montre une relation inverse; la stabilité décroît avec un accroissement de la rétention des sulfates.

Kurzreferat — Aluminiumionen, wie auch Hydroxidniederschläge fördern eine verbesserte Extraktion von Eisen aus Kaoliniten während der Auswaschung. Die selektive Aggregation ultrafeiner Teilchen

in Kaoliniten, die offenbar durch Fällung von Aluminiumhydroxid ausgelöst wird, ergibt eine Verbesserung der Aufhellung über das Maß hinaus, das der Eisenextraktion zugeschrieben werden kann. Die Aggregation von Anatas—dem wichtigsten aufhellenden Bestandteil, dessen Vorkommen weitgehend auf das feinkörnige Ende des Körnungsspektrums von Kaolinit beschränkt ist,— wird als Mechanismus für die ergänzende Aufhellung vorgeschlagen.

Die Fällung von Aluminiumhydroxid in Kaolinitssystemen verändert wesentlich die Flockungseigenschaften, die spezifische Oberfläche (Methylenblau) und die Strömungseigenschaften. Kanten-Kanten- und Kanten-Flächen-Flockung werden bei hoher Sulfatbindung gefördert und gehen bei Sulfatentzug zunehmend in Flächen-Flächen-Flockung über. Der Charakter der Flockung kann durch kombinierte Auswertung von Messungen der spezifischen Oberfläche und der Viskosität bei geringen Scherkräften gedeutet werden.

Der nach der Behandlung erreichbare Dispergierungsgrad von Kaoliniten nimmt mit steigender Sulfatrückhaltung zu. Die Stabilität von Suspensionen, die mit Polyphosphaten entflokt wurden, zeigt eine entgegengesetzte Beziehung: sie nimmt mit steigender Sulfatrückhaltung ab.

Резюме — Алюминиевые ионы как и осадки гидроокиси вызывают улучшенную экстракцию ионов из каолинитов во время выщелачивания. Селективная агрегация мельчайших частиц в каолинитах, очевидно вызванная осаждением гидроокиси алюминия на столько улучшают блеск, что это невозможно приписать экстракции железа. Полагают, что анатаз — первичный обесцвечиватель — удерживаемый большей частью мелкозернистым каолинитом, является механизмом добавочного улучшения блеска.

Осаждение гидроокиси алюминия в системах каолинита значительно изменяет характеристики флокуляции, поверхностный слой (метиловая синь) и реологию. Флокуляция «ребро-ребро» и «ребро-грань» вызывается когда имеется высокое удерживание сульфата, а при удалении сульфата реакция прогрессивно становится «грань-грань». Характер флокуляции можно объяснить совместным использованием площади поверхности и низким сдвигом данных вязкости.

Степень до которой можно диспергировать каолиниты после обработки поднимается в соответствии с повышенем удержания сульфата. Стабильность суспензии диспергированной полифосфатами дает обратное соотношение — она понижается с увеличением удержания сульфата.