ALUMINUM CHEMISTRY IN ACID SULFATE SOILS

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Aluminum is the most abundant metallic element in the earth's crust. Moreover, hydrolysis of the aluminum ion produces a moderately strong acidic environment so that it is not surprising that many of the properties of acid soils are controlled by the chemistry of aluminum. Indeed, aluminum bonding has been described as a unifying principle in soil science (Jackson 1963). In acid sulfate soils additional acidity is produced by the oxidation of sulfides to sulfuric acid, which may also react with many aluminum compounds in soil. The venerable topic of soil acidity has been examined recently in an excellent review by Coleman and Thomas (1967). Thus, the present analysis will take a somewhat different path. First, we will consider the reactions of aluminum in aqueous solutions and then examine how these reactions may be modified in clay suspensions; then, the chemistry of aluminum in soils will be examined; and finally, we will consider the effects of aluminum on the physical properties of clays and soils.

ALUMINUM CHEMISTRY IN AQUEOUS SOLUTIONS

Hydrolysis

Chemically, the hydrolysis of aluminum in aqueous solutions has been assumed to proceed via the first-stage hydrolysis reaction:

$$Al^{3+} + H_2O = AlOH^{2+} + H^+ \qquad (1)$$

where water of hydration is omitted for convenience. Expressing ion activities as negative logarithms, the thermodynamic equilibrium constant for this reaction is given by:

$$pK = pAlOH + pH - pAl \qquad (2)$$

where the valences of the ions are omitted for convenience. There have been numerous determinations of this hydrolysis constant (Sillen and Martell, 1964,1971) with most investigators agreeing that pK is approximately 5.0. However, many feel that this reaction does not exist or that other hydrolytic species must also be considered.

A partial explanation for these different viewpoints is provided by work of Frink and Peech (1963), who showed that aqueous aluminum solutions become super-

saturated with respect to $Al(OH)_3$ on dilution or addition of base. Hence, at low basicities, the first-stage hydrolysis reaction appears to be satisfactory (Frink and Peech, 1963a; Holmes et al. 1968; Raupach, 1963; Schofield and Taylor, 1954; Srinivasan and Rechnitz, 1968). At higher basicities numerous polynuclear species have been reported (Brosset et al. 1954; Fripiat et al. 1965; Matijević et al. 1961, 1964; Rausch and Bale 1964; Ruff and Tyree, 1958). These conflicting interpretations appear throughout the study of aluminum chemistry in solutions, clay suspensions, and in soils, and will become familiar topics as we proceed.

Recently, the effect of basicity on the apparent mechanism of hydrolysis has been re-examined by analysis of potentiometric titration curves of dilute aluminum salt solutions. Frink and Sawhney (1967) pointed out that these titration curves present two apparent anomalies. First, although the monomeric hydrolysis mechanism satisfactorily describes the changes in pH on dilution of aluminum salt solutions, no inflection point corresponding to the completion of first-stage hydrolysis is observed in titration curves. Second, the pH of an aluminum solution at 50% neutralization is not a constant, as is the case with other weak acids, but instead is a function of initial aluminum concentration. They proposed that the neutralization of an aluminum salt solution could be considered to proceed by stoichiometric precipitation of $Al(OH)_3$ by added base, and that the pH was controlled by first-stage hydrolysis of the aluminum remaining in solution. Discrepancies between calculated and observed pH near the equivalence point were attributed to anion penetration of the solid phase $Al(OH)_3$.

Turner (1968a, 1968b) has examined this proposal in considerable detail. His results indicate that, while the conclusions reached by Frink and Sawhney (1967) were essentially correct for rapid titrations, other reaction products including polynuclear cations were formed during slow titrations. Turner and Ross (1969) examined the solid phase formed during the neutralization of $AlCl_3$ solutions and found that its composition changed during the course of the titration and could not be represented by $Al(OH)_3$. They concluded that the initial product formed during the neutralization of $AlCl_3$ solutions is a solid phase of variable composition and that polynuclear hydroxyaluminum cations form slowly at the expense of the solid phase.

Other evidence for the occurrence of monomeric hydrolysis has been provided recently by measurements of dissociation field effect relaxation times in dilute aqueous aluminum chloride solutions by Holmes et al. (1968). Their observations agreed with earlier findings of Frink and Peech (1963a) that monomeric rather

than polymeric mechanisms best described these solutions. Srinivasan and Rechnitz (1968) measured rates of formation of aluminum fluoride complexes and concluded that the simple monomeric mechanism provided the best fit to their experimental data. Sullivan and Singley (1968) analyzed titration curves of dilute aluminum perchlorate solutions and concluded that the major species present in 10^{-3}M and 10^{-4}M solutions were Al^{3+}, $AlOH^{2+}$, and $Al(OH)_3$.

Hem (1968) has examined the reaction products formed during serial titrations of aluminum salt solutions by a variety of techniques. He found crystalline gibbsite in solutions with OH/Al ratios between 2 and 3 after aging for as little as 10 days. Particle diameters were of the order of 0.1 micron and Hem (1968) feels that these crystalline products may have been overlooked by earlier investigators. He further examined various proposed polymers by considering OH^- to exist either in non-structural positions as in the monomer $AlOH^{2+}$ or in structural bridges in polymers. As a result of analyses of rates of reaction of these two kinds of hydroxyls with acid, he concluded that at equilibrium all non-structural OH^- is present as the monomer $Al(OH)^{2+}$ and that all structural OH^- is present as a polymer with formula $Al(OH)_3$. Hence, he agreed with the proposals of Frink and Sawhney (1967) that polynuclear hydroxyalyminum cations could be ignored. However, Hem (1968) does caution that equilibrium is only slowly attained and metastable complex species may exist for some time so that the concept may have limited practical usefulness.

Solid Phase and Polynuclear Species

Although considerable progress has been made in understanding the neutralization of aluminum salt solutions, neither the composition of the solid phase nor the nature of the various metastable polynuclear hydroxyaluminum species that have been proposed is known with certainty. The solubility product of gibbsite, the thermodynamically stable phase of $Al(OH)_3$, has been measured and found to correspond to $pK_{sp} = 33.5$ (Frink and Peech, 1962). However, equilibrium is established very slowly, particularly in undersaturated solutions. Kittrick (1966) found $pK_{sp} = 34.0$ for solutions aged for four years and concluded that his sample of gibbsite might be more crystalline than that of Frink and Peech (1962). Supersaturated solutions had an ion product for $Al(OH)_3$ corresponding to an apparent pK_{sp} of 31.8 (Frink and Sawhney 1967) and seeding with gibbsite had little effect. Other precipitates of varying crystallinity and basicity have been reported by a number of workers (Hsu and Bates 1964). In their recent studies, Turner and Ross

(1969) found that the $Al(OH)_3$ precipitated during neutralization contained variable amounts of Cl^- depending on the Cl^- concentration in solution and the degree of neutralization. Singh (1969) and Singh and Brydon (1969) have identified a crystalline basic aluminum sulfate, basaluminite, with formula $Al_4(OH)_{10}SO_4 \cdot 5H_2O$ and $pK_{sp} = 117.3$, as a metastable phase formed during the neutralization of aluminum sulfate solutions. Ross and Turner (1971) have postulated that the rate of $Al(OH)_3$ crystallization is inversely proportional to the tendency for anions to penetrate the solid phase. In their studies, the tendency for gibbsite to precipitate was greatest in the presence of ClO_4^-, less in the presence of NO_3^-, and least in the presence of Cl^-. Although the exact mechanism for the crystallization of gibbsite is not resolved, these studies do suggest the role that various anions may play in the precipitation process.

The nature of the various polynuclear hydroxyaluminum cations that have been proposed is even more uncertain than the composition of the solid phase. It is evident that potentiometric methods alone are not always adequate to distinguish amongst the various species, since Brosset et al. (1954) showed that either a single species $Al_6(OH)_{15}^{3+}$ or an infinite series of complexes would fit their neutralization data equally well. Matijević, et al. (1961, 1964) studied the coagulation of aqueous sols of silver halides and proposed the species $Al_8(OH)_{20}^{4+}$. However, as Hahn and Stumm (1969) point out, specific sorption on colloid surfaces may alter the distribution of species to the point where they feel it is impossible to draw conclusions regarding the nature of a specific polynuclear species in solution. From ultracentrifugation and acidity measurements, Aveston (1965) found that two species, $Al_2(OH)_2^{4+}$ and $Al_{13}(OH)_{32}^{7+}$, provided the best fit to his experimental data. Light scattering measurements by Ruff and Tyree (1958), however, showed that the average size of the aggregates decreased on dilution or with decreasing basicity. Fripiat et al. (1965) from infrared absorption spectra found evidence for the existence of a series of polymers of the form $Al\left[(OH)_8Al_3\right]_n^{+4}$. Their assignment of frequencies to various forms of OH^- bonded to aluminum seems rather speculative, however. Rausch and Bale (1964) used small-angle X-ray scattering in 1M $Al(NO_3)_3$ solutions to measure the size of clusters from the radius-of-gyration parameter. They reported their measurements were consistent with the presence of $\left[Al_{13}O_4(OH)_{24}(H_2O)_{12}\right]^{+7}$, a species also said to be present in some solid phase basic salts. Turner (1968b) and Turner and Ross (1969) used the 8-hydroxyquinoline method developed by Okura et al. (1962) to measure monomeric aluminum ions in solution and concluded that the OH/Al ratio of the polynuclear ions was near 2.5. This basicity is close to that reported by many pre-

vious workers and probably is a reasonable approximation of the apparent basicity of many polynuclear hydroxyaluminum species. However, it is evident that the exact size and charge of these species is not constant but is a function of experimental conditions. Hence, considerable caution should be exercised in extrapolating from the results of one investigation to describe the aluminum species existing under different conditions in other investigations. Indeed, in view of the transitory nature of these various hydroxyaluminum species, it is questionable whether further efforts to identify particular ions are worthwhile.

Summary

It appears that the simple monomeric hydrolysis mechanism can be used to calculate the pH and aluminum ion activities of dilute solutions at low basicities. When base is added to these dilute solutions, a solid phase consisting of $Al(OH)_3$ with various degrees of anion substitution is formed, and at high basicities significant amounts of metastable polynuclear hydroxyaluminum cations may be present in solution in addition to simpler monomeric species. In more concentrated aluminum salt solutions, which by virtue of their acidity are considerably undersaturated with respect to $Al(OH)_3$, relatively large amounts of base can be added before precipitation occurs. Under these conditions, higher concentrations of a variety of polynuclear hydroxyaluminum species can be present in solution.

ALUMINUM CHEMISTRY IN CLAY SUSPENSIONS

Inasmuch as the chemistry of aluminum in aqueous solutions is not completely understood, it is not surprising that the reactions of aluminum in clay suspensions are the subject of some confusion and controversy. Before pursuing this subject we should consider briefly the preparation of H- and Al-saturated clays since much early work was done with mixed clays and hence misinterpreted. Coleman and Thomas (1967) have reviewed the history of the discovery that H-clays rapidly decompose to form partially Al-saturated clays. Barshad and Foscolos (1970) studied this "interchange" reaction and found that the rate of replacement of H^+ by Al^{3+} or Mg^{2+} in montmorillonite, vermiculite, and illite is directly proportional to surface charge density and MgO content. Riley and Arnold (1969) examined kaolinite, montmorillonite, and seven soils, and showed that the amount of exchangeable Al^{3+} produced was controlled by the amount of exchangeable H^+ present. In acid sulfate soils, decomposition of H-clays and their subsequent conversion to Al-clays would presumably be quite rapid.

Many methods for preparing pure H-clays have been proposed; the most recent utilizes extraction with a chelating agent followed by successive reactions with H-, OH- and H-resins (Barshad 1969). Less attention has been given to the preparation of Al-clays. Most investigators have obtained satisfactory results by treating the clay with a concentrated aluminum salt solution and removing the excess electrolyte by washing with some solvent. There are indications, however, that considerable hydrolysis occurs during prolonged washing. This question will be examined in greater detail in subsequent sections.

Hydrolysis

Considering now the effect of clay on the simple monomeric hydrolysis reaction, Ragland and Coleman (1960) reported that aluminum salt solutions undergo increased hydrolysis in clay suspensions when compared with aqueous solutions of the same pH. Frink and Peech (1963b) have disagreed with this choice of a reference solution, and concluded that hydrolysis is suppressed in clay suspensions when compared with a solution of the same total aluminum concentration. This disagreement may be largely semantic (Coleman and Thomas 1967); however, both studies show that the adsorption of hydrolytic species of aluminum on a clay surface does not alter the numerical value of the hydrolysis constant pK as shown in equation (2). Moreover, these two studies show that addition of base to an Al-clay has the same effect as addition of base to an aqueous aluminum salt solution: some form of $Al(OH)_3$ is precipitated.

Although theoretical considerations suggest that simple electrostatic adsorption of aluminum on a negatively charged surface has no effect on the mechanism of hydrolysis, adsorption by many clays appears to involve specific sorption reactions. Jackson (1963a,b) has proposed several mechanisms to describe the effectiveness of clays in promoting or enhancing the hydrolysis of aluminum. Kaddah and Coleman (1967 a,b) have recently examined the reactions of Al-saturated vermiculites in some detail. They showed that freshly prepared or aged Al-vermiculites contain predominantly trivalent aluminum as anticipated. However, extractions with various salt solutions induce variable amounts of hydrolysis, depending on the nature of the replacing cation and its concentration. At high salt concentrations interplate diffusion is unrestricted and hydrolysis is little enhanced so that primarily trivalent aluminum is exchanged. At low salt concentrations or in the presence of ions causing lattice closure, in-situ hydrolysis of surface adsorbed aluminum is greatly enhanced. According to Kaddah and Coleman

(1967 a,b) the hydrolysis product retained by the clay has a composition corresponding to $AlOH^{2+}$. Although it is not clear why this species should be specifically sorbed, consideration of equation (1) indicates that indeed such sorption would result in enhanced hydrolysis. Recent work by Kissel, et al. (1971) and by Rich (1970) indicates a similar salt-induced hydrolysis may occur in montmorillonite. Hence, prolonged washing of Al-saturated clays to remove excess electrolyte may well alter their properties significantly. Moreover, it is evident that we need to know more about the energy status of various adsorbed hydrolytic aluminum species.

Exchange

Measurements of the exchange of aluminum are complicated by hydrolysis, and, if base is added, by the precipitation of a solid phase. In this section, we will consider only the simple exchange reactions of Al^{3+} and H^+, reserving precipitation reactions for later discussion. Early studies of the exchange of H^+ and Al^{3+} ions were confounded by the difficulties of preparation of homoionic clays. Gilbert and Laudelout (1965) found the affinity for exchange of hydrogen by montmorillonite was as follows:

$$Li^+ < Na^+ < H^+ < K^+ < NH^+ < Rb^+ < Cs^+$$

although they considered the position of H^+ to be approximate owing to the tendency of the clay to decompose. Recently, Foscolos and Barshad (1969) have used new techniques in the preparation of H-montmorillonite and report that the affinity for H^+ exchange is below that for Na^+, although the differences in affinity are not great. Thus, these studies indicate that hydrogen occupies its usual place in the selectivity sequence demonstrated for common strong-acid cation exchangers (Helfferich 1962). However, since clays rapidly decompose when hydrogen-saturated, these findings are perhaps of limited practical importance.

Foscolos (1968) has demonstrated that the position of Al^{3+} in the selectivity sequence of Wyoming bentonite (with CEC = 90 me/100 g) is:

$$H^+ < Na^+ < Mg^{2+} < Ca^{2+} < K^+ < Al^{3+} .$$

For Otay montmorillonite with a higher charge density (CEC = 125 me/100 g) the sequence is:

$$H^+ < Na^+ < Mg^{2+} < Ca^{2+} < Al^{3+} < K^+ .$$

In Jeffersite vermiculite (CEC = 175 me/100 g) the sequence is:

$Mg^{2+} < Ca^{2+} < H^{+} < Al^{3+} < Na^{+}$.

Foscolos (1968) did not include K^{+} in the study of vermiculite to avoid the complications of lattice collapse; however, he states that K^{+} would be preferred over Al^{3+} by vermiculite. On the basis of these results, he concluded that as the surface charge density increases, univalent cations are preferentially adsorbed over ions of higher valence.

In studies of Ca:Al exchange equilibria, Coulter and Talibudeen (1968) found that Al^{3+} was preferred to Ca^{2+} by all soils and clays studied. Moreover, the preference for Al^{3+} relative to Ca^{2+} was in the order:

vermiculite >> illite > montmorillonite.

This increase in the preference for trivalent over divalent cations was attributed to increasing charge density in the series montmorillonite-illite-vermiculite, in agreement with considerations of electrical double layer theory, while findings by Foscolos (1968) seem in contradiction. Subsequently, Coulter (1969) found that for montmorillonite, Al^{3+} was strongly preferred over K^{+}. In vermiculite and illite, not all K^{+} could be easily exchanged by Al, but, even if corrections were made for this "difficultly exchangeable K", these minerals showed preference for K^{+} over Al^{3+}. The relative preference of minerals for K^{+} versus Al^{3+} was in the order:

vermiculite, illite >> montmorillonite.

These findings indicate that the exchange of aluminum with other ions is not yet well understood. Miller and Brown (1969) measured activation energies of mixtures of NaCl and $AlCl_3$ and of clays and resins containing various amounts of Na^{+} and Al^{3+}. They concluded that competition between the two ions for developing separate and incompatible order in the water surrounding them may lead to antagonistic effects between these ions. Similar competition between hydroxyaluminum and Ca^{+2} for exchange sites is suggested by work of Kozak and Huang (1971). These complications could likely affect measurements of exchange constants in clay systems. Corrections for hydrolysis may well be the largest uncertainty, since extraction with salt solutions enhances hydrolysis under some circumstances. Coulter (1969) and Coulter and Talibudeen (1968) assumed the presence of $Al(OH)_2^{+}$ in order to interpret their results. Foscolos (1968) reports that his values for exchange constants were corrected for the fact that adsorbed trivalent aluminum only exists below pH 3.0. The manner in which this correction was made, or its necessity, is not clear. These studies all suggest, however, that Al^{3+} is not as strongly sorbed as its valence would otherwise predict.

Titration Curves

As with aqueous aluminum solutions, considerable useful information has been obtained from titration curves of aluminum- and hydrogen-saturated clays. As Jenny (1961) points out, however, interpretation of the data seems to lag behind its collection. Early studies were of course confounded by the difficulties of preparing homoionic clays. Subsequent studies indicated that H-clays titrated as strong acids, Al-clays as weak acids, and that mixtures showed two buffer ranges corresponding to the neutralization of H^+ ions followed by Al^{3+} ions.

A third buffer range in the potentiometric titration of acid clays was reported by Schwertmann and Jackson (1963, 1964), which they attributed to the formation of basic aluminum compounds. Coleman and Thomas (1967) conclude that this work as well as that of Coleman and Thomas (1964) and Coleman et al. (1964) suggests that hydroxyaluminum compounds existing as coatings or interlayers are responsible for this third buffer range.

Independently, Mitra et al. (1963) reported the presence of a third buffer range in the titration of acid montmorillonite and suggested that this third range may be due to broken bond hydroxyl groups, structural hydroxyl groups, or Lewis acid sites. Sawhney and Frink (1966) examined titration curves of acid montmorillonite and also found three buffer ranges. Since the third buffer range was increased by increasing severity of acid treatment, they suggested that the weak acid titrated in this range was a complex alumino-silicate resulting from the decomposition of lattice edges. Recently, Mitra and Kapoor (1969) have reported four buffer ranges in the titration curves of acid montmorillonites. These are attributed to H^+ ions, Al^{3+} ions, basic aluminum ions, and weak acid groups assumed to be hydroxyl groups associated with aluminum at lattice edges.

A somewhat different approach has been taken by Turner et al. (1963) who assumed that two reactions occur when $Ca(OH)_2$ is added to Al-saturated clays:

$$2\ \text{Al-clay} + 3\ Ca^{2+} = 3\ \text{Ca-clay} + 2\ Al^{3+} \qquad (3)$$

$$Al^{3+} + 3\ OH^- = Al(OH)_3 \qquad (4)$$

combining the Ca:Al ion exchange constant and the solubility product of $Al(OH)_3$, they derived an equation to describe the relationship between the lime potential, pH-$\frac{1}{2}$pCa, and the percent base saturation. One difficulty with this approach is that the ion product of $Al(OH)_3$ does not appear to remain constant throughout the titration; hence allowance must be made for this variability if the prediction is to be precise (Turner and Clark 1965). Other variables, including

time of reaction, accompanying anions, and temperature, are also important (Singh 1967, 1972; Turner and Brydon 1965,1967). None of these workers have observed the variety of inflection points reported by others.

Shainberg and Dawson (1967) examined a variety of titrants for acid montmorillonite, including NaOH and the sodium salts of boric, acetic, formic and nitrous acids. They demonstrated that $Na_2B_4O_7$ is a strong enough base to titrate both exchangeable H^+ and Al^{3+}, while NaOAc will titrate only exchangeable H^+ since the equivalence point with Al^{3+} cannot be detected. Titration with NaOH neutralizes exchangeable H^+ and Al^{3+}, as well as some protons attached to clay hydroxyl groups. Depending on the choice of the end point, a possible titer due to aluminate formation was also reported in the NaOH titration. Interestingly, they attribute about 14 me/100 g to hydroxyl groups in Wyoming bentonite, a value surprisingly close to the figure of 15-16 me/100 g found by Mitra and Kapoor (1969) for the fourth buffer range and attributed by them to Al-OH groups at lattice edges.

Rich (1970) titrated various exchangers with NaOH, $Ba(OH)_2$ and $Na_2B_4O_7$. He found that titration to pH 8.0 gave better estimates of acidity than did inflection points because of adsorption by the exchanger of partially neutralized hydroxyaluminum species. He also observed, in agreement with Shainberg and Dawson (1967), that aluminate could be formed during titration with strong bases, leading to erroneously high results.

Thus, the soil acidity merry-go-round continues. Although it is not possible to reconcile all these conflicting observations, a tentative explanation will be attempted. Two groups of investigators (Schwertmann and Jackson 1963, 1964; Sawhney and Frink 1967) observed that the total potentiometric titratable acidity of acid clays in 1N NaCl decreased markedly on aging. They both observed three inflection points but disagreed on the interpretation of the third buffer range. Conductometric titrations (Mitra et al. 1963; Mitra and Kapoor 1969; Shainberg and Dawson 1967) do not show any decrease in titratable acidity on aging and suggest that the last buffer range in titration curves is due to lattice hydroxyls.

Hence, it is proposed that the third buffer range reported by Schwertmann and Jackson (1963, 1964) and later studied by Frink and Sawhney (1967) is in fact due to lattice hydroxyls as suggested by Mitra et al. (1963), Mitra and Kapoor (1969), and by Shainberg and Dawson (1967). The decrease in titratable acidity observed in potentiometric titrations of aged clays may then be attributed to the effect of salt on the titration of aluminum in the intermediate buffer ranges.

Sufficient evidence exists to indicate that salt may restrict the exchange of aluminum in both vermiculite (Kaddah and Coleman 1967 a,b) and montmorillonite (Rich 1970; Kissel et al. 1971). Restriction of exchange by salt apparently depends on various factors, such as time of equilibration, since it was not observed by Mitra and Kapoor (1969) when salt was added in their relatively slow potentiometric titration of aged acid clays. Neither was this restricted exchange observed in titration of fresh or aged Al-saturated montmorillonite by Frink and Sawhney (1967).

Recent studies by Schwertmann (1969) of the physical and chemical properties of various acid clays suggest that aging of concentrated suspensions at elevated temperatures leads to significant aggregation, accompanied by a decrease in exchangeable H^+ and Al^{3+} and an increase in non-exchangeable polynuclear hydroxyaluminum cations. Banin and Shaked (1969) aged dilute suspensions of H-montmorillonite at high temperatures and found them to remain well dispersed, with tactoids containing only one to two plates. They attribute this behavior to formation of some surface coating which prevents adherence of clay plates, while Schwertmann (1969) proposed that hydroxyaluminum polymers are responsible for the aggregation he observed. Both studies, however, indicated that Al-montmorillonites are well aggregated, with tactoids containing ten or more plates (Banin and Shaked 1969). The disparate effects of suspension concentration on the characteristics of aged clays suggests that the various effects of aging reported in potentiometric studies can be attributed in part to differing methods of sample preparation and hence aggregation.

Solid Phase and Polynuclear Species

As with aqueous aluminum salt solutions, a variety of solid phase aluminum compounds and partially neutralized hydroxyaluminum species have been reported in clay suspensions. The presence of clay offers an additional complication, however, since both polynuclear species and solid phase compounds may be retained by expanding layer silicates, giving rise to hydroxyaluminum interlayers or "chloritized" clays. Moreover, as Turner (1967) has pointed out, the reaction products obtained from neutralization of an Al-saturated clay are frequently different from those obtained if the aluminum salt solution is partially neutralized before it is added to the clay. Investigations of the various solid phases and polynuclear species found in clay suspensions have proceeded along two lines. In one, the aim has been to prepare synthetic hydroxyaluminum interlayered clays with properties similar to those found in soils. The second aim has been to study

the neutralization of Al-saturated clays as an aid in understanding the reactions assumed to occur during the liming of acid soils.

Rich (1968) has prepared an excellent review of the occurrence,formation, and properties of hydroxyl interlayers in layer silicates; consequently the present analysis will be limited to a brief summary and review of recent work. Aluminum interlayers may be formed in both vermiculites and montmorillonites by treating them with partially neutralized Al-salt solutions. The resulting clays have greatly reduced cation exchange capacities, generally attributed to the blocking of exchange sites by sorption of hydroxyaluminum species or by precipitation of continuous solid phases in interlayer positions. The adsorption of considerable amounts of $Al(OH)_x$ by illite and kaolinite (Turner and Brydon 1967) indicates that sorption on external surfaces can also be quite pronounced. Indeed, Tweneboah et al. (1967) suggested that minerals in acid soils may be coated with aluminum "outerlayers". In vermiculites, a structure with a 14Å basal spacing is created, which resists collapse to 10Å on K-saturation or heating. In montmorillonites, a similar structure is developed which resists expansion on Mg-saturation and glycerol solvation, as well as resisting collapse to 10Å on K-saturation or heating. After aging in the laboratory, gibbsite and other forms of $Al(OH)_3$ are frequently found as separate phases, depleting some aluminum from interlayer positions. This process is apparently more rapid in montmorillonite than in vermiculite suspensions (Brydon and Turner 1972).

Many investigators have attempted to determine the OH/Al ratio of interlayer material by relating the observed changes in exchange capacity to aluminum absorbed in or extracted from interlayer positions. According to Rich (1968), the outcome of these analyses indicates that the OH/Al ratio of even one interlayer may be variable since the degree of blocking of exchange sites varies with the amount of interlayer material. Sawhney (1968) found that the apparent OH/Al ratio of interlayer aluminum in vermiculite was close to the OH/Al ratio of the particular aluminum salt solutions used in preparation of the interlayered material, but concluded that the choice of a specific polynuclear species based on charge alone was uncertain. Weismiller et al. (1967) suggested that gibbsite-like rings of structure $\left[Al(OH)_2(H_2O_2)\right]_6^{6+}$ as proposed by Hsu and Bates (1964) would satisfy their observations of infrared adsorption spectra of montmorillonite containing interlayer material with OH/Al = 1.5. Little other direct evidence of the structure of interlayer material is available.

Recent studies by Colombera et al.(1971) show that the adsorption of hydroxyaluminum species by illite can be described by Langmuir adsorption isotherms at

constant OH/Al ratio. This behavior, as well as other aspects of the adsorption reactions, indicated that the process is not one of exchange, but rather involves the formation of hydrogen bonds between the surface of illite and the hydroxy-aluminum species similar to those formed by the sorption of hydroxy cations on silica (Stumm and O'Melia 1968). In contrast to reports by Hsu (1968) that the surface of montmorillonite is non-homogenous in its affinity for hydroxyaluminum species, Colombera et al. (1971) believe the surface of illite to be homogeneous with respect to adsorption of hydroxyaluminum species. Hence, it appears that earlier theories of the constancy of charge or of OH/Al ratio of interlayer material are probably in error. Moreover, the conclusions of Hahn and Stumm (1968) that the nature of solute species cannot be deduced from knowledge of sorbed species should certainly be kept in mind.

Considering briefly the solid phases and polynuclear species formed during neu - tralization of Al-saturated clays, we find less attention is given to the formation of interlayer material and more to the possible forms of $Al(OH)_3$ precipitated as a separate phase. This is certainly due in part to observations that few interlayers are formed during neutralization of dilute Al-clay suspensions (Frink and Peech 1963b; Ragland and Coleman 1960; Turner 1967). Most other studies of the solubility and identification of aluminum hydroxide have been conducted with soils and will be described subsequently.

Summary

Although theoretical considerations suggest that electrostatic adsorption by clays of the hydrolysis products of aluminum should not alter the simple monomeric mechanism, considerable evidence indicates that the presence of an indifferent electrolyte such as NaCl may well alter the reaction. Under conditions where interplate diffusion is restricted, in-situ hydrolysis is enhanced and various hydrolytic species may be specifically sorbed by clays.

When precautions are taken to prepare pure H-clays, H^+ is found to occupy its usual place in the so-called lyotropic series. The exchange of Al^{3+} is less well understood and is apparently influenced by differing charge densities of minerals, the nature of the counter ion and uncertainties in corrections for the hydrolysis of Al^{3+} itself. In general, Al^{3+} does not appear to be as strongly preferred in exchange reactions as its valence would suggest.

Titration curves of H- and Al-saturated clays have been studied for many years, but interpretation of the data has lagged behind its collection. It was formerly assumed that H-clays titrate as strong acids, Al-clays as weak acids, and mixtures

of the two exhibit two buffer ranges corresponding to the neutralization of H^+ ions followed by Al^{3+} ions. Recent reports of three and four buffer ranges have shown that the reactions occurring during titration are considerably more complex. All four buffer ranges are seldom resolved in a particular titration curve, so that interpretations are difficult. It is proposed that aluminum may give rise to two intermediate buffer ranges, while the fourth buffer range, recently reported, may be due to lattice hydroxyl groups.

Both solid phase and polynuclear aluminum species are adsorbed by expanding layer silicates and may produce hydroxyaluminum interlayers or artificially "chloritized" clays. Cation-exchange capacity is reduced and lattice expansion or collapse is considerably restricted. While early investigators attempted to assign specific structures and OH/Al ratios to interlayer material, recent work suggests that its composition is continuously variable from simple monomeric aluminum through various polynuclear species culminating in the precipitation of $Al(OH)_3$.

ALUMINUM CHEMISTRY IN SOILS

Having examined in some detail the reactions of aluminum in aqueous solutions and clay suspensions, we now inquire how these reactions relate to the chemical properties of acid soils in the field. In particular, we will examine factors controlling aluminum solubility in soil solutions, the reactions involved in neutralization of acid soils and the role of aluminum interlayers.

Aluminum in Soil Solutions

Lindsay et al. (1959) measured the solubility of aluminum in $CaCl_2$ extracts of three samples of an acid soil, one amended with sulfur, one with lime, and an untreated check, and found the ion product pH-1/3pAl to remain nearly constant for any one sample as the concentration of $CaCl_2$ varied from 0.001 to 0.1 M. This constancy can be predicted from considerations of double layer theory, provided the concentrations of Al^{3+} and H^+ on the clay surface remain constant, and does not necessarily imply the presence in soil of solid phase $Al(OH)_3$. In the three soils examined, pH-1/3pAl was 2.52 in the soil at pH 4.2, 2.66 in the soil at pH 4.8 and 2.86 in the soil at pH 5.3 Corresponding values of pH-1/3pAl for gibbsite vary from 2.67 (Kittrick 1966) to 2.83 (Frink and Peech 1962) depending on the crystallinity of the product. Hence, these soils at pH 4.8 and pH 5.3 could be at equilibrium with gibbsite. Subsequent studies (Frink and Peech 1962) of the solubility of synthetic gibbsite in soil solutions showed that equilibrium was established very slowly, particularly in undersaturated solutions with values

of pH-1/3pAl less than 2.67-2.83. The highest value of pH-1/3pAl for soils supersaturated with respect to gibbsite was 3.59, which was reduced only to 3.30 after equilibration with gibbsite for one month. Hence, it appears that forms of $Al(OH)_3$ more soluble than gibbsite can persist in soils for considerable periods of time.

Recently, Richburg and Adams (1970) have suggested that the apparent increase in the solubility of $Al(OH)_3$ with increasing soil pH is due to the inappropriate choice of the monomeric hydrolysis reaction, equation (1), for calculating the activity of trivalent aluminum. They report that use of the hydrolysis reaction:

$$6Al^{3+} + 15H_2O = Al_6(OH)_{15}^{3+} + 15H^+ \quad (5)$$

proposed by Brosset et al.(1954), considerably reduced the apparent dependency of the calculated ion product of $Al(OH)_3$ on soil pH. It should be noted, however, that this cannot be the sole criteria for testing the appropriateness of a proposed hydrolysis constant. Using their approach, for example, one could assign arbitrary values to the monomeric hydrolysis constant until the dependence of the ion product for $Al(OH)_3$ on pH is minimized. However, such a revised constant would then not predict the observed changes in pH on dilution of aluminum salt solutions. Since the proposed mechanism, equation (5), does not meet this criteria either (Frink and Peech 1963a), it is doubtful if it should be assumed to describe Al^{3+} activity in soil extracts. Although Richburg and Adams (1970) imply that $Al_6(OH)_{15}^{3+}$ is the sole hydrolysis product, they report that the calculated activity of Al^{3+} was not altered significantly if both the monomeric and polymeric hydrolysis reactions were assumed to proceed simultaneously. This seems consistent with the findings of Turner and colleagues (Turner et al.1968a, 1968b; Turner and Ross 1969)in their studies of titration curves of aluminum salt solutions, namely that polynuclear species may be present in addition to monomeric species, particularly at high degrees of neutralization. Thus, it appears possible that soil solutions supersaturated with respect to gibbsite, as were all soils examined by Richburg and Adams (1970), could be considered to contain polynuclear as well as monomeric aluminum ions. It also seems likely that the particular species will vary from one soil to another depending on past history as has been shown with aqueous aluminum salt solutions.

A number of partially neutralized or basic aluminum salts have been reported to precipitate from aqueous solutions and clay suspensions. Singh and Brydon (1967, 1969, 1970) have identified a crystalline basic aluminum sulfate, basaluminite, with formula $Al_4(OH)_{10}SO_4 \cdot 5H_2O$ and $pK_{sp} = 117.3$. Well-crystallized aluminum

sulfates have been found in acid sulfate soils (van Beers 1962) and may perhaps be basaluminite. Richburg and Adams (1970) examined the solubility product of basaluminite in a number of soils and found it to decrease from pK = 117 in soil at pH 4.4 to pK = 112 in soil at pH 5.6. They attributed this inconstancy to use of the monomeric hydrolysis mechanism; using the polymeric mechanism, the calculated pK was reasonably constant at approximately pK = 123. Since this compound is apparently much less soluble than that studied by Singh and Brydon, the question of the appropriate hydrolysis mechanism is again raised.

Soils may contain other solid phase aluminum compounds, but their role in controlling the solubility of aluminum in soil solution is not clear. Discrete amorphous aluminum compounds similar to boehmite have been reported in some soils (de Villiers 1969). Copious precipitates of white aluminum hydroxide have been found in acid sulfate soils (van Beers 1962). Allophane, an amorphous gel containing silica and alumina in mole ratios between 0.5 and 1.3, is formed in many soils derived from volcanic ash (Coleman and Thomas 1967). Amorphous material was reported by Yuan (1969) to constitute as much as 65% of the clay fraction in a variety of soils, yet little is known of its solubility.

Although aluminum forms many soluble complexes with the hydroxyl ion, it forms few other stable complexes with ions likely present in soil solutions. However, fluoride complexes of aluminum are quite stable (Sillén and Martell 1964, 1971) and must be considered if fluoride is present in soil extracts. Hem (1968) has shown, for example, that fluoride complexes with aluminum will predominate in many natural waters below pH 6.6 in the presence of as little as 10^{-5} M fluoride. Complexes with sulfate may also be important (Turner and Brydon 1965; Richburg and Adams 1970) and should be given more consideration in analyses of soil extracts. Calculations of Hem (1968) indicate that such complexes would be particularly important in acid sulfate soils. Although knowledge of the formation of complexes of aluminum with phosphate is fragmentary (Sillén and Martell 1964, 1971), recent evidence suggests they could easily be important in strongly acid soils (Bohn and Peech 1969).

Aluminum may also form complexes or chelates with soil organic matter. Schnitzer (1969) reports some provisional studies indicating that fulvic acid complexes of aluminum are more stable than complexes of divalent cations. Aluminum was reported to occur as $AlOH^{2+}$ in complexes with metal to fulvic acid ratios of 1:1,but as $Al(OH)_2^+$ in 3:1 and 6:1 complexes. As more aluminum was added, the complex precipitated, suggesting an explanation of the movement of aluminum in podzols

to the B horizon (Schnitzer 1969). Huang and Keller (1972) found the solubility of aluminum-bearing minerals to be enhanced by a number of organic acids. They also believe aluminum may be transported during weathering in organic complexes but subsequently precipitated by anions such as OH^-, PO_4^{3-} or SiO_4^{4-}. Complexes between aluminum and humic acid have also been reported (Khan 1969). According to Greenland (1971), aluminum will react with fulvic acid at pH 4.0 or below and be adsorbed in the interlayers of montmorillonite. These bonds, called "cation bridges" are rather weak and are readily broken by salt leaching. Aluminum sorbed by organic matter is believed to play an important role in soil structure and in the pH-dependent cation-exchange capacity of soils as described subsequently.

Neutralization of Acid Soils

The rationale for much of what has been discussed so far is the hope that it will aid in understanding the reactions of soil when amended with lime. Although controversy still exists over the nature of the beneficial effects of liming, we will proceed to examine the reactions of aluminum in limed soils.

One approach to the problem of predicting pH and solubility of aluminum as a result of adding lime has been taken by Turner et al.(1963) and was described briefly in a previous section. Clark and Nichol (1966) have shown that the value of the corrected lime potential follows that derived from the titration of Al-bentonite with $Ca(OH)_2$ for diverse acid and neutral mineral and organic soils. However Bache (1970) feels that correcting the solubility product of $Al(OH)_3$ does not correct a more basic problem, namely that equilibrium is not established in such titrations. He found that both pH-$\frac{1}{2}$pCa and pH-1/3pAl varied with time and solid-to-solution ratio and concluded that exchange isotherms must be measured to allow extrapolation to a point where no exchange of Al^{3+} or Ca^{2+} occurs.

A different approach to the neutralization reactions of acid soils assumes that at least three reactions occur when lime is added, and that these reactions correspond roughly to the various inflection points observed in the titration of acid clays. First, exchangeable hydrogen, if present, is neutralized; most soils contain little or no exchangeable hydrogen, however, unless free acid is present as is likely in acid sulfate soils (Dewan and Rich 1970). Next, exchangeable and non-exchangeable aluminum is neutralized over a pronounced buffer range. Although it is often assumed that this buffer range is centered at pH = 5.0, equivalent to the value pK = 5.0 for the first-stage hydrolysis constant of aluminum, the buffer range undoubtedly varies since even in aluminum salt solutions the pH of

maximum buffer capacity is a function of total aluminum concentration (Frink and Sawhney 1967). The final stage of neutralization involves edge sites of minerals and weak acid groups of soil organic matter. The neutralization of soils in these latter buffer ranges, above about pH 5.5-6.0, creates additional cation-exchange capacity, commonly referred to as pH-dependent CEC. Since this pH-dependent CEC can be detected in titration curves, but is not exchangeable with neutral salts, it is also included in measurements of titratable acidity (Coleman and Thomas 1967).

The presence of pH-dependent CEC in soils has at least two important consequences: it causes large differences in apparent lime requirements depending on the method of measurement, and also affects the availability of other cations.Methods of measurement of lime requirement have been ably reviewed by Coleman and Thomas (1967). Controversy still exists, however, as to whether soils should be limed to neutralize exchangeable Al^{3+} (Kamprath 1970; Reeve and Sumner 1970) or to raise the pH to nearer neutrality[+)]. The subject of the effect of liming on the availability of other cations, particularly potassium, is also one of some controversy. Recent evidence (Thomas and Coleman 1959; Bartlett and McIntosh 1969) suggests, however, that liming decreases potassium availability by increasing the CEC, thereby lowering the degree of potassium saturation of the exchange sites and, hence, its availability. Coleman and Thomas (1967) suggest that liming can also reduce CEC in the intermediate pH range of approximately 5.5 by precipitating aluminum and blocking exchange sites. This phenomenon has not been widely observed, however, in field studies.

Because of the importance of pH-dependent CEC in soils, considerable effort has been devoted to its description and measurement. Since clays containing synthetic aluminum interlayers exhibit pH-dependent CEC (de Villiers and Jackson 1967b) the pH-dependent CEC of soils is often attributed in large part to aluminum interlayers or sesquioxide coatings on clay surfaces (de Villiers and Jackson 1967a; Rich 1968). Soil organic matter also contributes to pH-dependent CEC (Coleman and Thomas 1967) and its contribution frequently may be large. In addition, an association of hydroxyaluminum with organic matter is often implied, which compounds the problem of separating the various components of pH-dependent CEC.

+) Lime Requirement of Soils-Inactivate Toxic Substances or Favorable pH Range? E.O.McLean, E.J.Kamprath. Ltrs. to the Editor. Soil Sci.Soc.Amer.Proc. 34: 363-364.

McLean and his colleagues have studied pH-dependent CEC in some detail; McLean and Owen (1969) found from multiple regression analysis that in a wide variety of soils, organic matter contributed about 20% of the CEC at pH 2.5, but more than 45% at pH 8.0. They also reported that organic exchange sites unable to sorb K^+ from KCl were inactivated by non-exchangeable aluminum. Liming appeared to reactivate these sites, presumably by deprotonation of hydroxyaluminum, in agreement with earlier results by Bhumbla and McLean (1965). Fiskell (1970) measured pH-dependent CEC in surface and subsurface horizons of varying organic matter and clay content and concluded that apparent pH-dependent CEC was mainly due to hydroxyyaluminum in interlayers and to that associated with organic matter.

Sawhney et al. (1970) proposed that contributions to pH-dependent CEC from organic matter and aluminum interlayers could be distinguished by measuring the reversibility of changes in CEC with pH. The increase in CEC from release of protons of weakly-dissociated organic matter should be eliminated by simply decreasing the pH again. Since raising the pH presumably would irreversibly precipitate aluminum interlayers or sesquioxide coatings, the increase in pH-dependent CEC from this source would be permanent. Most of the pH-dependent CEC in a number of spodosols from the Northeast was reversible and hence was attributed to weakly acidic organic matter groups. Unfortunately, aluminum bound to organic sites might also react in similar fashion, so the contribution of aluminum-organic matter complexes to pH-dependent CEC is not resolved by this technique. Sawhney, et al. (1970) did find, however, in agreement with other earlier studies, that the pH-dependent CEC was reasonably well correlated with amounts of aluminum extracted with NaOAc at pH 4.8. Subsequently, Sawhney and Norrish (1971) showed that kaolinite, halloysite, imogolite and allophane can contribute significantly to reversible pH-dependent CEC when present in soils. Irreversible components of pH-dependent CEC were shown to be very small in soils of tropical regions.

Pionke and Corey (1967) have defined "non-exchangeable acidic aluminum" as the difference between Al extracted by pH 4.8 N NH_4OAc and that extracted by 1N KCl. This "non-exchangeable acidic aluminum" reached a maximum in soils at about pH 5.0 and decreased in more acid or alkaline soils. Since this non-exchangeable acidic aluminum was correlated better with soil organic matter than with pH or clay content, they proposed it was complexed by soil organic matter according to the scheme:

$$
\begin{array}{ccccc}
 & & Al(OH)_3 & & \\
 & & \downarrow\uparrow & & \\
 & & Al_y(OH)^{z+}_{3y-z} & & \\
 & & \downarrow\uparrow & & \\
 & & Al(OH)^{2+} & & \\
 & & \downarrow\uparrow & & \\
Al\text{-}OM & \rightleftharpoons & Al^{3+} & \rightleftharpoons & Al\text{-}X
\end{array}
$$

where OM represents organic matter and X the clay component. Although the proposed reaction seems reasonable, the coincidence of the observed maximum in solubility with the pH of the extracting solution makes it possible that this is an artifact, i.e., the solubility of aluminum in soils more acid than the extractant might be reduced while the solubility in less acid soils would be increased.

Subsequently, Pionke et al.(1968) compared the ability of various soil properties to predict lime requirement, and ranked them in the order: pH-dependent sites on organic matter > non-exchangeable acidic aluminum > exchangeable Al^{3+} $\geq$ pH-dependent sites on clays. The regression relationship obtained accounted for nearly 90% of the observed variability in lime requirement as measured by neutralization with $CaCO_3$ to pH 6.0 in 1N KCl.

In oxisols, Reeve and Sumner (1971) have found little relationship between pH and exchangeable Al^{3+}[3], a finding contrary to much earlier work. They propose that the scheme presented by Pionke and Corey (1967) be modified as follows:

$$
\begin{array}{ccc}
 & Al_y(OH)^{z+}_{3y-z} & \\
 & \downarrow\uparrow & \\
\text{Exch } Al^{+3} \rightleftharpoons & [(CEC - AEC) - \text{Exch bases}] & \\
 & \downarrow\uparrow & \\
 & OM - Al &
\end{array}
$$

where net CEC (the CEC less anion exchange capacity, AEC) and exchangeable bases control exchangeable Al^{3+} in equilibrium with hydroxyaluminum species and complexes with organic matter.

Thus, these various schemes suggest that exchangeable Al^{3+} exists in relatively small amounts in soils but is in equilibrium with a relatively large pool of non-exchangeable aluminum. Early studies attributed much of this non-exchangeable aluminum to aluminum interlayers and oxide coatings. Present evidence, however, indicates that organic matter complexes are also important. Coleman and Thomas

(1967) suggested that "neutralization of organic matter in acid soils may be no more a titration of a weak acid than is neutralization of clay", and subsequent studies indicate they may well be correct.

Aluminum Interlayers

Aluminum interlayers are found in expanding layer silicates in a wide variety of soils and sediments, yet the optimum conditions favoring their formation, even under laboratory conditions, are not known completely. Moreover, aluminum interlayers found in soils are in general more resistant to heat treatment and chemical extractants than synthetic laboratory samples. Rich (1968) is of the opinion that formation of aluminum interlayers in soils is favored by: active weathering to provide aluminum, moderate pH (4.6-5.8), low organic matter content and frequent wetting and drying. In tidal sediments in California, Lynn and Whittig (1966) found that under reducing conditions chlorite containing ferrous iron apparently was formed. Other studies (Rich 1968) indicate that magnesium may be an important component of interlayers in marine sediments.

According to Jackson (1963a) in acid soils aluminum interlayers form via the weathering sequence:

$$\text{mica} \rightleftharpoons \text{vermiculite} \rightleftharpoons \text{14A intergrade.}$$

The interlayer material may then degrade through the sequence:

$$\text{14A intergrade} \rightleftharpoons \text{Al-chlorite} \rightleftharpoons \text{kaolinite.}$$

Considerable evidence exists that these reaction sequences are indeed reasonable (Rich 1968). Less is known, however, of the reversibility of weathering sequences. Lynn and Whittig (1966) found undrained sediments contained montmorillonite, chlorite, mica and kaolinite. Sediments drained for six years developed typical cat-clay characteristics, yet the clay minerals were unaltered. After 60 years of drainage, however, all crystalline minerals showed deterioration and diffuse X-ray diffraction patterns. Chlorite had decreased the most and apparently had been converted to montmorillonite (or a high charge mica), hence reversing the weathering process. Frink (1969) reported that chloritized vermiculite transported from a watershed of acid soils into a neutral lake environment was apparently stripped of aluminum interlayers and partially converted to illite. Efforts to demonstrate dechloritization by comparison of paired wooded and cultivated soils were not successful.[+)]

+) Frink C.R. 1968. Aluminum interlayers in wooded and cultivated soils. Agron. Abstr. p.151.

As with clays containing synthetic aluminum interlayers, the cation-exchange capacity of soils is reduced by aluminum interlayers. Although these interlayers are often thought to be to be the source of pH-dependent CEC, we have seen that organic matter in soils also plays an important role. Changes in exchange capacity on extraction with reagents which remove aluminum have been used to measure the extent of interlayer formation (Frink 1965); however, it is likely that some of the increase found is merely a manifestation of pH-dependent CEC.

Aluminum interlayers also affect the fixation of K^+, NH_4^+, Cs^+, and Rb^+ by layer silicates. The interlayer material tends to prop open layer silicates and reduce K^+ fixation by preventing layer collapse in vermiculite and soil clays containing vermiculite (Rich 1968). Selectivity of minerals for K-size ions is also altered since they may enter partially opened mica layers without causing collapse (Rich 1968). Although most mechanisms proposed to explain the selectivity for K^+ in minerals (Sawhney 1972) suggest that aluminum interlayers should decrease selectivity for K^+, Kozak and Huang (1971) report enhanced selectivity in interlayered vermiculite and K-depleted biotite. They propose that, in addition to the "propping effect" on K^+ fixation, aluminum interlayers increase the apparent K/Ca selectivity by interfering with calcium exchange.

Summary

The solubility of aluminum in some acid soils appears to be controlled by the solubility of gibbsite. However, soils at higher pH appear to be supersaturated with respect to gibbsite. Such soils may contain more soluble forms of $Al(OH)_3$ or, perhaps, soluble polynuclear species. Soluble complexes of aluminum with phosphate, sulfate, fluoride, and organic matter may also be present in soils. Other solid phase aluminum compounds are found in soils, but their role in controlling aluminum solubility is uncertain.

The neutralization of acid soils is believed to involve at least three reactions: first, neutralization of exchangeable hydrogen, present only in very acid soils; second, neutralization of exchangeable and non-exchangeable aluminum; and third, neutralization of a rather vague collection of acids including edge sites of minerals and organic matter. This latter range corresponds roughly to pH-dependent CEC which in turn influences lime requirement and the availability of other cations. Studies of pH-dependent CEC in soils suggest that relatively small amounts of exchangeable aluminum occur in equilibrium with a relatively large pool of non-exchangeable acidic aluminum. Earlier studies associated this latter category with interlayer aluminum; present evidence indicates that complexes with organic matter should also be considered.

Aluminum interlayers reduce soil CEC and reduce the ability of vermiculites to fix K^+ and other ions of similar size and charge. Optimum conditions for their formation are moderate pH, low organic matter content, and frequent wetting and drying. Once formed, they may weather ultimately to kaolinite or, if environmental conditions change, as in draining of acid sulfate soils, they may revert to precursors in the weathering sequence.

ALUMINUM AND SOIL PHYSICAL PROPERTIES

In view of the extensive studies of the chemistry of aluminum in soils, it is somewhat surprising that little is known of the effect of aluminum on the physical properties of soils. We will begin by examining some of the effects of aluminum on physical properties of clays and then examine physical properties of acid soils in the field.

Observations of Al-saturated montmorillonite by Banin and Shaked (1969) and Schwertmann (1969) indicate that such clays are well aggregated, with tactoids containing ten or more plates. Davey and Low (1971) observed that a mixed Na-Al montmorillonite became viscous and gelation commenced in 2% suspensions, while the same behavior was not noted in pure Na-saturated clays until the suspension concentration reached 4%. The tensile strength of montmorillonite was found to increase as the valence of the saturating cation increased; however, Dowdy and Larson (1971) felt some of the tensile strength of Al-montmorillonite was due to the formation of hydrous oxides. Kidder and Reed (1972) found that macroscopic swelling of montmorillonite was greatly reduced by introduction of synthetic aluminum interlayers. Similarly, Tamura (1957) had reported that removal of aluminum interlayers from a soil montmorillonite permitted it to swell on glycerol solvation. Quigley (1969) pointed out that adsorbed aluminum causes problems in soil mechanics research, since the usual chemical pretreatments to prepare "clean" clays may remove adsorbed aluminum, making engineering test data unreliable in the field. Quigley (1969) felt that adsorbed aluminum particularly affected the measurements of Attenberg plastics limits. Thus, all of these reports suggest that aluminum may act to hold clay particles together and presumably should have some effect on soil structure.

Iron oxides have long been thought to be the primary agent cementing clay particles together providing the various kinds of structure observed in field soils. However, recent evidence suggests that aluminum may be more important than iron in many soils. Flach et al. (1969) suggest too much importance may have been

ascribed to iron, due to its obvious coloration and ease of extraction, and that aluminum cementing agents should be examined more thoroughly. Deshpande et al. (1968) have reviewed earlier work and have also conducted extensive studies of the relationship between changes in the physical structure of red soils and amounts of iron, aluminum, silica and organic matter removed by various extractants. They concluded that most of the free iron oxides in such soils exist as discrete particles with little effect on soil physical properties, and that aluminum, along with minor amounts of iron and silica, plays the major role in cementation of soil particles into structural units. Saini et al.(1966) examined aggregate stability in the B-horizon of spodosols and found a better correlation of stability with aluminum oxides than with iron oxides. Reeder et al. (1967) presented evidence suggesting that aluminum is involved in creating structural stability in solonetzic soils when the pH is lowered.

Other studies have not shown aluminum to be involved in formation of some soil structures. Grossman and Carlisle (1969), for example, have reviewed available information on fragipan formation and concluded that aluminum is not the principle cementing agent in these pans. Aluminum interlayers might be expected to reduce measured clay contents of soils unless drastic dispersants are used prior to mechanical analysis. However, studies in this laboratory of the clay contents of interlayered soils described by Frink (1965) have failed to show any difference between clay content determined before or after extraction with sodium citrate. Similarly, Dixon et al.(1968) compared particle sizes determined after the conventional sodium metaphosphate dispersion and those found following a more drastic treatment with citrate-dithionite-bicarbonate. Even though some of the soils studied contained very stable aluminum interlayers, particle sizes by the two methods were nearly identical. Hence, aluminum is apparently not a universal cementing agent in all soils. These studies do emphasize, however, that continued attention should be given to the role of aluminum in soil aggregation as suggested some time ago by Jackson (1963a, 1963 b).

While it is quite likely that organic matter plays a most important role in the structure of clay soils (Boekel 1963), aluminum-organic combinations may also play some part. According to Edwards and Bremner (1967), microaggregate formation in soils involves the binding of organic matter by clay through linkage with polyvalent metals on exchange sites. Parfitt and Greenland (1970) found that soil polysaccharides were little adsorbed by Na- or Ca-montmorillonite but strongly adsorbed by Al-montmorillonite. However, Martin and Richards (1969) showed that iron and aluminum salts greatly reduced the influence of various polysaccharides

on soil aggregation and hydraulic conductivity. This may be due in part to increased bonding among individual polysaccharide molecules, since the effect was much less if the soil was treated first with the polysaccharide and then with the metal. Despite considerable accumulated information on the nature of soil polysaccharides (Swincer et al. 1969) and on the nature of clay-organic complexes (Mortland 1970), the role of aluminum in binding organic matter to soil is largely unknown.

Since acid soils are generally amended with lime to improve fertility, we should consider the effect of liming on soil structure. Emerson and Dettmann (1960), from a review of earlier work and studies of their own, concluded that liming decreases attractive forces between clay particles, presumably by neutralizing trivalent aluminum, and hence tends to reduce the stability of soil crumbs. However, liming and especially the presence of free $CaCO_3$ provides enough soluble Ca^{2+} to maintain flocculation and help keep drainage waters clear. In acid sulfate soils, flocculation of silt in drainage water by soluble aluminum has a similar effect; however, the tremendous accumulation of silt rapidly fills the canals, making frequent dredging necessary (Moormann 1963). Large amounts of $Ca(OH)_2$ (several percent by weight) are sometimes added to soil to reduce swelling and shrinking and improve its mechanical properties for roads and other structures. Most earlier studies of lime soil stabilization assumed that the reaction involved dissolution of existing clay minerals and the formation of new calcium silicate and calcium aluminum hydrates (Grim 1962). Recent work by Pettry and Rich (1971) shows that clay minerals are not completely dissolved, since an acid extraction restored the original X-ray diffraction patterns. Apparently, $CaCO_3$ is a major reaction product, along with some soil-$Ca(OH)_2$ reaction products found lining the interior walls of soil voids and as intergranular bridges. These reactions would not be expected, however, as a result of normal liming of agricultural soils.

Summary

Aluminum reacts with clays and causes increased aggregation, viscosity, and tensile strength and reduces macroscopic swelling. Although iron has long been thought to be the principal cementing agent in soils, present evidence indicates that aluminum is of major importance in creating structural stability in red soils and spodosols. The nature of the cementing agent in fragipans is not known, but it does not appear to be aluminum. Although aluminum interlayers are common in many acid soils, they are not stable enough to prevent dispersion of soils for mechanical analyses. While clay-organic matter complexes may be responsible

for structural stability in many soils, the role of aluminum in binding organic matter to clay is not yet clear. Liming of acid soils has been shown to reduce structural stability of soil crumbs, perhaps by neutralizing exchangeable aluminum.

SUMMARY AND CONCLUSIONS

The simple monomeric hydrolysis mechanism provides a satisfactory description of the pH and aluminum ion activity of dilute aqueous aluminum salt solutions at low basicities. When base is added, a solid phase of $Al(OH)_3$ is formed with varying degrees of anion substitution. At high basicities, significant amounts of various metastable polynuclear hydroxyaluminum cations may be present in solution. Present evidence indicates that the monomeric hydrolysis mechanism is still operative in such solutions, since there is no unequivocal proof of the superiority of any particular polymeric mechanism.

Theoretical considerations and experimental data show that the monomeric hydrolysis mechanism is not altered by simple electrostatic adsorption of hydrolysis products on clay surfaces. However, where diffusion is restricted by lattice collapse, in-situ hydrolysis is enhanced and various hydrolytic products may be specifically sorbed by clays. Studies of the exchange of aluminum are complicated by corrections for hydrolysis, but Al^{3+} does not seem to be as strongly preferred in exchange reactions as its valence might otherwise suggest. This behavior must also be attributed to specific sorption effects which are poorly understood.

The neutralization of acid clays involves several reactions: first, neutralization of exchangeable hydrogen; second, neutralization of aluminum, which may include both exchangeable and non-exchangeable forms; and third, neutralization of lattice hydroxyl groups. Titration curves may reveal three or four buffer ranges depending on how well these various reactions are resolved.

Both solid phase and soluble aluminum species may be adsorbed by expanding layer silicates, producing hydroxyaluminum interlayers. As a result, cation-exchange capacity is reduced and lattice expansion and collapse is considerably restricted. Interlayers also reduce the ability of vermiculite to fix K^+ and other ions of similar size and charge. While early investigators attempted to assign specific structures and OH/Al ratios to interlayer material, recent work suggests that the composition is continuously variable from simple monomeric aluminum through various polynuclear species culminating in the precipitation of $Al(OH)_3$. In soils, optimum conditions for the formation of aluminum interlayers

are moderate pH, low organic matter content, and frequent wetting and drying.

The solubility of aluminum in some acid soils appears to be controlled by the solubility of gibbsite. However, soils at higher pH appear to be supersaturated with respect to gibbsite. Such soils may contain more soluble forms of $Al(OH)_3$, or polynuclear species of aluminum may be present. Soluble complexes of aluminum with phosphate, sulfate, fluoride, and organic matter may also be present in soils under some circumstances.

The neutralization reactions of acid soils are similar to those of acid clays but also include reactions of soil organic matter. The third or final neutralization range in soils corresponds roughly to pH-dependent CEC which in turn influences lime requirement and the availability of other cations. Studies of the pH-dependent CEC of soils suggest that relatively small amounts of exchangeable aluminum occur in equilibrium with a relatively large pool of non-exchangeable acidic aluminum. Earlier studies associated this latter category largely with interlayer aluminum, but recent work indicates that complexes with organic matter must also be considered.

Aluminum reacts with clays, causing increased aggregation, viscosity, and tensile strength but reduces macroscopic swelling. Although iron has long been thought to be the principal cementing agent in soils, it now appears that aluminum is of major importance in creating structural stability in red soils and spodosols. The nature of the cementing agent in fragipans is not known, but it does not appear to be aluminum. Although aluminum interlayers are common in many acid soils, they are not stable enough to prevent dispersion of soils during mechanical analyses. While clay-organic matter complexes are responsible for structural stability in many soils, the role of aluminum in binding organic matter to clay is not yet clear. Liming of acid soils reduces the structural stability of soil crumbs, perhaps by neutralizing exchangeable aluminum.

Despite occasional pessimism that studies of aluminum chemistry in aqueous solutions can lead to an understanding of the reactions of acid soils in the field, the record indicates that considerable progress has been made. Promising areas for further research include studies of the hydration status of aluminum ions adsorbed on clay surfaces, investigations of the nature of soluble aluminum species in supersaturated solutions with the aim of simplifying the present bewildering array of proposed polynuclear species, and an examination of the complexes of aluminum with inorganic and organic ligands present in soils.

REFERENCES

AVESTON, J. 1965. Hydrolysis of the aluminium ion: Ultra-centrifugation and acidity measurements. J. Chem. Soc. 4438-4443.

BACHE, B.W. 1970. Determination of pH, lime potential, and aluminium hydroxide potential of acid soils. J. Soil Sci. 21: 28-37.

BANIN, A. and SHAKED, D. 1969. Particle size and surface properties of acidic montmorillonite. Int. Clay Conf., Proc. Vol.1 (Tokyo, Japan), 669-682. Israel Universities Press, Jerusalem.

BARSHAD, I. 1969. Preparation of H saturated montmorillonites. Soil Sci. 108: 38-42.

BARSHAD, I. and FOSCOLOS, A.E. 1970. Factors affecting the rate of the interchange reaction of adsorbed H^+ on the 2:1 clay minerals. Soil Sci.110:52-60.

BARTLETT, R.I. and McINTOSH, J.L. 1969. pH-dependent bonding of potassium by a spodosol. Soil Sci. Soc. Amer. Proc. 33: 535-539.

BEERS, W.F.J.van. 1962. Acid sulphate soils. Int. Institute for Land Reclamation and Improvement. Bull. 3. 31 p. Wageningen, The Netherlands.

BHUMBLA, D.R. and McLEAN, E.O. 1965. Aluminum in soils: VI. Changes in pH-dependent acidity, cation-exchange capacity, and extractable aluminum with additions of lime to acid surface soils. Soil Sci. Soc. Amer. Proc. 29: 370-374.

BOEKEL, P. 1963. The effect of organic matter on the structure of clay soils. Neth. J. Agr. Sci. 11: 250-263.

BOHN, H.L. and PEECH, M. 1969. Phosphatoiron (III) and phosphatoaluminum complexes in dilute solutions. Soil Sci. Soc. Amer. Proc. 33: 873-876.

BROSSET, C., BIEDERMANN, G. and SILLEN, L.G. 1954. Studies on the hydrolysis of metal ions. XI. The aluminum ion, Al^{+3}. Acta Chem. Scan.8: 1917-1926.

BRYDON, J.E. and TURNER, R.C. 1972. The nature of Kenya vermiculite and its aluminum hydroxide complexes. Clays and Clay Minerals 20: 1-11.

CLARK, J.S. and NICHOL, W.E. 1966. The lime potential-percent base saturation relations of acid surface horizons of mineral and organic soils. Can. J. Soil Sci. 46: 281-285.

COLEMAN, N.T. and THOMAS, G.W. 1964. Buffer curves of acid clays as affected by the presence of ferric iron and aluminum. Soil Sci. Soc. Amer. Proc. 28: 187-190.

COLEMAN, N.T. and THOMAS, G.W. 1967. The basic chemistry of soil acidity. In R.W. Pearson and F. Adams (eds.): Soil acidity and liming. Agronomy 12: 1-41. Amer. Soc. of Agr.,Madison, Wisconsin.

COLEMAN, N.T., THOMAS, G.W., LEROUX, F.H. and BREDELL, G. 1964. Salt-exchangeable and titratable acidity in bentonite-sesquioxide mixtures. Soil Sci. Soc. Amer. Proc. 28: 35-37.

COLUMBERA, P.M., POSNER, A.M. and QUIRK, J.P. 1971. The adsorption of aluminium from hydroxy-aluminium solutions on to Fithian illite. J.Soil Sci.22:118-128.

COULTER, B.S. 1969. The equilibria of K:Al exchange in clay minerals and acid soils. J. Soil Sci. 20: 72-83.

COULTER, B.S. and TALIBUDEEN, O. 1968. Calcium:aluminium exchange equilibria in clay minerals and acid soils. J.Soil Sci. 19: 237-250.

DAVEY, B.G. and LOW, P.F. 1971. Physico-chemical properties of sols and gels of Na-montmorillonite with and without adsorbed hydrous aluminum oxide. Soil. Sci. Soc. Amer. Proc. 35: 230-236.

DESHPANDE, T.L., GREENLAND, D.J. and QUIRK, J.P. 1968. Changes in soil properties associated with the removal of iron and aluminium oxides. J.Soil. Sci. 19: 108-122.

DE VILLIERS, J.M. 1969. Pedosesquioxides-composition and colloidal interactions in soil genesis during the Quaternary. Soil Sci. 107:454-461.

DE VILLIERS, J.M. and JACKSON, M.L. 1967a. Cation exchange capacity variations with pH in soil clays. Soil Sci. Soc. Amer. Proc. 31: 473-476.

DE VILLIERS, J.M. and JACKSON, M.L. 1967b. Aluminous chlorite origin of pH-dependent cation exchange capacity variations. Soil Sci. Soc. Amer. Proc.31: 614-618.

DEWAN, H.C. and RICH, C.I. 1970. Titration of acid soils. Soil Sci. Soc. Amer. Proc. 34: 38-44.

DIXON, J.B., McCRACKEN, R.J., PEELE, T.C. and RICH, C.I. 1968. Particle size analysis of soils compared by sodium metaphosphate and sodium carbonate dispersion methods. Soil Sci. Soc. Amer. Proc. 32: 734-735.

DOWDY, R.H. and LARSON, W.E. 1971. Tensile strength of montmorillonite as a function of saturating cation and water content. Soil Sci. Soc. Amer. Proc. 35: 1010-1014.

EDWARDS, A.P. and BREMNER, J.M. 1967. Microaggregates in soils. J. Soil Sci. 18: 64-73.

EMERSON, W.W. and DETTMANN, M.G. 1960. The effect of pH on the wet strength of soil crumbs. J.Soil Sci. 11: 149-158.

FISKELL, J.G.A. 1970. Cation exchange capacity and component variations of soils of southeastern USA. Soil Sci.Soc.Amer.Proc.34: 723-727.

FLACH, K.W., NETTLETON, W.D., GILE, L.H., and CADY, J.G. 1969. Pedocementation: Induration by silica, carbonates and sesquioxides in the Quaternary. Soil Sci. 107: 442-453.

FOSCOLOS, A.E. 1968. Cation-exchange equilibrium constants of aluminum-saturated montmorillonite and vermiculite clays. Soil Sci. Soc. Amer. Proc.32:350-354.

FOSCOLOS, A.E. and BARSHAD, I. 1969. Equilibrium constants between both freshly prepared and aged H-montmorillonites and chloride salt solutions. Soil Sci. Soc. Amer. Proc. 33: 242-247.

FRINK, C.R. 1965. Characterization of aluminum interlayers in soil clays. Soil Sci. Soc. Amer. Proc. 29: 379-382.

FRINK, C.R. 1969. Chemical and mineralogical characteristics of eutrophic lake sediments. Soil Sci. Soc. Amer. Proc. 33: 369-372.

FRINK, C.R. and PEECH, M. 1962. The solubility of gibbsite in aqueous solutions and soil extracts. Soil Sci. Soc. Amer. Proc. 28: 346-347.

FRINK, C.R. and PEECH, M. 1963a. Hydrolysis of the aluminum ion in dilute aqueous solutions. Inorg. Chem. 2: 473-478.

FRINK, C.R. and PEECH, M. 1963b. Hydrolysis and exchange reactions of the aluminum ion in hectorite and montmorillonite suspensions. Soil Sci. Soc. Amer. Proc. 27: 527-530.

FRINK, C.R. and SAWHNEY, B.L. 1967. Neutralization of dilute aqueous aluminum salt solutions. Soil Sci. 103: 144-148.

FRIPIAT, J.J., VAN CAUWELAERT, F. and BOSMANS, H. 1965. Structure of aluminum cations in aqueous solutions. J.Phys. Chem. 69: 2458-2461.

GILBERT, M. and LAUDELOUT, H. 1965. Exchange properties of hydrogen ions in clays. Soil Sci. 100: 157-162.

GREENLAND, D.J. 1971. Interactions between humic and fulvic acids and clays. Soil Sci. 111: 34-41.

GRIM, R.E. 1962. Applied clay mineralogy. McGraw Hill Book Co., New York. 422 p.

GROSSMAN, R.B. and CARLISLE, F.J. 1969. Fragipan soils of the eastern United States. Advances in Agron. 21: 237-279.

HAHN, H.H. and STUMM, W. 1968. Coagulation by Al (III). Adv. in Chem. 79: 91-111.

HELFFERICH, F. 1962. Ion exchange. McGraw Hill Book Co., New York. 624 p.

HEM, J.D. 1968. Aluminum species in water. Adv. in Chem. 73: 98-114.

HOLMES, L.P., COLE, D.L. and EYRING, E.M. 1968. Kinetics of aluminum ion hydrolysis in dilute solutions. J.Phys.Chem. 72: 301-304.

HSU, P.H. 1968. Heterogeneity of montmorillonite surface and its effect on the nature of hydroxy-aluminum interlayers. Clays and Clay Minerals 16: 303-311.

HSU, P.H. and Bates, T.F. 1964. Formation of X-ray amorphous and crystalline aluminum "hydroxides". Mineral Mag. 33: 749-768.

HUANG, W.H. and KELLER, W.D. 1972. Geochemical mechanics for the dissolution, transport and deposition of aluminum in the zone of weathering. Clays and Clay Minerals 20: 69-74.

JACKSON, M.L. 1963a. Interlayering of expansible layer silicates in soils by chemical weathering. p.29-46. In W.F.Bradley (ed.): Clays and Clay Minerals, Proc. 11th Conf. Macmillan Co. (Pergamon), New York.

JACKSON, M.L. 1963b. Aluminum bonding in soils: a unifying principle in soil science. Soil Sci. Soc. Amer. Proc. 27: 1-10.

JENNY, H. 1961. Reflections on the soil acidity merry-go-round. Soil Sci. Soc. Amer. Proc. 25: 428-432.

KADDAH, M.T. and COLEMAN, N.T. 1967a. Salt displacement and titration of $AlCl_3$-treated trioctahedral vermiculites. Soil Sci. Soc. Amer. Proc. 31: 328-332.

KADDAH, M.T. and COLEMAN, N.T. 1967b. Salt displacement of acid-treated trioctahedral vermiculites. Soil Sci. Soc. Amer. Proc. 31: 333-336.

KAMPRATH, E.J. 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. Soil Sci. Soc. Amer. Proc. 34: 252-254.

KHAN, S.V. 1969. Interaction between the humic acid fraction of soils and certain metallic cations. Soil Sci. Soc. Amer. Proc. 33: 851-854.

KIDDER, G. and REED, L.W. 1972. Swelling characteristics of hydroxyaluminum interlayered clays. Clays and Clay Minerals 20: 13-20.

KISSEL, D.E., GENTZSCH, E.P. and THOMAS, G.W. 1971. Hydrolysis of non-exchangeable acidity in soils during salt extractions of exchangeable acidity. Soil Sci. 111: 293-297.

KITTRICK, J.A. 1966. The free energy of formation of gibbsite and $Al(OH)_4^-$ from solubility measurements. Soil Sci. Soc. Amer. Proc. 30: 595-598.

KOZAK, L.M. and HUANG, P.M. 1971. Adsorption of hydroxy-Al by certain phyllosilicates and its relation to K/Ca cation exchange selectivity. Clays and Clay Minerals 19: 95-102.

LINDSAY, W.L., PEECH, M. and CLARK, J.S. 1959. Determination of aluminum ion activity in soil extracts. Soil Sci. Soc. Amer. Proc. 23: 266-269.

LYNN, W.C. and WHITTIG, L.D. 1966. Alteration and formation of clay minerals during cat clay formation. p.241-248. In W.F. Bradley (ed.): Clays and Clay Minerals, Proc. 14th Conf. Macmillan Co. (Pergamon), New York.

MARTIN, J.P. and RICHARDS, S.J. 1969. Influence of the copper, zinc, iron and aluminum salts of some microbial and plant polysaccharides on aggregation and hydraulic conductivity of Ramona sandy loam. Soil Sci. Soc. Amer. Proc. 33: 421-423.

MATIJEVIĆ, E., JANAUER, G.E. and KERKER, M. 1964. Reversal of charge of lyophobic colloids by hydrolyzed metal ions. I. Aluminum nitrate. J.Colloid.Sci. 19: 333-346.

MATIJEVIĆ, E., MATHAI, K.G., OTTERWILL, R.H. and KERKER, M. 1961. Detection of metal ion hydrolysis by coagulation. III. Aluminum. J.Phys.Chem. 65:826-830.

McLEAN, E.O. and OWEN, E.J. 1969. Effects of pH on the contributions of organic matter and clay to soil cation exchange capacities. Soil Sci. Soc.Amer.Proc. 33: 855-858.

MILLER, R.J. and BROWN, D.S. 1969. The effect of exchangeable aluminum on conductance and diffusion activation energies in montmorillonite. Soil Sci. Soc. Amer. Proc. 33: 373-378.

MITRA, R.P. and KAPOOR, B.S. 1969. Acid character of montmorillonite: titration curves in water and some non-aqueous solvents. Soil Sci. 108: 11-23.

MITRA, R.P., SHARMA, B.K. and KAPOOR, B.S. 1963. Three stages in the titration of montmorillonite in water and in acetonitrile-benzene mixtures. Ind. J. Chem. 1: 225-226.

MOORMANN, F.R. 1963. Acid sulfate soils (cat-clays) of the tropics. Soil Sci. 95: 271-275.

MORTLAND, M.M. 1970. Clay-organic complexes and interactions. Adv. in Agron.22: 75-117.

OKURA, T., GOTO, K. and YOTUYANAGI, T. 1962. Forms of aluminum determined by an 8-quinolinolate extraction method. Anal. Chem. 34: 59-63.

PARFITT, R.L., and GREENLAND, D.F. 1970. Adsorption of polysaccharides by montmorillonite. Soil Sci. Soc. Amer. Proc. 34: 862-866.

PETTRY, D.E. and RICH, C.I. 1971. Modification of certain soils by calcium hydroxide stabilization. Soil Sci. Soc. Amer. Proc. 35: 834-838.

PIONKE, H.B. and COREY, R.B. 1967. Relations between acidic aluminum and soil pH, clay, and organic matter. Soil Sci. Soc. Amer. Proc. 31: 749-752.

PIONKE, H.B., COREY, R.B. and SCHULTE, E.E. 1968. Contributions of soil factors to lime requirement and lime requirement tests. Soil Sci. Soc. Amer. Proc. 32: 113-117.

QUIGLEY, R.M. 1969. Soil mechanics research problems caused by aluminum and iron adsorption on clay minerals. Int. Clay Conf., Proc. Vol. 1 (Tokyo, Japan) 793-803. Israel Universities Press, Jerusalem.

RAGLAND, J.L. and COLEMAN, N.T. 1960. The hydrolysis of aluminum salts in clay and soil systems. Soil Sci. Soc. Amer. Proc. 24: 457-460.

RAUPACH, M. 1963. Solubility of simple aluminum compounds expected in soils. II. Hydrolysis and conductance of Al^{+3}. Aust. J. Soil Res. 1: 36-45.

RAUSCH, W.V. and BALE, H.D. 1964. Small-angle X-ray scattering from hydrolyzed aluminum nitrate solutions. J. Chem. Phys. 40: 3391-3394.

REEDER, S.W., ARSHAD, M.A. and ODYNSKY, W. 1967. The relationship between structural stability and chemical criteria of some solonetzic soils of northwestern Alberta. Can. J. Soil Sci. 47: 231-237.

REEVE, N.G. and SUMNER, M.E. 1970. Lime requirements of Natal oxisols based on exchangeable aluminum. Soil Sci. Soc. Amer. Proc. 34: 595-598.

REEVE, N.G. and SUMNER, M.E. 1971. Cation exchange capacity and exchangeable aluminum in Natal oxisols. Soil Sci. Soc. Amer. Proc. 35: 38-42.

RICH, C.I. 1968. Hydroxy interlayers in expansible layer silicates. Clays and Clay Minerals 16: 15-30.

RICH, C.I. 1970. Conductometric and potentiometric titration of exchangeable aluminum. Soil Sci. Soc. Amer. Proc. 34: 31-38.

RICHBURG, J.S. and ADAMS, F. 1970. Solubility and hydrolysis of aluminum in soil solutions and saturated-paste extracts. Soil Sci. Soc. Amer. Proc.34:728-734.

RILEY, D. and ARNOLD, P.W. 1969. Hydrogen-magnesium, hydrogen-sodium exchange equilibria and the formation of "exchangeable" aluminum. Soil Sci. 108: 414-418.

ROSS, G.J. and TURNER, R.C. 1971. Effect of different anions on the crystallization of aluminum hydroxide in partially neutralized aqueous aluminum salt solutions. Soil Sci. Soc. Amer. Proc. 35: 389-392.

RUFF, J.K. and TYREE, S.Y. 1958. Light-scattering studies on aqueous aluminum nitrate solutions. J. Amer. Chem. Soc. 80: 1523-1526.

SAINI, G.R., MACLEAN, A.A. and DOYLE, J.J. 1966. The influence of some physical and chemical properties on soil aggregation and response to VAMA. Can. J. Soil Sci. 46: 155-160.

SAWHNEY, B.L. 1968. Aluminum interlayers in layer silicates: Effect of OH/Al ratio of Al solution, time of reaction and type of structure. Clays and Clay Minerals 16: 157-163.

SAWHNEY, B.L. 1972. Selective sorption and fixation of cations by clay minerals: A review. Clays and Clay Minerals 20: 93-100.

SAWHNEY, B.L. and FRINK, C.R. 1966. Potentiometric titration of acid montmorillonite. Soil Sci. Soc. Amer. Proc. 30: 181-184.

SAWHNEY, B.L., FRINK, C.R. and HILL, D.E. 1970. Components of pH dependent cation exchange capacity. Soil Sci. 109: 272-278.

SAWHNEY, B.L. and NORRISH, K. 1971. pH dependent cation exchange capacity: Minerals and soils of tropical regions. Soil Sci. 112: 213-215.

SCHNITZER, M. 1969. Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. Soil Sci. Soc. Amer. Proc. 33:75-81.

SCHOFIELD, R.K. and TAYLOR, A.W. 1954. The hydrolysis of aluminium salt solutions. J. Chem. Soc. 4445-4448.

SCHWERTMANN, U. 1969. Aggregation of aged hydrogen clays. Int. Clay Conf., Proc. Vol. 1 (Tokyo, Japan) 683-690. Israel Universities Press, Jerusalem.

SCHWERTMANN, U. and JACKSON, M.L. 1963. Hydrogen-aluminum clays: A third buffer range appearing in potentiometric titration. Science 139: 1052-1053.

SCHWERTMANN, U. and JACKSON, M.L. 1964. Influence of hydroxy aluminum ions on pH titration curves of hydronium-aluminum clays. Soil Sci. Soc. Amer. Proc. 28: 179-183.

SHAINBERG, I. and DAWSON, J.E. 1967. Titration of H-clay suspensions with salt solutions. Soil Sci. Soc. Amer. Proc. 31: 619-626.

SILLÉN, L.G. and MARTELL, A.E. 1964. Stability constants of metal-ion complexes. Special Publ. No. 17, 754 p. The Chemical Society, Burlington House, London.

SILLÉN, L.G. and MARTELL, A.E. 1971. Stability constants of metal-ion complexes. Supplement No. 1. Special Publ. No. 25, 865 p. The Chemical Society, Burlington House, London.

SINGH, S.S. 1967. Sulfate ions and ion activity product $Al(OH)^3$ in Wyoming bentonite suspensions. Soil Sci. 104: 433-438.

SINGH, S.S. 1969. Neutralization of dilute aqueous aluminum sulfate solutions with a base. Can. J. Chem. 46: 663-667.

SINGH, S.S. 1972. The effect of temperature on the ion activity product $Al(OH)^3$ and its relation to lime potential and degree of base saturation. Soil Sci. Soc. Amer. Proc. 36: 47-50.

SINGH, S.S. and BRYDON, J.E. 1967. Precipitation of aluminum by $Ca(OH)_2$ in the presence of Wyoming bentonite and sulfate ions. Soil Sci. 103: 162-168.

SINGH, S.S. and BRYDON, J.E. 1969. Solubility of basic aluminum sulfates at equilibrium in solution and in the presence of montmorillonite. Soil Sci. 107: 12-16.

SINGH, S.S. and BRYDON, J.E. 1970. Activity of aluminum hydroxy sulfate and the stability of hydroxy aluminum interlayers in montmorillonite. Can.J.Soil Sci. 50: 219-225.

SRINIVASAN, K. and RECHNITZ, G.A. 1968. Reaction rate measurements with fluoride ion-selective membrane electrode. Anal.Chem.40:1818-1825.

STUMM, W. and O'MELIA, C.R. 1968. Stoichiometry of coagulation. J. Amer. Water Works Assoc. 60: 514-539.

SULLIVAN, J.H.Jr. and SINGLEY, J.E. 1968. Reactions of metal ions in dilute aqueous solution: Hydrolysis of aluminum. J. Amer. Water Works Assoc. 60: 1280-1287.

SWINCER, G.D., OADES, J.M. and GREENLAND, D.J. 1969. The extraction, characterization and significance of soil polysaccharides. Adv. in Agron.21:195-235.

TAMURA, T. 1957. Identification of the 14A clay mineral component. Amer. Mineral. 42: 107-110.

THOMAS, G.W. and COLEMAN, N.T. 1959. A chromatographic approach to the leaching of fertilizer salts in soils. Soil Sci. Soc. Amer. Proc.23: 113-116.

TURNER, R.C. 1967. Aluminum removed from solution by montmorillonite. Can.J. Soil Sci. 47: 217-222.

TURNER, R.C. 1968a. Conditions in solution during the formation of gibbsite in dilute Al salt solutions: I. Theoretical treatment of the effect of the formation of mono- and polynuclear hydroxy aluminum ions, precipitations and crystallization on curves representing the titration of $AlCl_3$ with a base. Soil Sci. 106: 291-296.

TURNER, R.C. 1968b. Conditions in solution during the formation of gibbsite in dilute Al salt solutions: II. Effect of length of time of reaction on the formation of polynuclear hydroxy aluminum cations, the substitution of other anions for OH^- in amorphous $Al(OH)_3$ and the crystallization of gibbsite. Soil Sci. 106: 338-344.

Summary

This introductory lecture reviews and summarizes recent achievements in aluminum chemistry in relation to soil acidity. Subsequently are considered the aluminum reactions in aqueous solutions, in clay suspensions and in soils. The explanation of aluminum behaviour is difficult because of uncertainties about both the nature of the solid phase and monomeric and polynuclear dissolved species. Aluminum interactions with clay minerals, organic matter and metaloid ions further complicate this picture. All the same considerable progress has been made in distinguishing various of the aluminum species and in recognizing their very important role in soil reaction, cation exchange reactions and stabilization of soil structure, especially in acid soils.

Résumé

Cette introductoire passe en revue et résume les résultats récents de la chimie d'aluminum par rapport à l'acidité du sol. Consécutivement ont été traitées les réactions d'aluminum dans les solutions aqueuses, dans les suspensions argileuses et dans les sols mêmes. L'interprétation de la conduite de l'aluminum est difficile à cause des incertitudes autour du caractère de la phase solide et des espèces dissolues monomériques et polynucléaires. En plus l'interprétation est compliquée par les interactions d'aluminium avec les minéraux d'argiles, la matière organique et les ions métalloides. Néanmoins on a réussi à déterminer plusieurs d'espèces d'aluminium et leurs influence sur la réaction du sol, l'échange de cations et la stabilisation de la structure, surtout dans les sols acides.

Resumen

Esta ponencia da una resena de las resultas recientes en la química de aluminio relacionado al acidez de suelo. Se ha tratado consecutivamente las reacciones de aluminio en soluciones acuosas, en suspenciones arcillosas y en suelos. Es muy dificil el interpretar del comportamiento del aluminio debido a las incertidumbres relativo al caracter de la fase solida y de las especies disueltas monoméricas y polinuclearias. Luego se complica el concepto por las reacciones de aluminio antes de minerales arcillosas, materia organica y iones metaloides. Sin embargo se ha avanzado en medida progresiva en determinando especies de aluminio y reconosciendo su influencia en la reacción del suelo, los procesos de intercambio de cationes y la stabilisación de la estructura, sobre todo en los suelos ácidos.

Zusammenfassung

Diese Einleitung ist eine Zusammenfassung der letzten Entwicklungen im Gebiet der Aluminiumchemie in Beziehung zur Bodensäure. Nacheinander werden behandelt die Aluminiumreaktionen in Wasserlösungen, in Tonsuspensionen und in Böden. Die Erklärung des Aluminiumbenehmens wird erschwert durch Unsicherheiten über das Naturell der festen Phase und der aufgelösten monomerischen und polynukleären Aluminiumarten. Weiterhin wird das Bild kompliziert durch die Wechselwirkung zwischen Aluminium und Tonmineralien, organischen Substanzen und metalloiden Ionen. Trotzdem hat man wichtige Fortschritte gemacht namentlich in der Determination von verschiedenen Aluminiumarten und im besseren Kenntnis derer spezifischen Wirkungen auf die Bodensäure, Kationen-Austauschkapazität und Stabilität der Bodenstruktur.