

SPECIATION OF INORGANIC ALUMINUM SOLUTIONS AND MODELING
THEIR KINETICS AND MECHANISMS OF ADSORPTION ON SELECTED
SOLIDS

by

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Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY
in
Agronomy

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November, 1985
Blacksburg, Virginia

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(ABSTRACT)

Kinetics and mechanisms of Al adsorption on Ca-saturated kaolinite, montmorillonite, and peat were studied using miscible displacement methods. Unneutralized and partially neutralized Al solutions ($\text{OH}/\text{Al}=1.0$) were leached through monomineralic columns and effluent analyzed for monomeric and polymeric Al, titratable acidity, and desorbed Ca as a function of time. Observed breakthrough curves (BTC) for continuous injection of the various Al solutions through kaolinite suggested the existence of at least two mechanisms for Al adsorption. It was shown that a relatively rapid reaction, where solution Al was in equilibrium with the solid phase, involved Ca-Al exchange and a slower reaction involved Al polymerization on the adsorbent. This scenario was supported by rigorous modeling of observed BTC with nonequilibrium transport theory, analysis of desorbed Ca effluent, and potentiometric titrations of effluent solutions. The occurrence of two mechanisms for Al adsorption on montmo-

rillonite and peat was also evident. Polymeric Al was preferentially adsorbed by kaolinite throughout the displacement experiment whereas montmorillonite preferentially adsorbed monomers at short times and polymers at longer times. Selective adsorption of either form of Al on peat was not evident.

In order to accurately distinguish between monomeric and polymeric Al in solution and on solids, a method was developed which evaluates the interaction of ferron with Al. The colorimetric complexation of aqueous Al with ferron was largely described by a binary species first-order rate function. Based on the differential kinetic reactions of ferron with monomeric and polymeric Al, the fraction of the former species was well predicted using the binary species model. The method avoids arbitrary separation times for the distinction of monomeric and polymeric Al since the duration of monomer interactions with ferron depend on the initial basicity of the Al solution.

ACKNOWLEDGEMENTS

I wish to express my most sincere gratitude to my major professor, Dr. Lucian W. Zelazny, for his guidance and intense friendship during my graduate program. I will always appreciate the time he has given to listen and understand the many problems I have encountered during my stay at Virginia Tech. He has allowed me to grow and become a more complete individual. I am as well grateful to Dr. John "Jack" C. Parker who, like Lucian, has provided considerable assistance and support during my research endeavors and manuscript preparations. Their ability to bring great pressure to bear on knotty research problems deserves special thanks. Appreciation is extended to the remaining members of my committee Drs. James C. Baker, Dave C. Martens, and James D. Rimstidt for their valuable advice, time, and friendship. Special thanks is also expressed toward Dr. John G. Mason who devoted several moments of his time to share research ideas and thoughts.

I would like to thank _____ for his fine support and friendship during my graduate studies. Our timeless research and lunch-hour discussions will be cherished. I also appreciate the many graduate students and technical staff especially, _____ , _____ , _____

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Chapter I

INTRODUCTION

Understanding the process of acid deposition on soil and the need for analytical control of water treatment requires acute knowledge concerning the chemical partitioning of aqueous and solid phase Al. The deposition of atmospheric pollutants has been found to accelerate the transport of nutrient cations from terrestrial to aquatic systems and increase soil mineral weathering, Al solubilization, and soil acidity. It is thought that the readily soluble Al is responsible for recent declines of certain flora and aquatic life. Aluminum salts, however, are commonly used in the physico-chemical treatment of water and waste-waters to remove suspended matters, to precipitate inorganics such as fluorides and phosphates, and to eliminate organic micro-pollutants. For this reason speciation of aqueous Al into its various organic and inorganic forms and optimizing operational conditions for efficient treatment of waste-water becomes very important.

Aware of the complexities of physical and chemical processes that govern solid-solution partitioning of Al, research projects were conducted to investigate the reaction of different forms of Al with various soil constituents and

develop speciation methods for the chemical partitioning of solid and solution phase Al. More specifically the objectives of the study were to investigate the kinetics and mechanisms of monomeric and polymeric Al adsorption on various soil constituents using transient displacement experiments and to speciate hydrolyzed aqueous Al into its monomeric and polymeric forms.

Chapter II

LITERATURE REVIEW

2.1 INTRODUCTION

Aluminum occupies a somewhat anomalous position among the biological elements, in that it is a very common and important constituent of many inorganic materials of the biosphere, but is quite rare and usually an unimportant component of living matter (Hutchinson, 1945). Although Al is typically found in low amounts in plant and animals, the Al content of most soils is generally quite high. Such Al is usually not readily available and is primarily contained in the internal structure of aluminosilicate clays (Jackson, 1963b). As soils become acidified through the actions of weathering, leaching of bases, and by the effects of acid rain, the aluminosilicate clays and the hydroxides and oxides of Al solubilize releasing Al in its readily available elemental forms. The newly released Al may be reabsorbed onto the solid surfaces of the soil colloids or remain in the soil solution where it is in direct contact with rooting systems of living plants.

The occurrence of Al in the extracts of acid soils was first observed by Veitch in 1902. Unfortunately the impor-

tance of his findings were overlooked for many years and soil scientists continued to support the well entrenched theory that acid soils were primarily the result of adsorbed hydronium ions on soil colloids. The ideas proposed by Veitch (1902) however, slowly began to circulate amongst the soil and plant scientists. Ruprecht (1915) and Hartwell and Pember (1918), utilizing the knowledge provided by Veitch, obtained evidence suggesting that the injurious effects of acid soils on certain plants was due to Al rather than to the hydronium ion. Similar results confirming this idea were obtained by Mattson and Hester (1933). The H-clay theory also met disfavor when Paver and Marshall (1934) provided evidence strongly suggesting that soil acidity was mainly associated with the Al ion. Not until the work of Grim (1942), Chernov (1947), and Schofield (1949) did soil and plant scientist begin to accept that soil acidity was primarily related to the Al ion and not the hydronium ion.

Over the years studies on the interaction of Al with plants and various soil constituents has advanced our current knowledge of soil acidity only slightly. Earlier investigators had failed to consider the important reactions of Al hydrolysis both in solution and on the exchange phase. Not until recently have the precise conditions of hydrolysis been considered when determining the nature and quantity of

polymeric species, colloidal particles or amorphous phases which form in Al salt solutions.

2.2 CHARACTERIZATION OF ALUMINUM SPECIES IN PURE SOLUTIONS

The characterization of various Al species in the soil solution is of great importance to both the soil and plant scientist. Knowledge of the various species has provided ideas pertaining to the mode of interaction between Al, soils, and plants.

In dilute aqueous Al salt solutions with a pH close to 3.0, Al exists primarily as the trivalent cation, with six water molecules in octahedral coordination (e.g. $\text{Al}(\text{OH}_2)_6^{+3}$). The coordinated water molecules are oriented with the oxygen toward the central Al ion. The oxygen-hydrogen bonds of the coordinated water are under considerable stress due to the high charge of the Al ion. This situation facilitates the removal of a proton when the pH of the solution is raised only slightly. This initial hydrolysis of Al was first proposed by Bjerrum (1928). Much research has been conducted in determining a precise pK value for the hydrolysis scheme (Fauchere, 1948; Lacroix, 1949; Schofield and Taylor, 1954; Frink and Peech, 1963a). These initial investigations of the hydrolysis of Al^{+3} assumed that the only significant hydrolysis product in dilute aqueous solu-

tions was $\text{Al}(\text{OH})^{+2}$. Recent studies have shown however, that earlier techniques for measuring Al hydrolysis in dilute solutions were not sensitive enough to distinguish between $\text{Al}(\text{OH})^{+2}$ and possible species of the general formula $\text{Al}_x(\text{OH})_{2x-1}$ (Baes and Mesmer, 1976). Variations in concentrations, pH, and temperature of aqueous Al salt solutions further complicates the proposed monomeric hydrolysis schemes. Strong evidence suggest that under appropriate conditions the association of monomeric Al species occurs, resulting in the formation of various sized Al polymers. The types and sizes of such polymers will vary relative to the concentration of Al and OH^- ions in solution, and relative to the temperature of the system. Variations in size will also be greatly dependent on the methodology used in adding OH^- ions to the Al solutions.

Varying the concentration of Al in solution, Faucherre (1954) reported that the cation $\text{Al}_2(\text{OH})_2^{+4}$ (Al dimer) formed in solutions where the concentration of Al exceeded 1.1×10^{-2} M. At concentrations below 5.1×10^{-3} M, however, the monomer $\text{Al}(\text{OH})^{+2}$ was predominate. This was in agreement with the results of Matijevec and Tezak (1953) who initially proposed the dimer species. In a similar fashion, Nair and Prenzel (1978) suggested that the dimer species was insignificant from pH 1 to 9 at Al concentrations of 10^{-3} , $10^{-4.5}$,

and 10^{-6} M. Their conclusions were based on theoretically determined equilibrium diagrams. Nail et al. (1976b), investigating the structure of the initial precipitates of aluminum hydroxide gels, suggested however that the dimer could easily form by union of two deprotonated octahedra (e.g. $\text{Al}(\text{OH})^{+2}$). The dimer species was believed to be the precursor for the formation of other more complex polymers. They suggested that the dimer could join to form either a chain structure or a ring structure according to their proposed deprotonation-dehydration mechanism. Investigating Al speciation in very dilute solutions, Hem and Roberson (1967) also suggested formation of the dimer species. Hsu (1977) disagreed with these arguments, suggesting that $\text{Al}_2(\text{OH})_2^{+4}$ could not form since a considerable repulsive force exist between the two Al monomers in solution.

The dimer species is the smallest proposed Al polymer that can exist in solution. Many larger and more complex polynuclear species have been proposed based on evidence provided by pH measurements, potentiometric titrations, light scattering, cryoscopy, coagulation and diffusion reactions. Brosset et al. (1954) concluded that the main Al species in their solution was probably $\text{Al}_6(\text{OH})_{15}^{+3}$ although no definite decisions could be made since their method could not distinguish between several conceivable formulas (e.g.

$\text{Al}_6(\text{OH})_{15}^{+3}$, $\text{Al}_8(\text{OH})_{20}^{+4}$, etc). Their proposed speciation was based on the monitoring of aged Al solutions and crystallographic evidence. In order to distinguish between such species, Matijevic et al. (1961) suggested that information on molecular weight, size, charge, etc. of the hydrolyzed species must be available. Nail et al. (1976b,c) suggest that the proposed species of $\text{Al}_6(\text{OH})_{15}^{+3}$ is most likely not a major hydrolysis product in Al solutions. The authors note that the structure $\text{Al}_6(\text{OH})_{15}^{+3}$ consist of a six membered ring with the extra hydroxide groups attached by single bonds to alternate Al atoms in the ring. The presence of these "nonstructural" hydroxide groups cause larger basicity values to occur than those predicted from the authors proposed deprotonation-dehydration scheme which considered only double hydroxide bridge formations. Thus Nail et al. (1976b) suggest that a complex of 32 aluminum atoms, derived from the $\text{Al}_6(\text{OH})_{15}^{+3}$ species is the maximum size of the polymer that can be postulated. This size limitation seems unreasonably small since others have suggested that Al polymers with over a hundred Al ions per structure are present in solution (Smith and Hem, 1972). The $\text{Al}_6(\text{OH})_{15}^{+3}$ species has also met disfavor with Hem and Roberson (1967). They argue that no structural basis exists for supposing that the small partly polymerized unit, $\text{Al}_6(\text{OH})_{15}^{+3}$, would be likely

to persist over any wide range of pH or OH/Al mole ratio value.

In contrast to the proposed species $\text{Al}_6(\text{OH})_{15}^{+3}$, Matijevic et al. (1961) concluded that between pH 4 and 7, the Al species could be defined as $\text{Al}_8(\text{OH})_{20}^{+4}$ as noted from studies on the coagulation of aqueous sols of silver halides. Rubin and Hayden (1973) also found that $\text{Al}_8(\text{OH})_{20}^{+4}$ was the principle Al species of their solutions. Again, Hem and Roberson (1967) argued that no structural basis exists for supposing that the polymer $\text{Al}_8(\text{OH})_{20}^{+4}$ should exist in solution.

Sillen (1954a,b) and Heitanen and Sillen (1954) presented many experimental, mathematical, and graphical techniques for determining the form and stability of many polynuclear complexes. It was noted that the Al ion seemed to form a considerable number of complexes containing fundamental units with a varying number of attached units. Using the theoretical treatment developed by Sillen (1954, 1961), Fripiat et al. (1965) proposed a mechanism of unlimited polymerization for the formation of $\text{Al}[(\text{OH})_8\text{Al}_3]_n^{+4}$ complexes. Based on spectroscopic data of concentrated Al solutions and using their proposed mechanism of polymerization, Fripiat et al. (1965) suggested that the species $\text{Al}_4(\text{OH})_8^{+4}$ was the principal form in solution. Again, this polynuclear species

violates the structural mechanisms proposed by Hem and Robertson (1967) who worked with very dilute, partially neutralized Al solutions.

Akitt et al. (1969, 1972), using nuclear magnetic resonance (NMR), concluded the following forms of Al occurred in their solutions over a variety of pH values: Al^{+3} , $\text{Al}_2(\text{OH})_2^{+4}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$, and $\text{Al}_8(\text{OH})_{20}^{+4}$. The polynuclear species $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ has previously been proposed by Johanson (1960) following his studies of the crystals of basic aluminum sulfate. Rausch and Bale (1964) also assumed this polynuclear Al species using small-angle x-ray scattering. They prepared Al solutions of basicities varying between 1.5 and 2.25 and heated them to 70°C for 1 hr. Monitoring the solution with small-angle x-ray they found a polymer with a radius of gyration 4.3A which was assumed to be $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$. Waters and Henty (1977), using Raman spectroscopy, also suggested that this latter polymeric species was the major constituent of their hydrolysed Al salt solutions when $\text{OH}/\text{Al}=2.5$. More recently Bottero et al. (1980), investigating the hydrolysis and precipitation process of Al using ^{27}Al NMR spectroscopy, concluded that their 0.1M AlCl_3 solutions, of varying basicity from 0 to 2.5, contained the polymers $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ and a dimer whose formula was $\text{Al}_2(\text{OH})_x(\text{H}_2\text{O})_{10-x}^{(6-x)+}$. Later in the investi-

gation, Bottero et al. (1980) ran experimental potentiometric titrations and tried to repredict the curves using theoretical considerations. In order to improve the superimposition of the theoretical curve on the experimental curve, the authors decided to modify the charge of the polymer $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ and its dissociation constant to $\text{Al}_{13}\text{O}_4(\text{OH})_{28}^{+3}$ and $k=10^{-105}$, respectively. Further investigations of the hydrolysis of aqueous solutions of Al were conducted by Bottero et al. (1982) using small-angle x-ray scattering. Using 0.1M AlCl_3 with a $\text{OH}/\text{Al}=2.0$, and assuming the principal species in solution as $\text{Al}_{13}\text{O}_4(\text{OH})_{28}^{+3}$, the experimentally calculated radius of gyration was 9.8A which corresponds to an ionic radius of 12.6A. This value demonstrates that the solvation layer of the polymer has substantial thickness. The polymer proposed by Johanson (1960), $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$, and a derivative of this proposed by Bottero et al. (1980), $\text{Al}_{13}\text{O}_4(\text{OH})_{28}^{+3}$, have icosahedral structures where a tetrahedral central Al is symmetrically surrounded by 12 octahedral Al. Some believe the icosahedral structure of these polymers is quite unstable based on theoretical calculation (G.N. White, personal communication). Recalling the formula: bond strength = valence/coordination number and considering that the 3 tetrahedral oxygens, each of which is bound to 3 octahedra, have a net

valence of 5/4, we find that in order to have a net balance of charge amongst the bonds, we need to have the valence of the octahedral bonds to be 5/12. This is 1/12 less than theory would predict resulting in an unstable structure or a structure where the 12 "uncharged waters" in reality have 7/12 bond strength. This latter statement most likely is not the case. Akitt and Farthing (1981 c,d) have recently provided experimental evidence which verifies that the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ polymer is in fact unstable in partially neutralized Al solutions. They postulate its formation by suggesting that rapid addition of base with Al results in localized concentrations of $\text{Al}(\text{OH})_4^-$ which serves as a central nucleus for the binding of 12 octahedrally coordinated Al units. With age, the polymer fragments into units of varying proportion which are of a hexagonal arrangement. Bertsch et al. (1986) has also shown that the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ polymer is a kinetic artifact of the method of preparation. The $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ polymer was observed at $\text{OH}/\text{Al} (n) > 0.25$ using base injection rates of 0.6 and 1.2 mL min^{-1} and its concentration was found to increase linearly as a function of n. For $n=2.5$ the concentration of the polymer decreased at the 1.2 mL min^{-1} base injection rate but increased linearly at the base injection rate of 0.6 mL min^{-1} . After 9 months of aging, the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ species was no longer

evident in solutions synthesized at 1.2 mL min^{-1} but still remained in solutions made at 0.6 mL min^{-1} . Bertsch et al. (1986) has also shown that the existence of the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ polymer is dependent on the concentration of initial solution Al. Concentrations of $3.34 \times 10^{-3} \text{ M Al}$ and less were found not to contain the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ polymer in detectable amounts until $n \geq 1.5$.

Many of the authors discussed to this point, with the exception of Hem and Roberson (1967) and Smith and Hem (1972) have utilized rather high concentrations of Al in their studies which does not serve to mimic the soil environment very well. Many of these studies dealt with partially neutralized solutions where the OH^- ions were added to the Al solutions rather rapidly. Vermeulen et al. (1975) have shown that such a procedure results in localized concentrations of OH^- which could cause premature precipitation of solid $\text{Al}(\text{OH})_3$. Thus many of previous studies may have prepared polymers in solutions which may be very unrealistic in soil systems. Acknowledging the factors contributing to the nature of Al hydrolysis, Hem and Roberson (1967) prepared dilute, partially neutralized Al solutions (4.53×10^{-4} to $4.53 \times 10^{-5} \text{ M}$) by "slowly" adding base to the vigorously stirring Al solutions. The precise rate of base addition and whether or not it was added below the surface of

the Al solution was not mentioned however. Nevertheless their method minimized, if not eliminated, the localized precipitation effect which hampered results of so many investigators before them. Hem and Roberson (1967) proposed a mechanism of polymer formation based on a process involving deprotonation and dehydration of solution Al ions. This process initially results in the formation of the of the dimer species which contains a double hydroxide bridge between aluminum ions. The dimers can then join to form either a branched chain structure or a ring structure by the same deprotonation-dehydration mechanism. The general formula for the branched chain structure would be $Al_x(OH)_{2x-2}(OH_2)_{2x+4}^{x+2+}$ which has a finite length. Hem and Roberson (1967) suggest that the statistical probability of forming long straight chains is low since the mutual directional bonding forces between Al^{+3} and OH^- ions which form the double bridges require that no two adjacent bridges lie in the same plane. This is in agreement with the structure of gibbsite which is a common and stable constituent of many soils. The authors further suggest that rapid addition of hydroxide to Al solutions probably produces various chain lengths. Nevertheless, the ring structure can also be formed by joining dimers. The ring formation is composed of 6 octahedrally coordinated Al ions joined together by double

OH bridges. These six-membered rings may then coalesce further by continued polymerization which follows the deprotonation-dehydration mechanism. Stol et al. (1976), working also with very dilute Al solutions of varying basicity, proposed a structural model for Al polymer formation and suggested that hexamers and their cyclic derivatives were the most common species of Al polymers. The authors further added that other Al structures may be present but their contribution towards the total population is much less than that of the hexameric species. Hsu and Rich (1960) and Hsu and Bates (1964) had also suggested that a "gibbsite-like" ring structure of Al was the primary polymer in their solutions. According to Hsu (1973) and Bersillon et al. (1978), polymeric Al species consist of sheetlike units which grow in size in the a and b directions and whose size depends on the initial basicity of the Al solution. Vertical combination of particles may occur and this mechanism of polymer growth involves H-bonding between the adjacent sheetlike layers. Based on infrared (IR) studies of the development of order in Al hydroxide gels, Nail et al. (1976a) also concluded that Al polymers and precipitates preferential grow in the ab plane suggesting the formation of thin platelet structures.

2.3 INTERACTIONS OF ALUMINUM WITH PURE CLAYS AND PEAT

The final rejection of the H-clay theory which occurred in the early to mid 1950's, prompted countless investigations on the interaction of Al with various constituents of the soil and its implications on soil acidity as a whole. The ever growing evidence suggesting that Al was the adsorbed species in many acid soils and not H_3O^+ was supported by Rich and Obsenshain (1955) who found evidence suggesting nonexchangeable Al existed in interlayer positions of vermiculite in their acid soil. From such knowledge, numerous studies were conducted on the interaction of Al with various soil constituents in order to model actual reactions in true heterogeneous soil systems.

Rich (1960) treated trioctahedral vermiculite with Al solutions of varying basicities and allowed the samples to age. He suggested that some hydrolysis of the adsorbed Al had occurred, but since the Al was held tightly in the vermiculite interlayer space this hydrolysis was probably limited. Artificial Al interlayers were also synthesized in vermiculite by Hsu and Bates (1964). Hydroxy-Al solutions, prepared by addition of 0.1N NaOH dropwise into 0.2M $AlCl_3$ solutions and then diluted to give various OH/Al mole ratios, were added to vermiculite resulting in the fixation of Al polymers on the clay. The species $Al_6(OH)_{12}^{+6}$ (ring

structure) and $\text{Al}_{10}(\text{OH})_{22}^{+8}$ (double ring) were presumed to be present as single layers in the interlayer space. It was suggested that at high Al concentrations in the interlayer space, further sorption in this space may be impeded either physically (size of polymer) or chemically (unfavorable charge distribution). They also indicated that Al hydrolysis was enhanced in the presence of the vermiculite clay. The adsorption of the polynuclear species $\text{Al}_6(\text{OH})_{12}^{+6}$ into the interlayer spaces of montmorillonite was also suggested by Weismiller et al. (1967) using infrared analysis. Carstea (1968) formed hydroxy-Al interlayers in both montmorillonite and vermiculite at various temperatures and found that the formation of Al interlayers in both minerals increased with increasing temperature. He suggested the higher degree of interlayering in montmorillonite as compared to vermiculite of a similar size fraction was related to the difference in the amount and location of charge between the minerals. Since vermiculite should hold the Al polymer more tightly than montmorillonite, it was suggested that a lesser degree of hydrolysis should occur for the adsorbed ions in the former clay. Cotten (1965) studying the hydrolysis of Al as a function of the degree of cross-linkage in a synthetic cation exchanger, Dowex-50, found that the extent of hydrolysis increased as the degree of cross-linkage (and charge

density) decreased. Sawhney (1968) also proposed that the expanded interlayer space in montmorillonite, which has a lesser charge density than vermiculite, provides an ideal locale for the enhanced polymerization of Al while the interlayer space of vermiculite restricts it. Barnhisel and Rich (1963) complied with this argument by suggesting that an increased number of negative charges on a clay surface may delay precipitation of Al as do anions such as Cl^- and SO_4^{-2} . The effect of anions on precipitation of $\text{Al}(\text{OH})_3$ in pure solutions has been investigated extensively (Ross and Turner, 1971; Serna et al., 1977; Akitt and Farthing, 1981d). Jackson (1960), however, had previously proposed the idea of "steric pinching" in the interlayer space. This idea arose from the fact that ions located in a high charge density interlayer were in very close association with their coordinated water molecules. Thus it was suggested that a greater opportunity for hydrolysis and polymerization existed resulting in a higher degree of polymerization. Rich (1970) supported this argument suggesting that narrow and more extensive interlayer spaces with high charge densities may provide a better environment for hydrolysis. Veith (1977), however, revealed evidence of only slight hydrolysis of adsorbed Al^{+3} on vermiculite. In contrast to all the above arguments, Frink and Peech (1963b) totally disagree with the entire idea of clay enhanced Al hydrolysis reactions.

Whether hydrolysis is enhanced by the presence of negatively charged colloids or not, is still an issue of debate today. Even so, the mechanism of Al sorption on interlayered clays is still not completely understood either. Grim and Johns (1954) considered that hydroxy-Al interlayers existed as "islands" which were randomly dispersed in the interlayer spaces. Chakravarti and Talibudeen (1961) and Dixon and Jackson (1962) felt that the hydroxy-Al species were concentrated near the edges. This was supported by Frink (1965) who suggested that Al interlayers exist as "atolls" where the concentrated portion of hydroxy-Al polymers occurred at the clay mineral edges. Barshad (1960) further suggested that polynuclear Al species tend to be more strongly preferred by interlayered clays relative to monomeric Al species. Veith (1977, 1978) has shown that montmorillonite adsorbs rather large polynuclear Al species from solution while vermiculite adsorbs smaller hydroxy-Al complexes. This is related to the nonexpansibility of the vermiculite clay. Hodges and Zelazny (1983a) also have shown that the amount of Al fixed by montmorillonite decreased with decreasing concentration of Al in solution suggesting the preferential adsorption of hydrolyzed, polynuclear species. The more dilute solutions tend to contain a larger percentage of monomeric Al species. Whether or not

the adsorbed polymers on the mineral surface further polymerize to form precipitates of amorphous $\text{Al}(\text{OH})_3$ or gibbsite is debatable. Strong evidence tends to suggest however, that precipitates of amorphous or crystalline gibbsite can form in the interlayer spaces of montmorillonite but not in those of vermiculite. Whether this is related to charge density considerations or to the expansible nature of the clays is unknown presently. Multilayer sorption of hydroxy-Al polymers was noted in montmorillonite interlayers by Sawhney (1968). With aging, the sorbed Al species further polymerized to form gibbsite. This phenomena was not found to occur in vermiculite and was attributed to the fact that interlayer spaces in montmorillonite provide a favorable condition for the organization of hydroxy-Al ions into gibbsite structure. Turner and Brydon (1967) also found gibbsite formation in aged, partially neutralized Al-montmorillonite samples. Once gibbsite had formed in the interlayer space (OH/Al approaching three), the clay-Al complex was no longer stable and the gibbsite was eventually released from the surface. Singh and Brydon (1967) also artificially formed interlayers in montmorillonite using the salt $\text{Al}_2(\text{SO}_4)_3$. The interlayer material that initially formed, disappeared from the interlayer space and a crystalline basic aluminum sulfate formed in solution. The preci-

pitated Al interlayer material was not stable with sulfate present at the low OH/Al mole ratio of 2.2. Veith (1977) suggested that the formation of gibbsite on clays requires extensive time of aging and may occur at a value as low as OH/Al=0.6 provided "enough" solution is added to increased the basicity of the adsorbed Al to the point beyond which gibbsite is formed. Recently, Hodges and Zelazny (1983a) found that montmorillonite fixed Al with basicities ranging from 2.1 to 2.9 suggesting that possible precipitates had formed. The formation of gibbsite was later verified using differential scanning calorimetry (DSC).

The complex nature by which Al interacts with both montmorillonite and vermiculite is apparent. The difficulties in mechanistic interpretation of the sorption processes of Al are further complicated when one considers the clay mineral kaolinite. Turner and Brydon (1967) added various concentrations of AlCl_3 to kaolinite clay samples which then had $\text{Ca}(\text{OH})_2$ added dropwise until a basicity of 2.5 was reached. At high concentrations of Al in solution, precipitates rapidly formed on the clay and were soon released due to some apparent instability of the precipitate on the solid. When smaller amounts of Al were added, the precipitates formed were permanently held on the surface of kaolinite. It was assumed that the precipitate occurred on the clay

mineral edges, where the primary seat of charge is located, rather than on planar surfaces. Brown and Hem (1975) however, found that the adsorption of polymeric Al species on clay surfaces was more closely related to surface area than CEC. They also suggested that polymeric Al adsorbed on mineral surfaces was not readily transformed to gibbsite. Barnshisel and Rich (1965) concluded that kaolinite could act as a template for the formation of gibbsite. They added 5.3 mmole of partially neutralized Al solution to kaolinite and found that although a precipitate formed, it was very poorly crystalline. El-Swaify and Emerson (1975), investigating the effect of Al and Fe oxides on the swelling and aggregate stability of clays after drying, suggested that the presence of kaolinite prevented the hydroxides from crystallizing in the form of gibbsite. In the absence of the clay, however, it was found that identical solutions were able to precipitate gibbsite. Roberts et al. (1974) also investigating flocculation and aggregate stability relations with Al, suggested that hydrolyzed Al, most likely $Al_8(OH)_{20}^{+4}$, acted as an "anchor point" to attach the negatively charged polymer, polyacrylamide, to the surface of kaolinite and enhance flocculation of the clay suspension. Hodges and Zelazny (1983a,b) have recently investigated the interaction of dilute, partially neutralized Al solutions

with kaolinite. They found that kaolinite strongly adsorbed Al primarily in the form of polymers. It was noted that the average basicity of adsorbed Al decreased with increasing aging on kaolinite suggesting that kaolinite may be capable of dehydroxylating the hydrolyzed Al added. The fixation of Al on the kaolinite resulted in basicity values ranging from 2.1 to 2.4. Even so, no gibbsite was detected using DSC. The authors suggest that a strong "anti-gibbsite" effect occurs with Al on kaolinite solids. The "anti-gibbsite" effect has previously been proposed by Jackson (1963a).

A meager amount of research has been conducted on the interactions of Al with "soil mica" (illite) and the primary minerals biotite and muscovite. Huang and Kozak (1970), investigating the adsorption of hydroxy-Al polymers by muscovite and biotite, suggested that the increase in adsorption with a decrease in particle size is attributed to the increase in external surfaces. This seems reasonable since no available interlayer spaces should exist in K-saturated mica particles. Kozak and Huang (1971) again found that K-saturated biotite and muscovite samples adsorbed only small amounts of Al polymers which were related to external planar and edge sites of the minerals. Depletion of some K from the interlayer spaces of biotite and muscovite resulted in a larger quantity of adsorbed Al in the former mineral, but

had a negligible effect on the adsorption of Al in the latter mineral. This appeared to be due to charge effects and steric hindrance of the Al polymer in the interlayers of K depleted muscovite. El-Swaify and Emerson (1975), investigating the effect of precipitated Al and Fe hydroxides on the swelling and aggregate stability of clays after drying, suggested that hydroxy-Al interlayers appeared to be formed in soil mica reducing the relative double-layer charge and hence swelling tendencies. Turner and Brydon (1967) also suggested the formation of hydroxy-Al interlayers in soil mica. Columbera et al. (1971), on the other hand, found that soil mica adsorbed hydroxy-Al polymers according to a Langmuir isotherm and suggest that the adsorption process was not one of exchange, but involved the formation of hydrogen bonds between the OH groups of the polymer and siloxane groups on the illite surface. Investigating the systems of Al-illite and Al-montmorillonite, Edwards et al. (1965) showed positive Cl^- adsorption on the Al-clays and suggested that it was associated with the tendency of the cation to undergo hydrolysis. The authors noted that Al hydrolysis was less on the illite relative to the montmorillonite and suggested it was the result of the higher charge density of the former clay which protected the bound Al from extensive hydrolysis.

Another important constituent of many heterogeneous soil systems is organic matter. Its complex polymeric structure has been discussed by Theng (1968) and Schnitzer (1978). Aluminum interactions on peat and humic acid have been studied by many researchers in order to model actual Al interactions with organic matter found in many mineral soils. Pionke and Corey (1967) suggested that Al-organic matter complexes were quite strong since nonexchangeable Al correlated best with organic matter. They assumed however, that nonexchangeable Al was the difference between 1N NH_4OAc pH 4.8 extracted Al and KCl extractable Al. Thomas (1975) also found that Al extracted from acid soils using 1N KCl was lower as the organic matter content increased at any given pH level. This suggested that Al was tightly bound to organic matter and helped explain why no adverse effect was found on corn growth in high organic matter surface soils with pH values as low as 3.8. Spyridakis et al. (1967) observed the formation of kaolinite from the alternation of biotite to hydroxy-Al interlayered vermiculite in sand cultures in which coniferous seedlings were grown. Where organic matter was added in the culture medium, kaolinite did not form and it was suggested that the organic matter may have complexed the Al released by weathering which was essential for kaolinite formation. The strong binding of Al

species with organic matter has also been suggested by Hoyt (1976) and Sivasubramaniam and Talibudeen (1972). Coleman and Thomas (1967) suggested that most of the pH buffering in acid soils is due to hydrolysis of Al on organic matter exchange sites and not necessarily associated with organic derived hydrogen ions. This agrees with the observations of Bloom et al. (1979) who concluded that hydrolysis of organically bound Al is a major source of buffering in the pH range of 4 to 5. White and Thomas (1981) suggested that weakly acidic carboxyl groups acted as sinks for protons released during the hydrolysis and polymerization of Al on organic matter. They found a close correlation between apparent pK_a of the acid groups (from titration curves at 50% neutralization) and the basicity of the adsorbed Al suggesting that Al was more extensively hydrolyzed the weaker the average acid strength of the carboxyl groups of the exchanger. Using muck samples and a carboxylic resin to serve as a model for soil organic matter, Hargrove and Thomas (1982) suggested that it would be unlikely that Al could occupy all the reactive sites of organic matter since it is always hydrolyzed to some degree and H_3O^+ ions will be adsorbed on weakly ionized acidic groups. The average basicities of adsorbed Al on the mucks ranged from 0.88 to 2.07. The upper limit of this range agrees well with those of

White and Thomas (1981) who used acid peat and humic acid to mimic soil organic matter. Bloom et al. (1979) and Bloom and McBride (1979) suggested that hydroxy-Al ions were more preferred on organic matter than Al^{+3} . They suggest hydroxy-Al ions have a lower charge and hydration energy allowing them to more closely approach a binding site and possibly maximize the binding energy. However, Bloom (1981) further mentioned that the hexameric polymers postulated by Hsu and Rich (1960), probably are not sorbed by peat since the geometry of the peat carboxyl sites would limit, if not prevent, association with the six charges of the small ring. Hargrove and Thomas (1982) suggest however, that three, or even two, simultaneously dissociating carboxyl groups are not necessary for complexing Al^{+3} . The stability of an Al complex with humic acid was shown by Arai and Kumada (1981) to increase with decreasing distance between two adjacent carboxylic groups in the humic acid or with increasing basicity of Al species bound to the exchanger. Hodges and Zelazny (1983a) have most recently investigated the interaction of dilute, partially neutralized Al solutions with peat. They noted that the exchanger fixed Al with basicities very near that of the equilibrium solution used and that no gibbsite could be detected on the solid using DSC. The lack of Al precipitation on the peat was indirectly sug-

gested to be associated with the high charge density of the exchanger, as is the case with vermiculite.

The modeling of Al reactions with various constituents of the soil has provided much information concerning the mechanisms of retention and release of the ion in heterogeneous soil systems. However, a substantial amount of research yet remains in the application and integration of these models to true soil systems.

2.4 THE USE OF REACTION KINETICS AND ION EXCHANGE EQUILIBRIA TO CHARACTERIZE ALUMINUM INTERACTIONS IN SOIL

In order to further understand the nature of soil acidity, many researchers have attempted to characterize Al interactions in soils using the theories of ion exchange equilibria and reaction kinetics. The latter condition has been primarily concerned with kinetics and mechanisms of the autotransformation of H-clays and soils to Al-clays and soils. The interest in such studies stems from the phenomena of soil weathering and subsequent promotion of soil acidity. Eeckman and Laudelout (1961), investigating the spontaneous evolution of hydrogen montmorillonite into Al montmorillonite, noted that the reaction proceeded by an apparent first-order rate mechanism and conformed to the parabolic diffusion law. It was determined that the structure of the

tetrahedral silica layer remained essentially undisturbed during acid dissociation but that peripheral dissociation of the gibbsitic layer did occur however. These findings agree with those of Davis et al. (1962) who also investigated the autotransformation of H-montmorillonite to Al-montmorillonite. They also suggested that variations in the properties of the H-Al-montmorillonite suspensions after heating for different periods of time, may be associated with differences in the state of hydrolysis of the released Al. The reaction of H ions with the magnesian chlorite, penninite, has also been shown to follow a similar mechanism of decomposition (Brindley and Youell, 1951). Coleman and Craig (1961) prepared H-clays using the method suggested by Alrich and Buchanan (1958). They noted that H-kaolinite altered more slowly than H-montmorillonite, which agrees with the idea that kaolinite has a more stable mineral structure. They suggested congruent dissolution of the montmorillonite by H ions. A similar mechanism for H dissolution of montmorillonite was also proposed by Miller (1965). He observed the release of Al obeyed pseudo-first-order kinetics with the reaction occurring on all surfaces. The dissolution of H-kaolinite was incongruent, however, and the release was found to conform to pseudo-zero-order kinetics. Miller (1965) suggested that a diffusion controlled edge attack of

H on the kaolinite was responsible. In an in depth study on the kinetics of the conversion of Na- or Ca-saturated clay to H-Al-clay, Banin and Ravikovitch (1965) provided evidence of a two stage reaction of H ions with the montmorillonite surface. In the first stage of the reaction several facts showed that the exchangeable Al was not liberated by crystal structure decomposition. It was postulated that its appearance was the result of a rapid dehydroxylation of hydroxy-Al groups located at plate edges or adsorbed on the basal planes of the mineral. During the second stage of the reaction, spontaneous self-decomposition of the clay structure then takes place. Banin and Ravikovitch (1965) suggest that almost all work done on the autotransformation process has dealt with the latter reaction only (Low, 1955; Laudelout and Eeckman, 1958; Eeckman and Laudelout, 1961; Coleman and Craig, 1961; Davis et al., 1962; Miller, 1965).

After the work of Banin and Ravikovitch (1965), little has appeared in the literature concerning the autotransformation of H-clays and soils to Al-clays and soils. Interest began to flourish in determining the rates of retention and release of Al which was present in soils as a product of weathering. Sivasubramaniam and Talibudeen (1972) and Cabrera and Talibudeen (1978) proposed a kinetic method for determining the amount of exchangeable Al in acid soils using

1N NH_4Cl and NH_4NO_3 (pH 3), respectively. The rate of release of exchangeable Al was found to follow pseudo-first-order kinetics and noted to be much slower than the rate of release of more basic alkali and alkaline earth cations. Since the extraction of Al depends on the valence and radius of the displacing cation and the pH used in the extraction, the method should be viewed qualitatively. Brown and Hem (1975), investigating the reactions of Al species with kaolinite, montmorillonite, and volcanic ash, found that the adsorption of the monomeric species Al^{+3} and $\text{Al}(\text{OH})_2^{+1}$ followed a cation exchange equilibrium model with the reaction being essentially complete after about 1hr. Rapid adsorption of polynuclear Al hydroxide species also occurred and was found to conform to the Langmuir adsorption isotherm. The loss of polymeric Al from solution was more closely correlated with surface area than to CEC. Brown and Hem (1975) suggest that such differences between monomers and polymers in the presence of an exchanger should be anticipated since a polymer cannot be expected to behave as a monomer where each individual Al atom is bound to a charged site. Also polymers are larger with less charge per Al ion, thus their mobility and diffusion rate in solution are likely to be slower. Hodges and Zelazny (1983a) indirectly suggested that kaolinite and montmorillonite react more rapidly with

dilute, partially neutralized Al solutions relative to peat. The complex polymeric structure of peat may be responsible for this observed difference. Diffusion of Al species into the interlayer space of montmorillonite was also suggested by Carstea (1968) to be the rate limiting step during the sorption process. Additional research has also considered the rate of release of Al from synthetic gibbsite and hydroxy-Al gels in acid media (Bloom, 1983, and Nail et al., 1976c, respectively).

The use of ion exchange equilibria to describe and characterize Al interactions in soils has also been attempted. Incorrect use of the classical equilibria theories (Vanselow, 1932; Gapon, 1933; Argersinger et al., 1950; Gaines and Thomas, 1952) to describe Al reactions in soils has resulted in much misinterpreted data. Many, if not all, investigations of this type have failed to recognize several important conditions that must be met in order to use thermodynamic equilibria to describe cation exchange reactions. Reversible reactions are of the essence when using equilibria models; something which is difficult to obtain when considering Al reactions with solid exchangers. The theory assumes one knows the valence and speciation of the cation which is present in solution and on the solid; something which has not yet been solved in Al chemistry. The theory

assumes all interactions of cations with the solid phase are coulombic in nature; this has not been totally verified for Al sorption reactions with soil exchangers. The list goes on and yet numerous researchers have attempted to apply their rather complex data to the oversimplified equilibria models (Nye et. al., 1961; Clark and Turner, 1965; Chen, 1965; Pleysier et. al., 1979; Baruah et al., 1983). Some attempts have been made to correct for the first hydrolysis step of Al in solution (Coulter and Talibudeen, 1968; Coulter, 1969). Even so, the speciation of sorbed Al on the solid phase is still grossly assumed as is the reversibility of the reaction. Recently McBride and Bloom (1977), proposed a statistical model which included the solution like nature of adsorbed Ca^{+2} , and the strongly adsorbed nature of the trivalent Al species, Al^{+3} . The model was complicated by hydrolysis and precipitation reactions of Al at higher pH values and such reactions could not be accounted for by the model. Reuss (1983) attempted to generate Ca-Al exchange isotherms based on equilibrium constants obtained from the literature and corrected them for the hydrolysis of Al. Unfortunately the equilibrium constants obtained were determined under conditions which violated many of the important assumptions that must be met in order to use thermodynamic equilibria theory.

Presently no satisfactory method has been found to describe Al equilibria reactions in clays and in soils. Until a better understanding is established on how Al interacts in solution and on solid exchangers, the use of classical thermodynamic equilibria to describe Al reactions will be invalid.

Chapter III

MECHANISMS OF ALUMINUM ADSORPTION ON CLAY MINERALS AND PEAT

3.1 ABSTRACT

Mechanisms of Al adsorption on Ca-saturated kaolinite, montmorillonite, and peat were studied by miscible displacement methods. Partially neutralized 1.0×10^{-4} M AlCl_3 solutions with basicities of 1.0 were leached through monomineralic columns and effluent analyzed for monomeric and polymeric Al, titratable acidity, and desorbed Ca as functions of time. Polymeric Al was preferentially adsorbed by kaolinite throughout the displacement experiment whereas montmorillonite preferentially adsorbed monomers at short times and polymers at longer times. Selective adsorption of monomeric or polymeric Al on peat was not evident. Aluminum adsorption kinetics on kaolinite, montmorillonite, and peat was described by two simultaneous reactions -- a relatively rapid reaction involving Al-Ca exchange and a slower reaction involving Al polymerization on the adsorbents. This scenario is supported by potentiometric titrations of effluent Al and by analyses of effluent Ca, and adsorbed, ex-

changeable and nonexchangeable Al basicities. Negligible adsorption of Al on gibbsite and quartz indicated that surface bound Al on kaolinite and montmorillonite may serve as a template for adsorption of more Al.

3.2 INTRODUCTION

Recent studies on the effect of acid deposition on soils have addressed problems associated with the transport of soluble constituents through porous media. Of particular concern is the transport of Al whose solid-solution partitioning is complicated by numerous physical and chemical processes (Prenzel, 1983; Reuss, 1983). Studies on the interaction of Al with soil adsorbents generally indicate that polynuclear Al species are preferred on exchangers relative to Al monomers (Barshad, 1960; Columbera et al., 1971; Brown and Newman, 1973; Bloom and McBride, 1979). Veith (1977, 1978) and Hodges and Zelazny (1983a) have shown that smectite preferentially adsorbs large hydroxy-Al complexes, leaving less basic Al species in solution. This agrees with earlier studies which noted multilayer sorption of hydroxy-Al polymers in montmorillonite interlayers (Weismiller et

al., 1967; Sawhney, 1968; Carstea, 1968). Strong adsorption of polymeric Al on kaolinite and organic matter has also been suggested by Hodges and Zelazny (1983a,b) and Bloom et al. (1979), respectively.

Several reports indicate that Al hydrolysis is enhanced in the presence of a charged adsorbent (Rich 1960; Hsu and Bates, 1964; Veith, 1977) while others contend the reverse (Frink and Peech, 1963b; Hodges and Zelazny, 1983b). Carstea (1968) and Sawhney (1968) proposed that the more extensive hydrolysis of Al on montmorillonite as compared to vermiculite reflects lower charge densities of the former phyllosilicate. Jackson (1960) and Rich (1970), however, suggested that narrow and more extensive interlayer spaces with high charge densities may provide a more favorable environment for Al hydrolysis. Hydrolysis of organically bound Al has been shown to be a major source of buffering in acid soils (Coleman and Thomas, 1967; Bloom et al. 1979) and White and Thomas (1981) suggest that weakly acidic carboxyl groups of organic matter act as sinks for protons released during the hydrolysis and polymerization of Al. Investigating the interactions of partially neutralized Al solutions with kaolinite, Hodges and Zelazny (1983a,b) suggested Al hydrolysis is initially enhanced in the presence of the clay but with increasing aging dehydroxylation of hydrolyzed Al

results. The former contention supports previous studies which suggested that kaolinite could act a template for the precipitation of Al (Barnhisel and Rich, 1965; Turner and Brydon, 1967).

The complex interactions between aqueous and adsorbed Al are a source of much confusion. Little is known about the mechanisms and transformations of adsorbed Al in soils. In this study, we investigate some of the mechanisms of monomeric and polymeric Al adsorption on various soil constituents.

3.3 MATERIALS AND METHODS

3.3.1 Sample Preparation

Samples of poorly crystalline Georgia kaolinite and Arizona montmorillonite ("Cheto") were obtained from the Clay Minerals Repository, Dept. of Geology, Columbia, Mo. Size fractionation of the kaolinite was avoided to prevent possible concentration of trace impurities in the sample. Hodges and Zelazny (1983a,b) found no significant contaminants in this kaolinite with regard to Al sorption. Montverde peat (Evic, hyperthermic, Typic Medisaprists) from Palm Beach County, Fa., was lightly crushed and dry sieved through a 0.075 mm screen. Chemical and physical properties of this

sample have been reported by Zelazny and Carlisle (1974). Gibbsite (Reynolds Metal Company) and micron-sized silica (Min-U-Sil-5) were fractionated by standard methods and the <2- μm sample retained. Gibbsite purity was excellent as determined by differential scanning calorimetry. All samples were Ca-saturated by exhaustive leaching with 0.5 M CaCl_2 . Entrained salts were removed by several washings with 0.01 M CaCl_2 followed by washing with distilled water until a negative test for Cl^- was obtained by AgNO_3 . Duplicate subsamples of the Ca-saturated kaolinite, montmorillonite, peat, gibbsite, and quartz were extracted with five 50-mL aliquots of 0.1 M MgCl_2 and the cation exchange capacity (CEC) determined as 16.8, 1130, 1550, 0.5, 2.6, mmole kg^{-1} , respectively.

3.3.2 Al Solution Preparation

An acidified stock containing 0.01 M AlCl_3 was prepared using reagent-grade $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The amount of added acid was such that the diluted solution had a pH of 2.63. This insured that all Al initially present was trivalent (Baes and Mesmer, 1976; Stol et al., 1976). Partially neutralized Al solutions containing 1.0×10^{-4} M AlCl_3 ($2.70 \mu\text{g mL}^{-1}$ Al) were prepared by adding 10 mL of the stock solution to a li-

ter volumetric flask and diluting the sample nearly to volume with CO₂ free distilled water. A known amount of CO₂ free 4.19 x 10⁻³ M NaOH was added to the dilute Al solution using a Radiometer Autoburette so as to neutralize free acid and attain a basicity of 1.0. Base was injected into the rapidly stirred Al solution through a 0.2 mm opening in a tube immersed below the liquid surface. The rate of base addition was 0.086 mL min⁻¹ and the temperature of the mixture was kept at approximately 300 K. Following the addition of base, the solution was made to volume using CO₂ free water, mixed and stored under an N₂ atmosphere. The solution was used in the miscible displacement studies within 40 h of its final preparation. Preliminary studies have shown this solution to be stable for at least 260 h (Table 1) which was more than adequate for our purposes.

3.3.3 Miscible Displacement Experiments

Aluminum sorption on the various exchangers was studied by miscible displacement methods. Samples of 250-mg Ca-saturated kaolinite, gibbsite, and silica were placed separately in suspension with distilled water and syringe injected into 47 mm inner diameter filter apparatus containing 1.0 μm nuclepore filters. Homogenous suspensions of 20-mg

Table 1: The effect of aging on the chemical properties of 1.00×10^{-4} M AlCl_3 with a basicity of 1.1.

	Aging Time (hrs)						
	20	40	60	80	100	140	260
Solution Al ($\times 10^{-4}$ M)	1.00	1.02	1.02	1.01	1.01	1.00	1.01
Monomer Al Total soln. Al	0.602	0.592	0.585	0.602	0.608	0.619	0.592
Polymer Al Total soln. Al	0.398	0.408	0.415	0.398	0.392	0.381	0.408
pH	4.62	4.63	4.63	4.56	4.56	4.52	4.54
Average OH/Al	1.14	1.18	0.93	1.14	1.18	1.14	1.12

Ca-montmorillonite and 15-mg Ca-peat were syringe injected into filter apparatus of 20 mm inner diameter containing 0.2- μm Gelman filters. Preliminary studies indicated that Al was nonreactive with the filters (See appendix A). The samples were then leached for ~16 h at a flow rate of ~50 mL hr^{-1} with the dilute, partially neutralized Al solution and effluent was collected in ~15 mL aliquots with an automatic fraction collector. After the Al sorption process was terminated, excess solution in contact with the exchanger solid was removed using suction. The samples were immediately leached with 50 mL of 0.10 M BaCl_2 (pH 4.7) at a rate of 50 mL h^{-1} to obtain the amount of BaCl_2 -extractable Al available. Upon termination of the BaCl_2 leaching process, entrained solution was again removed from the samples before leaching subsequently with 25 mL of 0.002 M MgSO_4 in order to determine the basicity characteristics (OH/Al mole ratio) of nonexchangeable Al (Hodges and Zelazny, 1983a,b). All studies were done in duplicate and conducted under isothermal, isobaric conditions (301-303 K and atmospheric pressure, respectively). The concentration of Al was chosen to mimic that of a moderately acid soil solutions.

3.3.4 Analytical Procedures

The effluent obtained during Al sorption on the various soil constituents was analyzed for Ca using atomic absorption spectrophotometry (AAS), for titratable acidity with CO₂ free NaOH in an N₂ atmosphere using a Radiometer automatic titration system, and for Al by a colorimetric method using ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid). The BaCl₂ extract solutions were analyzed as above and for extractable Na to account for displacement of Ca by Na. The MgSO₄ extract solutions were analyzed for Mg using AAS. Effluent Al was analyzed as rapidly as possible with no sample aging more than 12 h.

The colorimetric method used for analysis of Al was similar to that proposed by Bersillon et al. (1980) except orthophenanthroline was added to the ferron solution to complex any free iron. Since ferron-Al interactions are kinetically controlled, it is possible to distinguish between Al monomers and Al polymers in solution (Hem and Rober-son, 1967; Smith, 1971; Seip et al., 1984). Difficulty arises in deciding the termination point of monomer interactions with ferron and subsequent initiation of polymer interactions. To determine this, a 10 µg mL⁻¹ Al stock solution was prepared by dissolving prescouring Al metal in a dilute HCl solution and adjusting to volume using distilled

water. Aluminum standards were prepared from this stock and all had a pH below 3.0 insuring that Al was trivalent. The interaction of standards with ferron color developing solution gave a pH of approximately 5.2 indicating that the acidity of standards did not influence normal color development (Bersillon et al., 1980). Ferron interactions with the trivalent Al standards were 90 to 95% complete within 0.5 min and 100% at 2.0 min. In samples which contain both monomeric and polymeric Al, the polymers may begin to break down and react with ferron after 0.5 min due to substantial loss of monomers within this time period. Thus, we assume that the equilibrium shift from monomer to polymer interactions with ferron occurs at 0.5 min. We render a 5 to 10% loss in monomer detection and an even lower loss in polymer detection. Since the standard curve must be conditioned at 0.5 min, the calculation of total Al involves correcting the final value obtained from the original standard curve to a curve where the standards have become stable (i.e. 2.0 min). The correction is on avg 5%. A more precise and accurate method for the speciation of monomeric and polymeric Al using ferron has been recently developed by the author but unfortunately was not used in the particular study. The reader is referred to Chapter V of this publication.

3.3.5 Calculations

The average basicity (OH/Al mole ratio) of effluent Al and BaCl₂ extractable Al was calculated as follows:

$$\text{OH/Al} = 3 - \frac{\text{titrated acidity (meq)}}{\text{Al by ferron (mmole)}} \quad (1)$$

The average basicity of adsorbed Al was determined by:

$$\text{OH/Al} = 3 - \frac{\text{meq Al adsorbed}}{\text{mmoles Al adsorbed}} \quad (2)$$

where the meq. of adsorbed Al was taken as the difference between the meq. of desorbed Ca and the meq. of extracted Na. The average basicity of nonexchangeable Al was obtained by:

$$\text{OH/Al} = 3 - \frac{\text{charge reduction (meq)}}{\text{nonexchangeable Al (mmole)}} \quad (3)$$

where the mmoles nonexchangeable Al was calculated from the difference between adsorbed Al and BaCl₂ exchangeable Al and the reduction of CEC was assumed equal to the meq. of nonexchangeable Al.

3.4 RESULTS

Effluent Al as a function of time for Ca-saturated kaolinite, montmorillonite, and peat displacement experiments are shown in figs. 1a, 2a, 3a. In general, the curves exhibit a rapid initial concentration increase which gradually slows and continues to long times. The transition between the rapid and slow Al concentration increase corroborates with the termination of desorbed Ca elution (Figs. 1a, 2a, 3a). This suggests that the initial rapid reaction involves Al-Ca exchange while further Al adsorption reflects nonelectrostatic interactions. The mechanism of this latter interaction will be discussed later in the paper.

The relative concentrations of monomeric and polymeric Al adsorbed [$1 - (\text{effluent monomer or polymer concentration} / \text{influent monomer or polymer concentration})$] on kaolinite as functions of time reveal preferential adsorption of Al polymers (Fig. 1b). Although both monomeric and polymeric Al exhibited equivalent decreases in adsorption with time, the fraction of total polymers adsorbed was always greater than monomers. Effluent Al basicities as a function of time for the kaolinite displacement experiment also suggest preferred adsorption of Al polymers on this phyllosilicate (Fig. 1c). Since basicities represent an average of all Al species in a system, inferences regarding exact speciation cannot be

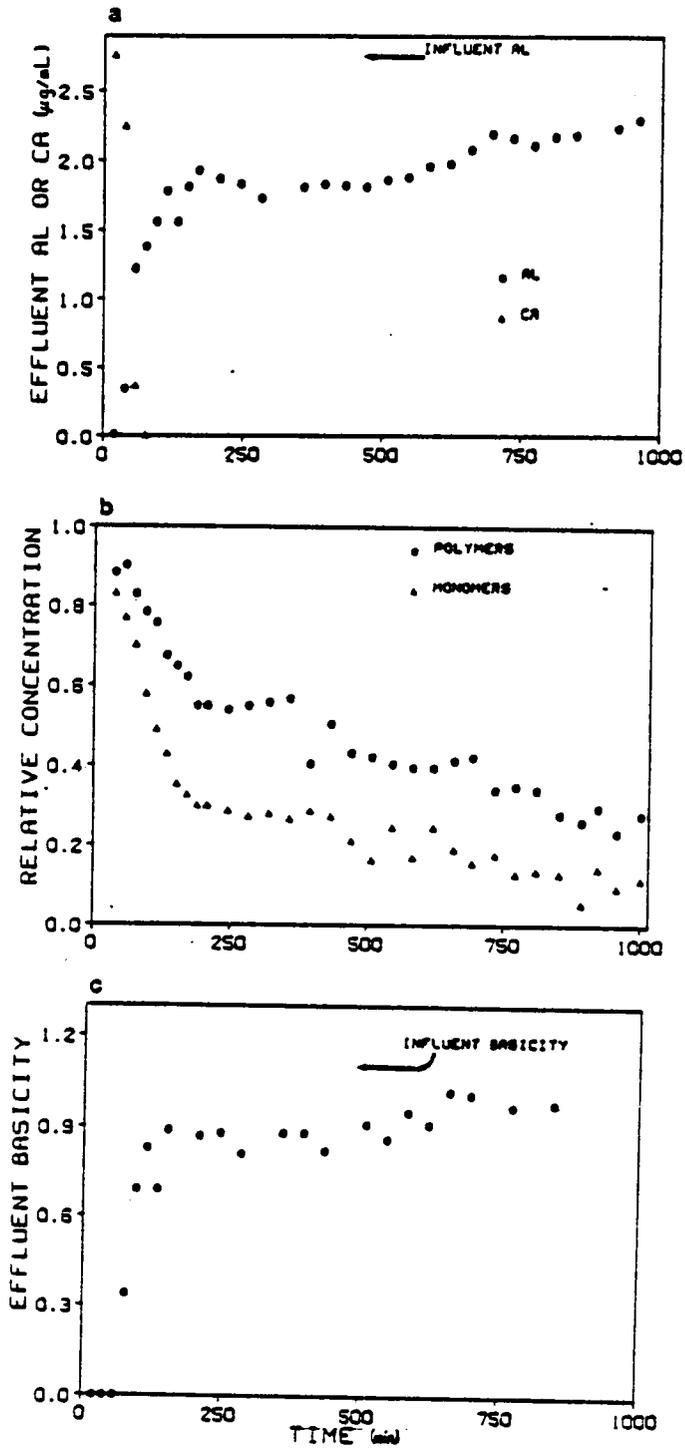


Figure 1. a) Effluent Al and Ca as a function of time for kaolinite b) Relative concentration of polymeric and monomeric Al adsorbed as a function of time on kaolinite c) Effluent Al basicities as a function of time on kaolinite.

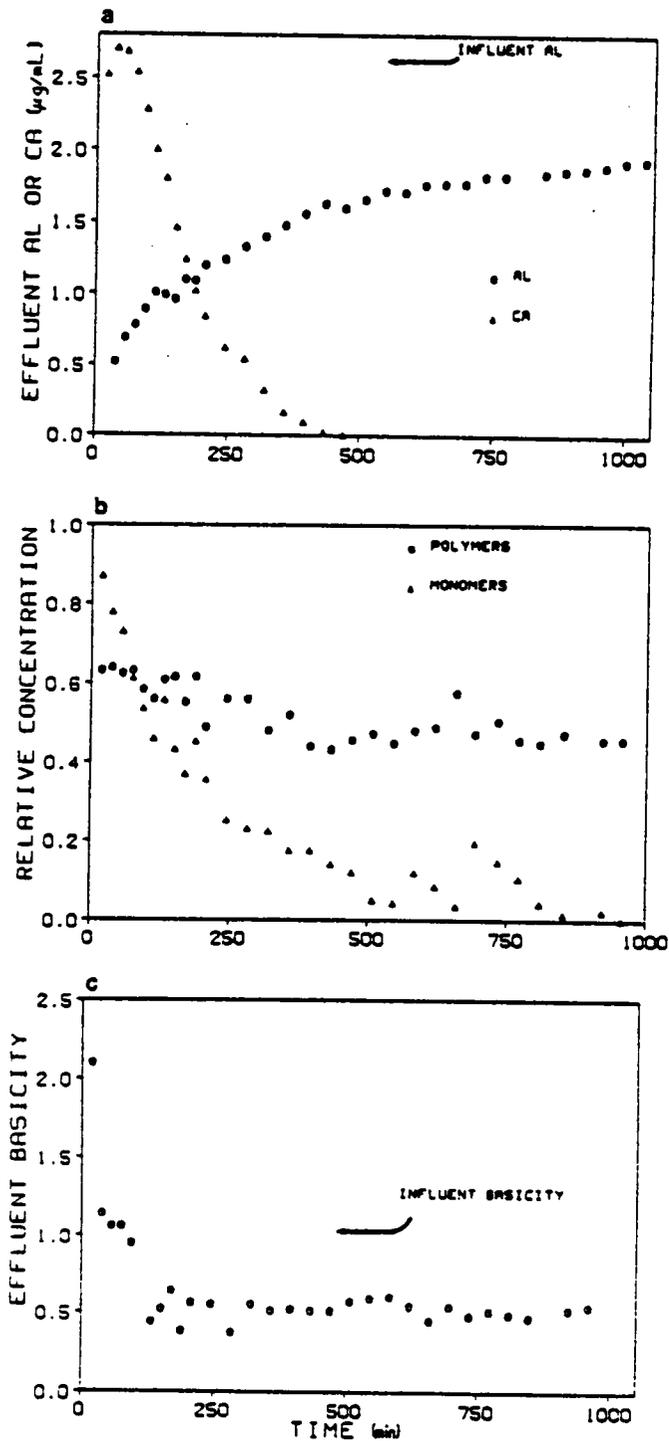


Figure 2. a) Effluent Al and Ca as function of time for montmorillonite b) Relative concentration of total polymeric and monomeric Al adsorbed as a function of time on montmorillonite c) Effluent Al basicities as a function of time on montmorillonite.

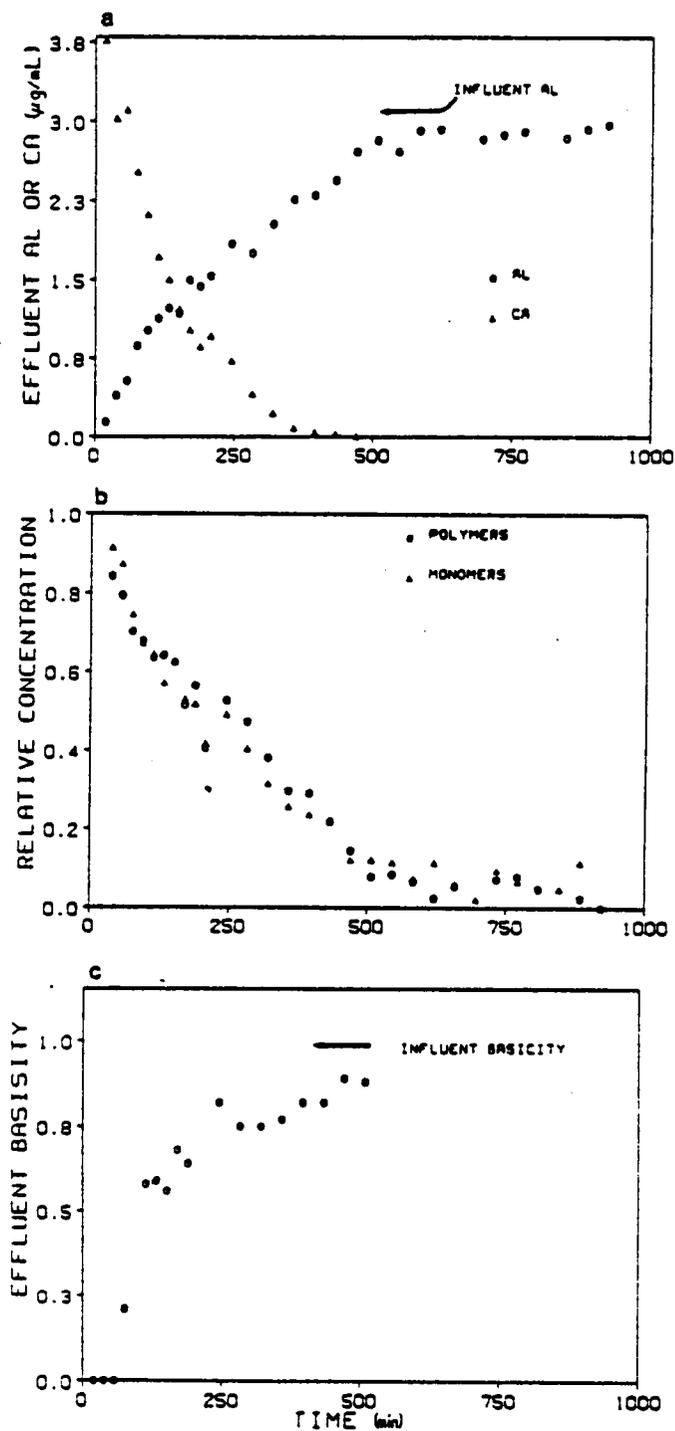


Figure 3. a) Effluent Al and Ca as a function of time for peat
 b) Relative concentration of total polymeric and monomeric Al adsorbed as a function of time on peat
 c) Effluent Al basicities as a function of time for peat.

drawn. Nevertheless, initially low effluent basicities imply that higher basicity Al species, most likely Al polymers, are removed from solution by adsorption on kaolinite. Effluent basicities increase with time but consistently remain less than the influent basicity again suggesting polymer preference on kaolinite at long times.

Interactions of Al with montmorillonite suggest an initial preference for monomeric Al followed by polymer preference at longer times (Fig. 2b). The decrease in monomer adsorption with time was much more rapid than the decrease in polymer adsorption reflecting the ability of montmorillonite to accumulate Al polymers in interlayers (Veith, 1977, 1978). The selectivity reversal for monomers and polymers of Al on montmorillonite is also evident from effluent basicities of the phyllosilicate as a function of time (Fig. 2c). Initially high effluent basicities imply that low basicity Al species, most likely Al monomers, are removed from solution and adsorbed on montmorillonite. As leaching continues, effluent basicities monotonically decrease below the influent basicity reflecting accumulation of Al polymers in interlayers of montmorillonite.

The fractions of total monomeric and polymeric Al adsorbed on peat as a function of time were nearly equal suggesting similar selectivity of both forms of Al (Fig. 3b).

However, effluent Al basicities as a function of time for the peat displacement study qualitatively suggested selective adsorption of Al polymers on the adsorbent (Fig. 3c) since effluent basicities consistently remained less than the influent basicity. The effect is difficult to quantify since average basicities provide limited information about Al selectivity. Bloom et al. (1979) have suggested the preferential adsorption of Al polymers on organic matter, however, Bloom (1981) cautioned that the adsorption of large Al polymers by peat may be limited by the geometry of the adsorbents carboxyl sites.

3.5 DISCUSSION

The rapid interaction of Al on Ca-saturated kaolinite, montmorillonite, and peat involves Al-Ca exchange while further Al adsorption reflects nonelectrostatic interactions (Figs. 1a, 2a, 3a). The latter reaction was much less significant on peat relative to the phyllosilicates. The nonelectrostatic interaction of Al with the exchangers is believed to involve Al polymerization on the solid phase and is supported by the following discussion.

Potentiometric titration curves of effluent from the kaolinite, montmorillonite, and peat displacement experi-

ments revealed the presence of H^+ inflections whereas titration curves of influent show no such inflections (Fig. 4). The presence of H^+ ions in the effluent suggests the enhanced hydrolysis of Al in the presence of the adsorbents. The more pronounced H^+ inflection on the titration curve for kaolinite effluent relative to the montmorillonite and peat effluent suggests the degree of Al hydrolysis on kaolinite is much more extensive. This point is seen more clearly by calculating the quantity of effluent H^+ from potentiometric titration curves for the various displacement experiments as a function of time (Fig. 5). The quantity of H^+ in the effluent for the kaolinite displacement experiment initially increases quickly to a maximum before gradually decreasing with continued leaching (Fig. 5). A more gradual and less dramatic increase of effluent H was noted for montmorillonite and peat followed by a slow decrease for the former adsorbent at longer times. Unfortunately, potentiometric titrations were not conducted on effluent Al at longer times for the peat displacement study, however, a decrease in effluent H with time would most likely occur. The larger quantity of H^+ in the kaolinite effluent as a function of time relative to the montmorillonite and peat, suggests the degree of Al hydrolysis on kaolinite is much more extensive.

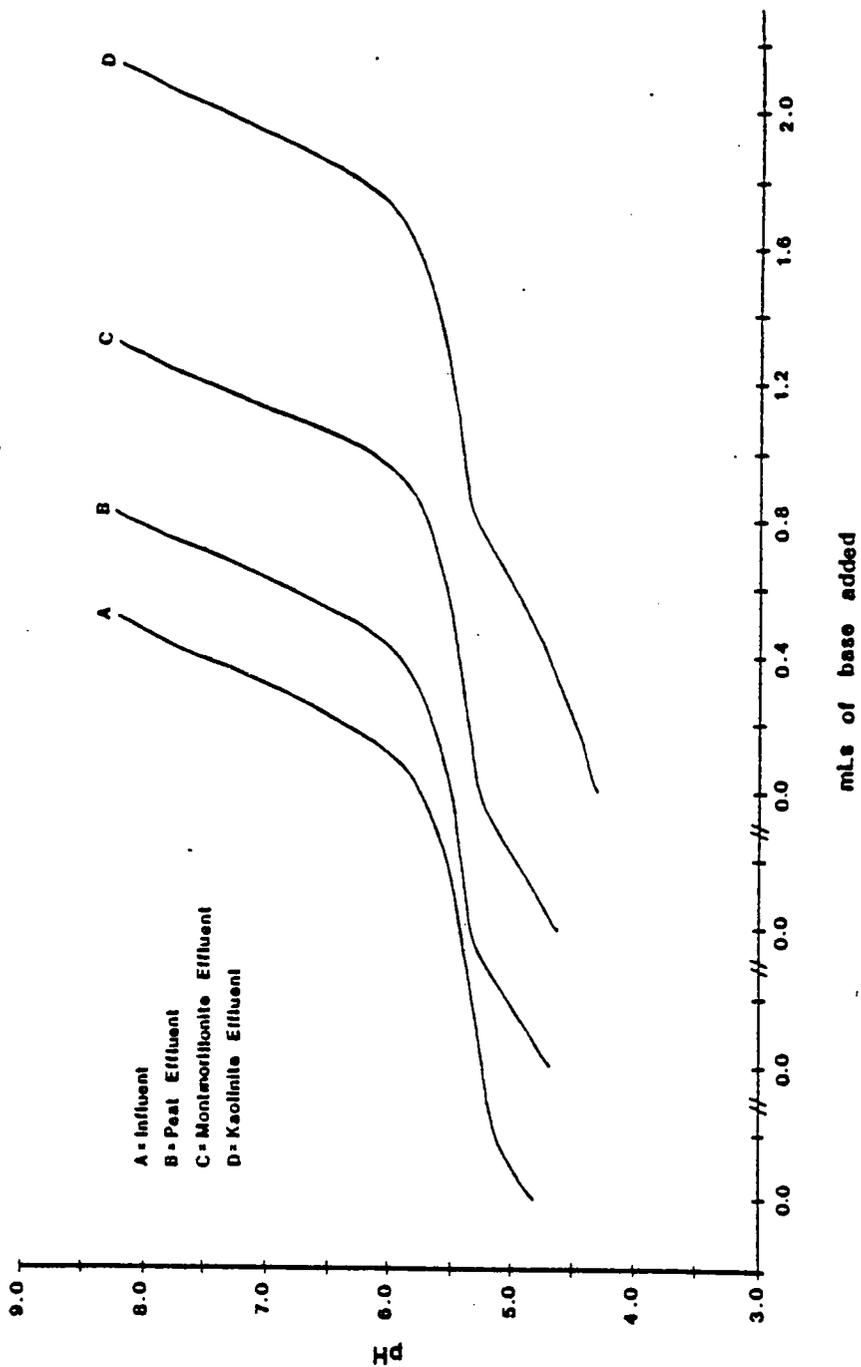


Figure 4. Example potentiometric titrations of influent and effluent Al for peat, montmorillonite, and kaolinite having similar levels of acidity.

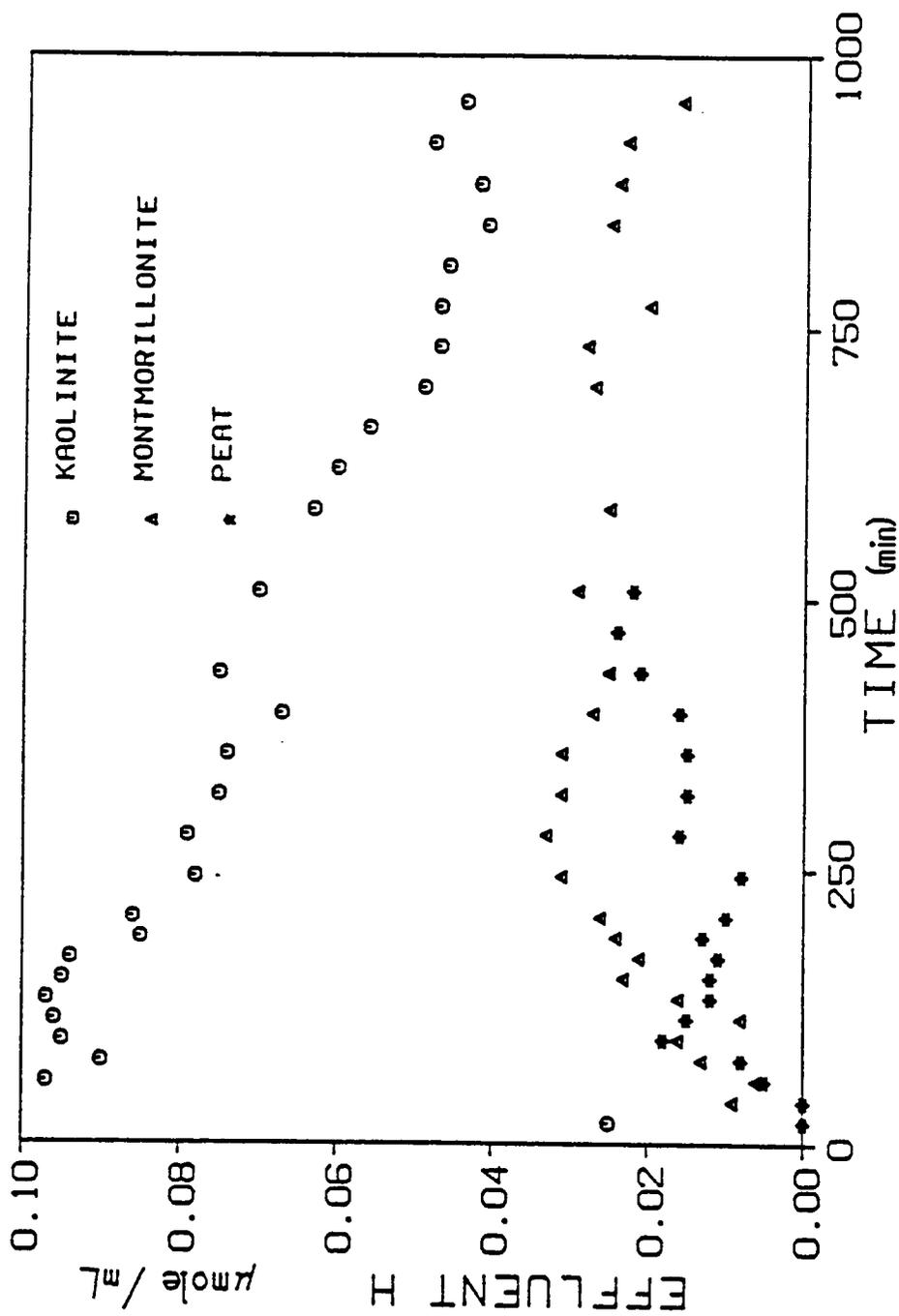


Figure 5. Effluent H as a function of time for kaolinite, montmorillonite, and peat.

Variations in effluent H with time indicate the loss of Al from solution is indeed the result of adsorption and not solution precipitation. The latter would result if the solution phase was supersaturated with respect to gibbsite when in contact with the adsorbent and effluent H would be constant as a function of time for these transient conditions. This is not the case for the displacement experiments presented and it appears that the loss of Al from solution is the result of adsorption onto the exchangers. The partially neutralized Al solution with no adsorbent (influent) was also not supersaturated with respect to gibbsite and was stable for at least 260 h (Table 1).

Enhanced hydrolysis of Al in the presence of kaolinite, montmorillonite, and peat is also reflected in the high average basicity values for adsorbed, exchangeable, and nonexchangeable Al (Table 2). Basicities were higher for kaolinite followed by montmorillonite and peat in agreement with the inferred degree of Al hydrolysis on the adsorbents (Figs. 4 and 5). This is consistent with the fact that although the amount of BaCl_2 -extractable Al was similar for all adsorbents, the fraction of polymeric Al extracted was higher for kaolinite than for montmorillonite and peat (Table 2). The average basicities for exchangeable and adsorbed Al for the various displacement experiments were also higher

Table 2. Chemical characteristics of BaCl₂ exchangeable Al and average basicities for adsorbed, exchangeable, and non exchangeable Al on kaolinite, montmorillonite, and peat.

Sample	-----BaCl ₂ extract-----				Average OH/Al	Average OH/Al total, ads. Al	Average OH/Al nonexchangeable Al
	BaCl ₂ ext. Al Total ads. Al	monomer Al BaCl ₂ ext. Al	polymer Al BaCl ₂ ext. Al				
Kaolinite	0.353	0.140	0.860	2.10	2.71	2.86	
Montmorillonite	0.290	0.299	0.701	1.82	2.41	2.85	
Peat	0.359	0.381	0.619	1.39	2.08	0.88	

than the average basicity of influent Al (i.e. $\text{OH}/\text{Al} = 1.0$). This suggests both the preferential adsorption of Al polymers and the enhanced hydrolysis of adsorbed Al by the exchanger. High basicity values for nonexchangeable Al on kaolinite and montmorillonite suggest the fixation of large hydroxy-Al polymers resulting from both adsorption from solution and extensive polymerization of surface bound Al (Table 2). The lower basicity value for nonexchangeable Al on peat implies that polymer adsorption and polymerization of surface bound Al are not as prevalent on this exchanger. This is consistent with the lesser amount of Al adsorbed by non-electrostatic interactions of Al with peat relative to the phyllosilicates (Figs. 1a, 2a, 3a). Hodges and Zelazny (1983a) have also found that kaolinite and montmorillonite fix Al of high basicity whereas peat tends to fix Al with basicities very near that of the influent solution.

Independent investigations of Al adsorption on $< 2 \mu\text{m}$ gibbsite and quartz from partially neutralized Al solutions, revealed negligible adsorption of Al. These minerals were used to mimic Al reactions on exposed octahedral surfaces and tetrahedral edges of phyllosilicates, respectively. The negligible adsorption on these minerals indicates that Al most likely is not binding to the uncharged octahedral surfaces and tetrahedral edges of kaolinite and montmorillo-

nite, but rather electrostatically-bound Al on kaolinite and montmorillonite may serve as a template for adsorption of more Al. Thus, the slow secondary reaction of Al on these phyllosilicates and peat may reflect Al polymerization on the solid phase.

Chapter IV

KINETICS AND MECHANISMS OF ALUMINUM ADSORPTION ON KAOLINITE USING A TWO-SITE NONEQUILIBRIUM TRANSPORT MODEL

4.1 ABSTRACT

Kinetics of Al adsorption on Ca-kaolinite at selected concentrations, pH, and column lengths were studied using a miscible displacement technique. Observed breakthrough curves (BTC) for continuous injection of pH 4.3, 0.75 - 7.75 $\mu\text{g mL}^{-1}$ Al solution were well-described by a two-site nonequilibrium transport model which assumes that sorption sites can be divided into two fractions: (1) instantaneous equilibrium sites and (2) sites following first-order reversible kinetics. Independent verification of the fitted parameter β , related to the fraction of type-1 equilibrium sites, was possible by assuming negative surface charge sites of kaolinite were in local equilibrium with the solution phase. Confirmation of the fitted parameter R, which is a measure of the total Al adsorbed, was not possible due to the non-singular nature of the equilibrium adsorption isotherm. First-order rate coefficients (α) for Al adsorption on kaolinite were unaffected by column length. Effects of infl-

uent Al concentration on α were small but suggested that kinetic reaction of Al with kaolinite was not strictly first-order. Decreasing the pH of influent solution from 4.3 to 4.0, eliminated type-2 kinetic sites. These effects indicate that kinetic reactions involve Al polymerization on kaolinite while equilibrium reactions reflect Ca-Al exchange. This scenario is supported by Ca desorption data of the effluent and by potentiometric titrations of effluent solutions.

4.2 INTRODUCTION

Analyses of reactive solute transport in porous media often assume local equilibrium occurs between solution and solid phases. The inadequacy, in many instances, of this assumption has spurred the development of more complex conceptual models (e.g. Villermanx, 1974; van Genuchten and Wierenga, 1976; Selim et al., 1977; Bhattacharya and Gupta, 1979; Chu and Sposito, 1981; Parker and Jardine, 1986) One approach has been to assume disequilibrium results from stagnant zones creating diffusional barriers between reac-

tion sites and the mobile fluid phase (Skopp and Warrick, 1974; De Smedt and Wierenga, 1979; Rao et al., 1980; Nkedi-Kizza et al., 1983). Other investigators have considered disequilibrium due to chemical kinetics of various reactions in heterogeneous systems (Cameron and Klute, 1977; Mathews and Weber, 1980; Chu and Sposito, 1981; Fluhler and Jury, 1983; Mironenko and Pachepsky, 1984). The latter models, commonly known as two-site nonequilibrium models, have been successfully employed to describe transport of a number of organic and inorganic species in soils (Hoffman and Rolston, 1980; Fluhler and Jury, 1981; van Genuchten, 1981).

Much research has been conducted on the interactions of Al with various adsorbents although few studies have addressed Al transport through porous media. The physical and chemical processes that govern solid-solution partitioning of Al are numerous and complex (Columbera, et al. 1971, Brown and Hem, 1975). Several reports indicate that Al hydrolysis is enhanced in the presence of a charged adsorbent (Hsu and Bates, 1964; Veith, 1977) while others contend the reverse (Frink and Peech, 1963). In recent investigations of the interaction of dilute, partially neutralized Al solutions with kaolinite, Hodges and Zelazny (1983 a,b) reported enhanced hydrolysis of Al in the presence of clay and found that Al was bound far in excess of the CEC. These findings

support previous investigations which suggested that kaolinite could act as a template for the precipitation of Al (Barnshisel and Rich, 1965; Turner and Brydon, 1967).

Little is known about the rates and mechanisms of Al sorption on various soil constituents. In this study, we investigate the kinetics and mechanisms of Al sorption on kaolinite by applying a two-site nonequilibrium transport model to transient displacement experiments.

4.3 MATERIALS AND METHODS

4.3.1 Theoretical

To analyze transient displacement experiments, we will employ the transport model of Selim et al. (1976) and Cameron and Klute (1977) which assumes that sorption sites may be partitioned into two types. Adsorption on "type-1" sites is assumed to be instantaneous and reversible, while adsorption on "type-2" sites is assumed to follow reversible first-order kinetics.

One-dimensional transport of a single reactive solute species during steady fluid flow in a homogeneous system is described by the convective-dispersive equation

$$\frac{\rho}{\theta} \frac{\partial S}{\partial t} + \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (4)$$

where s is the total adsorbed solute mass per unit mass of solid, c_r is the resident concentration of solute in the liquid phase, ρ is the porous medium bulk density, θ is the volumetric water content, D is a dispersion coefficient reflecting combined effects of diffusion and hydrodynamic dispersion on transport, v is the mean pore water velocity, t is time, and x is distance. At equilibrium, the interaction of solute with both type-1 and type-2 sites is assumed to be described by linear (or linearized) isotherms

$$s_1 = k_1 c_r \quad (5)$$

$$= Fk c_r$$

$$s_2 = k_2 c_r \quad (6)$$

$$= (1 - F)k c_r$$

where subscripts 1 and 2 refer to type-1 and type-2 sites, $k = k_1 + k_2$ is a net distribution coefficient, and $F = k_1/k$ is the fraction of type-1 sites present.

Because type-1 sites are always in equilibrium, it follows that,

$$\frac{\partial s_1}{\partial t} = Fk \frac{\partial c_r}{\partial t} \quad (7)$$

The adsorption rate for type-2 sites is described by

$$\frac{\partial s_2}{\partial t} = \alpha \{(1 - F)k c_r - s_2\} \quad (8)$$

where α is a first-order rate coefficient. Substituting Eqn. 7 into 4 and noting that $s=s_1+s_2$ yields

$$\left(1 + \frac{F_0 k}{\theta}\right) \frac{\partial C_r}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_2}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (9)$$

Equations 8 and 9 are solved subject to a uniform equilibrium initial condition and first-type inlet boundary condition for a semi-infinite medium appropriate for continuous injection and for flux-averaged solute detection in the effluent (Parker and van Genuchten, 1984). The solution is cast in nondimensionalized form and it will be convenient for discussion purposes to introduce the following scaled variables.

$$T = vt/L \quad (10)$$

$$P = vL/D \quad (11)$$

$$R_1 = 1 + \rho k_1/\theta \quad (12)$$

$$R = 1 + \rho k/\theta \quad (13)$$

$$\beta = R_1/R \quad (14)$$

$$\omega = \alpha(1 - \beta)RL/v \quad (15)$$

$$\bar{c} = (c_e - c_i)/(c_0 - c_i) \quad (16)$$

where L is the column length, T is the number of eluted pore volumes, P is a column Peclet number, R_1 is a retardation factor associated with type-1 sites, R is a net retardation

factor, β and w are reduced site distribution and rate constants, respectively, and \bar{c} is the reduced effluent concentration with c_e the effluent concentration, c_i the initial concentration and c_o the influent concentration.

For the miscible displacement experiments studied here involving Al solutions passing through Ca-kaolinite, values of the reduced parameters w , R , β , and P (corresponding to original parameters α , k , F , and D) are evaluated by fitting measured $\bar{c}(T)$ data to the mathematical model by least-squares inversion as described by Parker and van Genuchten (1984). Independent estimates of R and β from batch experiments were also evaluated for comparison with fitted values. It is assumed that Al-Ca exchange on kaolinite will be virtually instantaneous (type-1 sites) while type-2 behavior will arise due to non-electrostatic adsorption associated with surface Al polymerization reactions. Accordingly, an estimate of type-1 sites on kaolinite is made from Ca-Mg exchange capacity (CEC) measurements with the linearized adsorption coefficient estimated as

$$k_1^k = \sigma^k / c_o \quad (17)$$

where σ^k is the CEC of kaolinite expressed as an equivalent adsorbed mass of Al^{+3} per unit solid mass. Estimates of the adsorption coefficient k_1^C for cellulose powder used as filler in the displacement experiments were similarly evaluated. The net k_1 was then calculated as

$$k_1 = \frac{\rho^k k_1^k + \rho^c k_1^c}{\rho^k + \rho^c} \quad (18)$$

where superscripts k and c represent kaolinite and cellulose and ρ^k and ρ^c are masses of each component per unit total column volume. Given k_1 , the retardation factor R_1 may be obtained from Eqn. 12.

Estimates of $k^k = k_1^k + k_2^k$ were made from isohaline batch equilibrium isotherms of Al on Ca-kaolinite by assuming the area under a linearized isotherm is equal to that under the actual isotherm, i.e.:

$$k^k \int_{c_i}^{c_o} c_r dc_r = \int_{c_i}^{c_o} s^k(c_r) dc_r \quad (19)$$

where $s^k(c_r)$ is the experimental isotherm (van Genuchten, 1981). The corresponding value of k and hence R for the porous medium with cellulose filler was calculated in a manner analogous to Eqn. 18. Preliminary tests showed $k^c = k_1^c$ and since Al adsorption on cellulose was on average less than 5% of the total, no distinction between k^c and k_1^c was made.

4.3.2 Experimental

4.3.2.1 Sample Preparation

Samples of poorly crystalline Georgia kaolinite, obtained from the Clay Minerals Repository, Columbia Missouri, and Whatman CF11 fibrous cellulose powder were Ca-saturated by exhaustive leaching with 0.5 M CaCl_2 . Entrained salts were removed by several washings with 0.01 M CaCl_2 followed by washings with distilled water until a negative test for Cl^- was obtained using AgNO_3 . Fractionation of the kaolinite was avoided to prevent possible concentration of trace impurities in the sample. Hodges and Zelazny (1983 a,b) found no significant contaminants in this kaolinite with regard to Al sorption. The CEC of the kaolinite and cellulose was determined by Ca-Mg exchange and was found to be 16.8 and 2.2 mmole kg^{-1} , respectively.

4.3.2.2 Al Solution Preparation

An acidified stock containing 0.02 M AlCl_3 was prepared using reagent-grade $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The amount of added acid was such that the diluted solution had a pH of 2.65. This insured that all Al initially present was trivalent (Baes and Mesmer, 1976). Un-neutralized Al solutions ranging from 2.78×10^{-5} to 2.87×10^{-4} M AlCl_3 (0.75 - $7.75 \mu\text{g mL}^{-1}$ Al) were prepared by adding a known volume of the stock solution

to a one liter volumetric flask and diluting the samples with distilled water. Where pH adjustments were required, a known amount of dilute HCl was added to the Al solution prior to dilution. All solutions had a pH very close to 4.30 except those involved in the variable pH study in which solution pH ranged from 3.97 to 4.30. The pH adjustments were monotonic and hydroxyl ions were never added to the solutions. Experimental and theoretical investigations suggested that the un-neutralized, dilute Al solutions were primarily trivalent Al (Al^{+3}) and were very stable with time.

4.3.2.3 Miscible Displacement Experiments

The kinetics of Al sorption on kaolinite were studied using a miscible displacement technique. A sample of 250 mg Ca-kaolinite was mixed with varying amounts of Ca-cellulose (0-1.50 g) and placed in suspension with 7.5×10^{-5} M CaCl_2 . Plexiglass columns of 10mm inner diameter were fitted with 1 μm nuclepore filters supported on porous plastic disc at the column exit. Preliminary studies indicated that Al was non-reactive with the filters (See appendix A). Columns of varying length were prepared by wet packing kaolinite-cellulose mixtures under suction. They were then leached at a constant flow rate (Table 3) with dilute Al solution until the

effluent concentration nearly equaled that of the influent. Effluent of known volume was collected with an automatic fraction collector. All kinetic studies were conducted at 300 K and atmospheric pressure. The concentration of Al used in this study was chosen to mimic that of a moderately acid soil solution.

4.3.2.4 Analytical Procedures

Effluent obtained during kinetic analyses of Al sorption on kaolinite were analyzed for Ca using atomic absorption spectrophotometry and for Al by a colorimetric method using ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid). The latter method is similar to that proposed by Bersillon et al. (1980) except 1,10-phenanthroline was added to the ferron solution in order to complex any free iron. Several effluent solutions were also analyzed for titratable acidity using a Radiometer automatic titration system. The porosity and column lengths of the medium were measured for each experiment (Table 3). These measurements were made by conventional direct methods except for the case of the ca. 3 mm column with no cellulose filler. In order to determine the height of this column, the solid phase volume was calculated from the measured clay density and total mass. The total

Table 3. Physical parameters for column displacement experiments.

Experiment Number	Column Length mm	Influent Concentration $\mu\text{g mL}^{-1}$	pH	ρ kg m^{-3}	ρ_k/ρ	θ $\text{m}^3 \text{m}^{-3}$	v $\text{m s}^{-1} \times 10^5$
1	3.2	4.86	4.30	495	1.00	.810	6.11
2	22.0	5.06	4.28	448	.324	.803	19.83
3	42.5	4.85	4.30	364	.208	.787	21.03
4	64.3	5.18	4.29	333	.149	.784	21.11
5	38.6	0.73	4.29	397	.208	.805	21.09
6	38.7	1.51	4.28	395	.208	.809	20.99
7	39.4	2.37	4.38	389	.208	.814	20.87
8	39.7	7.75	4.20	385	.208	.817	20.79
9	39.2	1.56	4.08	385	.208	.825	20.59
10	39.7	1.50	3.97	385	.208	.808	21.02

sample volume was then calculated from the measured (saturated) water content and solid volume to obtain the sample length as the ratio of total volume and cross sectional area.

4.3.2.5 Batch Equilibrium Adsorption Experiments

Known amounts of Ca-kaolinite, ranging from 0.01-1.00 g, were added to 100 mL polyethylene centrifuge tubes and mixed with 50 mL of 1.90×10^{-4} M AlCl_3 (pH 4.30). The samples were sealed and shaken periodically for six days under constant temperature conditions (300 K). Preliminary investigations indicated this period of time was sufficient to attain equilibrium. The samples were then centrifuged and the supernatant analyzed for Al using the ferron procedure. Aluminum adsorption was taken as the difference between initial Al in solution and that remaining after equilibration.

4.4 RESULTS AND DISCUSSION

Observed Al breakthrough curves (BTC) for the Ca-kaolinite displacement experiments are shown in Figures 7-16 along with two-site model fitted curves using optimized values of parameters P , R , β , and ω . In general, the curves

exhibit a rather abrupt but retarded initial concentration increase followed by extended tailing which continues to long times. The abruptness of the initial breakthrough reflects the high column Peclet numbers (Tables 4-6) resulting from uniform packing. In the context of the two-site model, the initial increase in concentration should reflect saturation of type-1 sites (after R_1 pore volumes) while the duration of tailing is governed by the rate constant for type-2 sites.

Fitted Al BTC using the two-site model, shown as smooth curves in Figures 7-16, indicate quite good agreement with measured data. This does not necessarily substantiate the model since curve fitting may simply compensate for experimental artifacts. Thus, we wish to investigate possible independent means of evaluating the model parameters R and β . Consider first the estimation of R from the Al adsorption isotherm (Fig. 6). Following linearization with Eqn. 19 and correction for cellulose (ranging from 0 - 10% of the kaolinite adsorption capacity) R values denoted as R^{calc} were obtained which ranged from 0.95 - 2.95 times the fitted values (Tables 4-6). Several reasons seem apparent for these deviations. Colwell and Dranoff (1971) and Reardon (1981) have suggested that the application of a linear adsorption model to nonlinear processes may yield erroneous transport param-

Table 4. The effect of column length on various transport parameters at constant influent Al concentration and pH.

Experiment Number	Column Length mm	P	R _{calc}	R _{fit}	β_{calc}	β_{fit}	α_{fit} hrs ⁻¹
1	3.2	35.9	71.28	181.05	.160	.289	.147
2	22.0	26.2	23.48	22.35	.409	.399	.256
3	42.5	183.8	13.59	17.10	.325	.363	.262
4	64.3	171.4	9.90	13.47	.288	.354	.198

Table 5. The effect of influent Al concentration on various transport parameters at constant column length and pH.

Experiment Number	Influent Concentration $\mu\text{g mL}^{-1}$	P	R_{calc}	R_{fit}	β_{calc}	β_{fit}	α_{fit} hrs ⁻¹
5	0.73	53.9	40.21	51.77	.632	.620	.132
6	1.51	57.4	25.22	42.23	.415	.417	.124
7	2.37	58.4	16.78	49.62	.216	.261	.127
3	4.85	183.8	13.59	17.10	.325	.363	.262
8	7.75	114.3	*	11.97	.329	.385	.330

* Data not available from isotherm

Table 6. The effect of pH on various transport parameters at constant influent concentration and column length.

Experiment Number	pH	P	R <u>fit</u>	β <u>calc</u>	β <u>fit</u>	α <u>hrs⁻¹</u>
6	4.28	57.4	40.27	.415	.417	.124
9	4.08	97.5	20.05	.785	.782	.277
10	3.97	89.7	14.67	1.000	1.000	--

ters. Recently, however, Valocchi (1984) reported that such applications may yield minimal error if dispersion is low (i.e. high column Peclet number). In this study the Peclet numbers were all greater than or close to 50 (Tables 4-6). Thus it seems improbable that the linearization technique is responsible for the observed discrepancy between fitted and isotherm-derived R values.

Another more likely reason may be related to the non-singular nature of the isotherm. Unique, single-valued ion adsorption isotherms can only be obtained for binary systems kept at constant ionic strength and temperature. Later in the manuscript it will be shown how the hydrolysis of Al is enhanced in the presence of kaolinite. As the process occurs, H^+ ions are excluded from the hydration waters surrounding the ion. Thus, it appears that the assumed binary system is at least ternary. Since the isotherm is not unique, it is understandable why R values obtained from the "isotherm" are dissimilar to those indicated by the column experiments. The R values obtained from the latter method will closely correspond to the areas above the \bar{c} versus T curves which indicate the total Al adsorbed. This is approximated to within small error thus yielding estimates of R which are more meaningful for transient conditions than batch isotherm values.

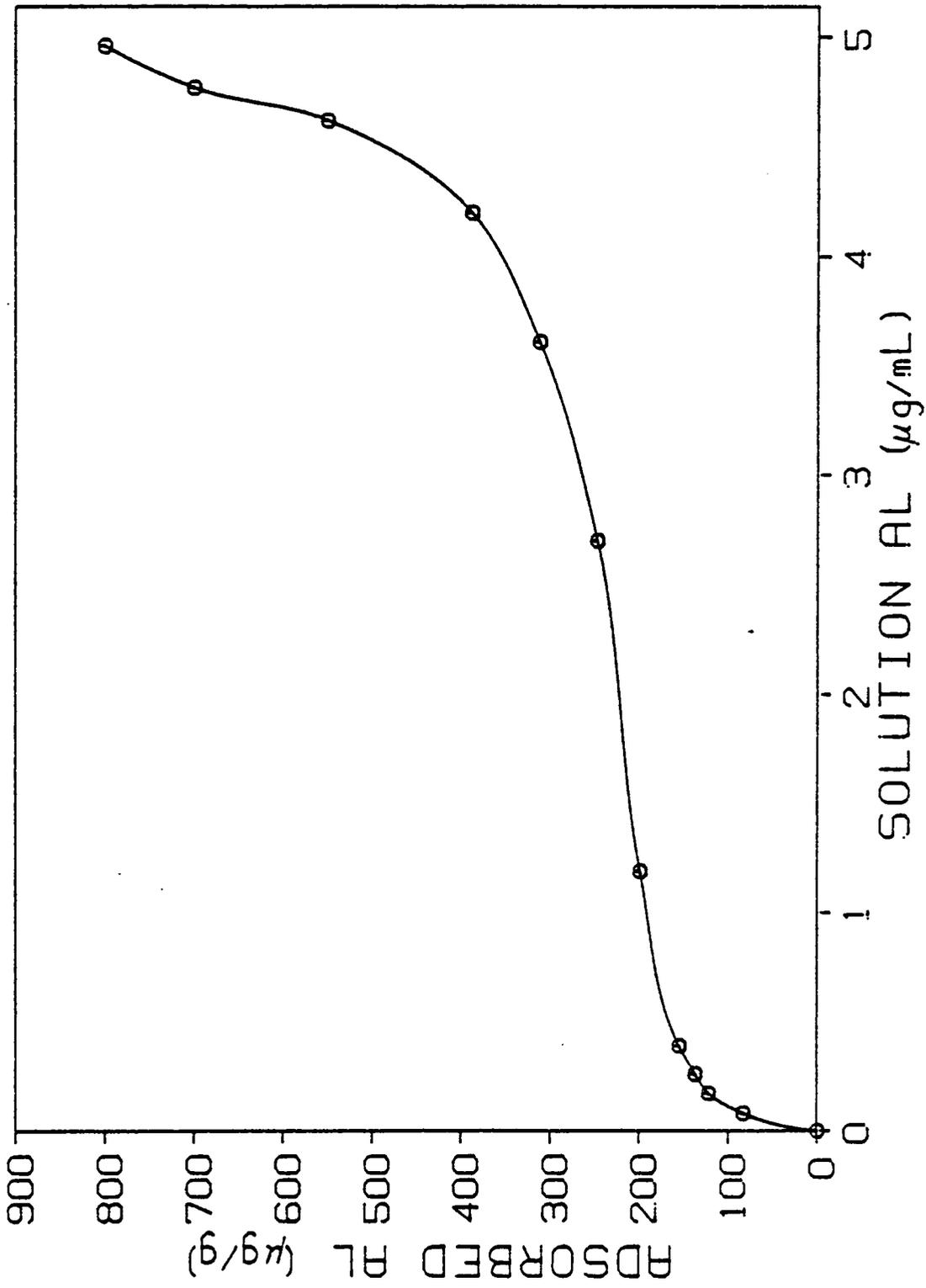


Figure 6. Batch equilibrium adsorption isotherm for Al on kaolinite.

Independent estimates of R_1 were obtained from CEC measurements and $\beta^{calc} = R_1/R$ calculated from these R_1 values and BTC-fitted R values. The calculated β compare well with BTC-fitted values (Tables 4-6) suggesting that the exchange sites of kaolinite, initially saturated with Ca, did indeed act as type-1 sites in local equilibrium with the solution phase. This is further supported by the simultaneous termination of Ca desorption with the change in slope of the Al BTC (Fig. 7). Recall the initial concentration increase of the Al BTC reflects saturation of type-1 sites. Slight deviations of CEC-calculated β values with the BTC-fitted values may reflect the variable charge nature of the kaolinite in the presence of a system whose pH is altered by Al hydrolysis. The general agreement between values of β , however, supports the validity of the model as a mathematical approximation for describing Al reactions on kaolinite.

Breakthrough curves which were fit by the two-site model were characterized by a rapid initial concentration increase followed by extended tailing. The slope and duration of the tailing is governed by the rate coefficient (α) for type-2 sites which are kinetically controlled. Varying column length, while holding influent Al concentration and pH constant, produced no consistent effect on values of α (Table 4, Figs. 8-11). The low value for α observed for the

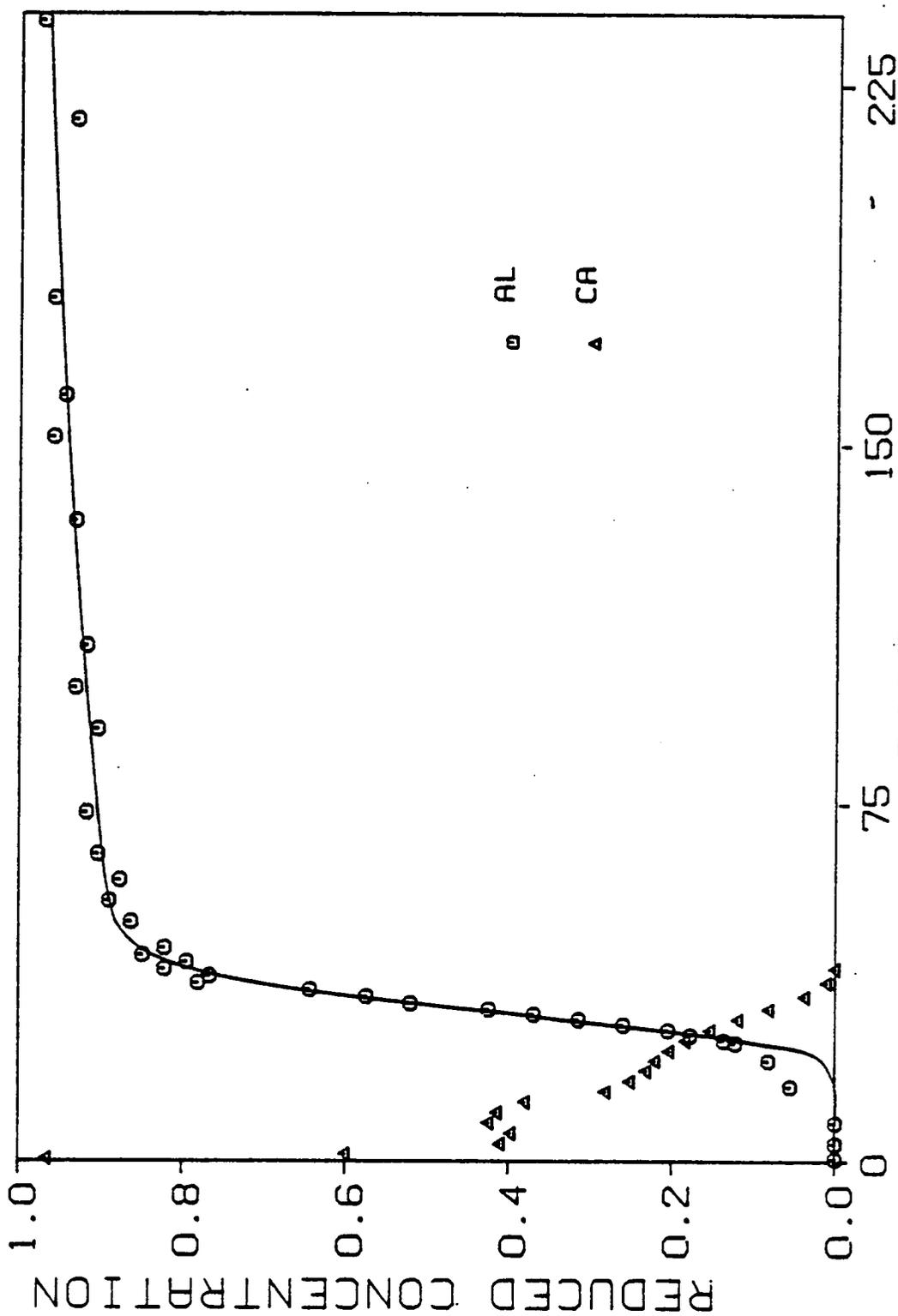


Figure 7. Breakthrough curve for $0.73 \mu\text{g mL}^{-1}$ Al at pH 4.29 on kaolinite with corresponding desorbed Ca. Solid line is the fitted curve from the nonequilibrium model. Note scales of abscissa for Figs. 7-16 differ.

shortest column may reflect the slower velocity at which the influent solution was leached through the clay (Table 3). If slower velocities caused reaction kinetics to be governed by diffusive mass transport, α could become dependent on v (Nkedi-Kizza et al., 1983). The impervious nature of this system, which had no cellulose filler, resulted in severe back-pressures which limited the pump's ability to maintain a higher flow rate. Because clay mass was held constant, increasing column length resulted in lower clay density ρ^k (Table 3) thus causing R to decrease with increasing L (Table 4).

Variations of influent Al concentration, at nearly constant pH and column length, appeared to have a slight effect on predicted α values (Table 5, Figs. 7,10,12,13, and 14). If the reaction is strictly first-order, α should be independent of the influent concentration of Al. Since the present system varies in its concentration of H_3O^+ and Al as transport occurs, deviations from first-order kinetics may be expected. The enhanced hydrolysis of Al on the kaolinite will result in a system which is at least second-order. Nevertheless, it appears that quasi-first-order kinetics serves as a good approximation of this transport problem for given influent characteristics. Calculated and fitted values for $R_1=R\beta$ decreased as the concentration of influent Al

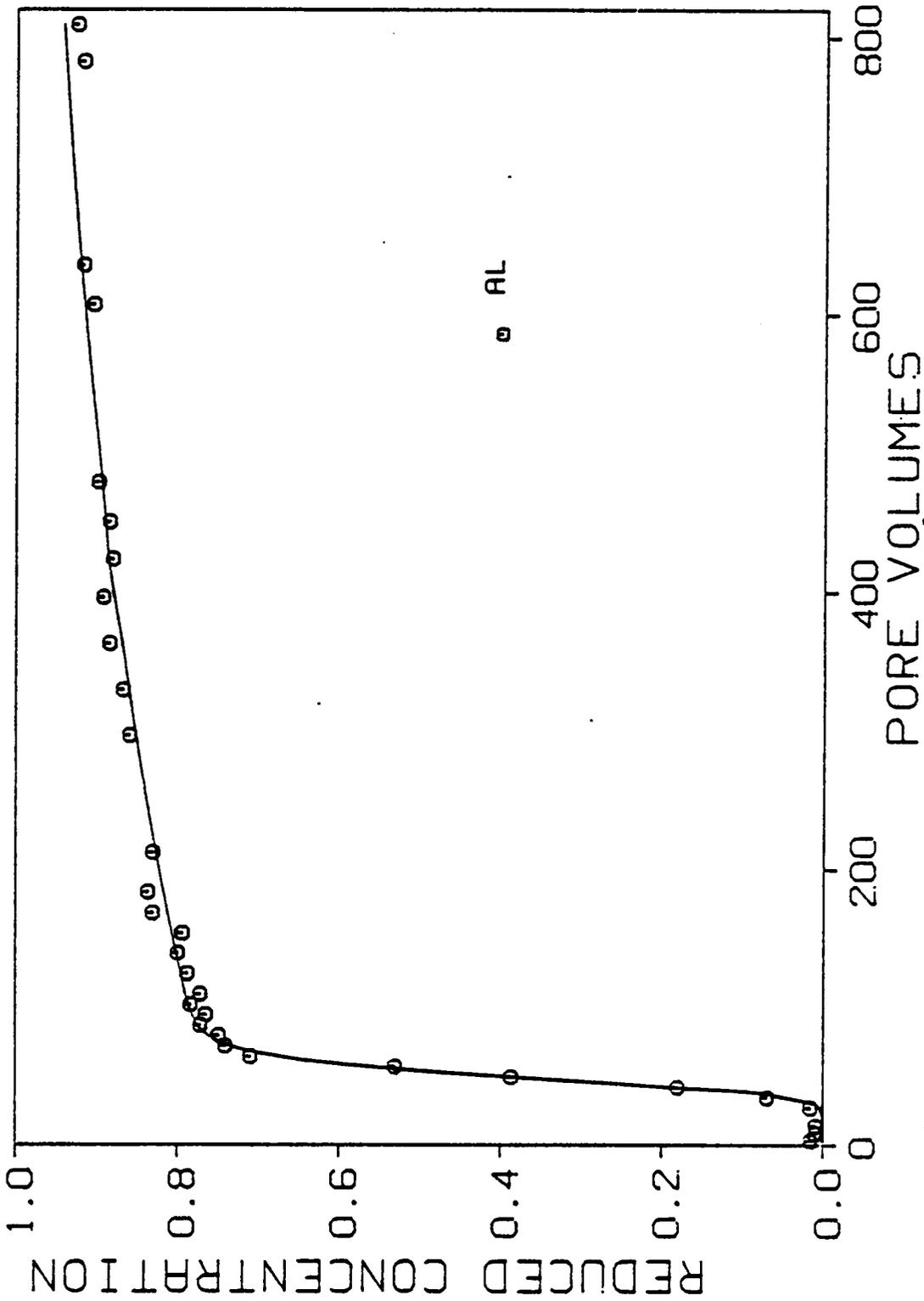


Figure 8. Breakthrough curve for $4.86 \mu\text{g mL}^{-1}$ Al at pH 4.30 on kaolinite with a column length of 3.2 mm. Solid line is the fitted curve from the nonequilibrium model.

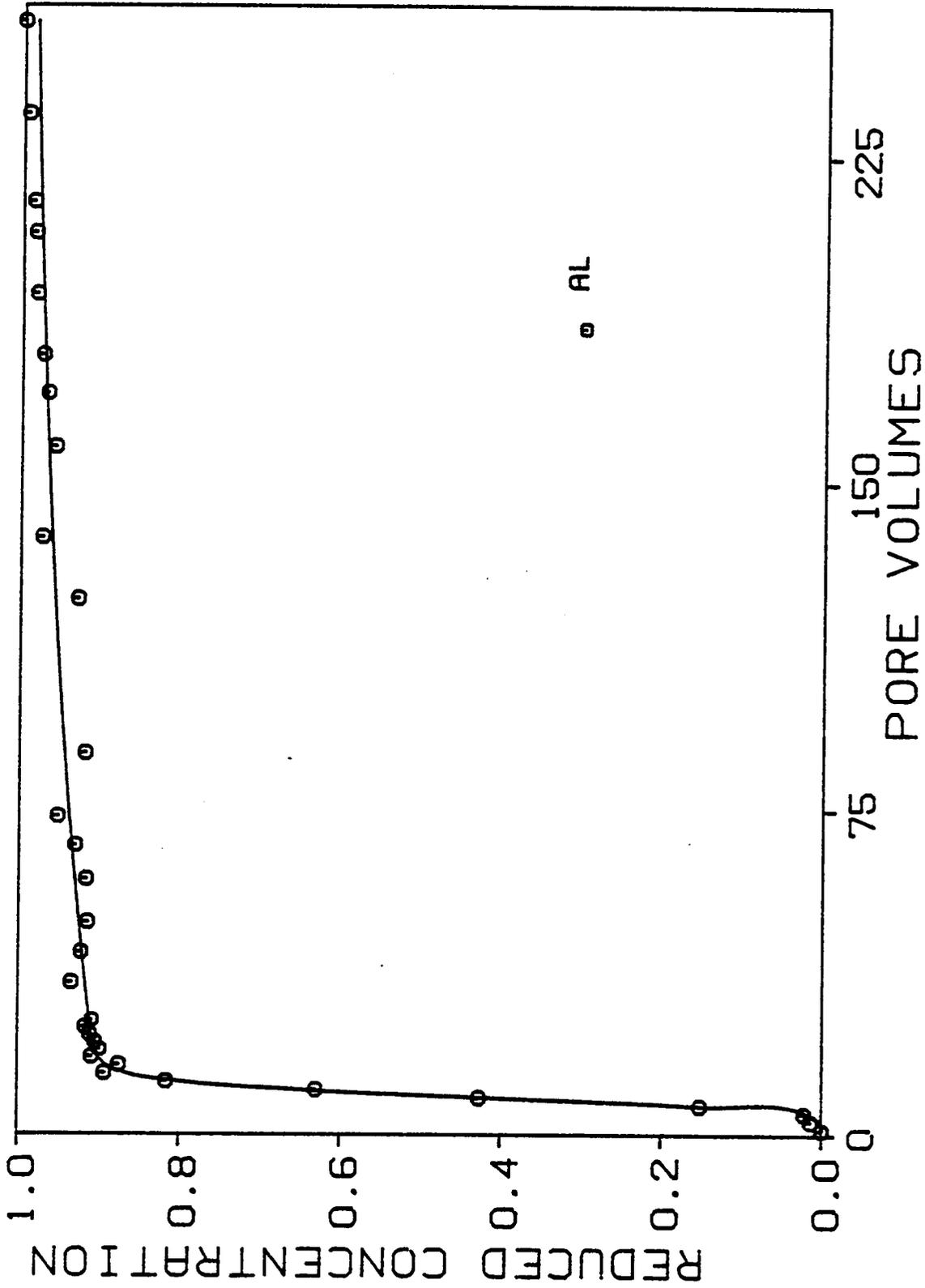


Figure 9. Breakthrough curve for 5.06 $\mu\text{g mL}^{-1}$ Al at pH 4.28 on kaolinite with a column length of 22.0 mm. Solid line is the fitted curve from the nonequilibrium model.

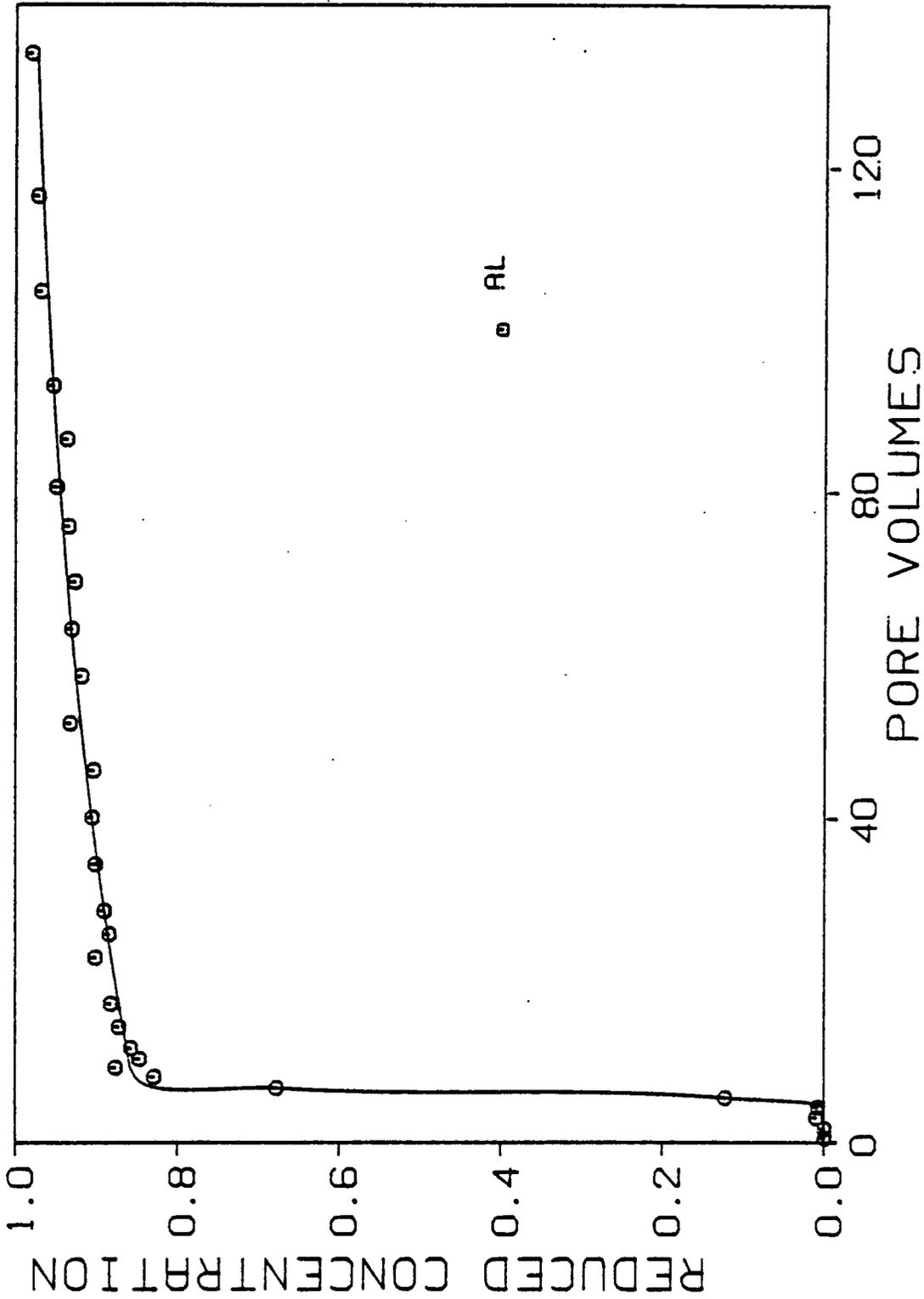


Figure 10. Breakthrough curve for $4.85 \mu\text{g mL}^{-1}$ Al at pH 4.30 on kaolinite with a column length of 42.5 nm. Solid line is the fitted curve from the nonequilibrium model.

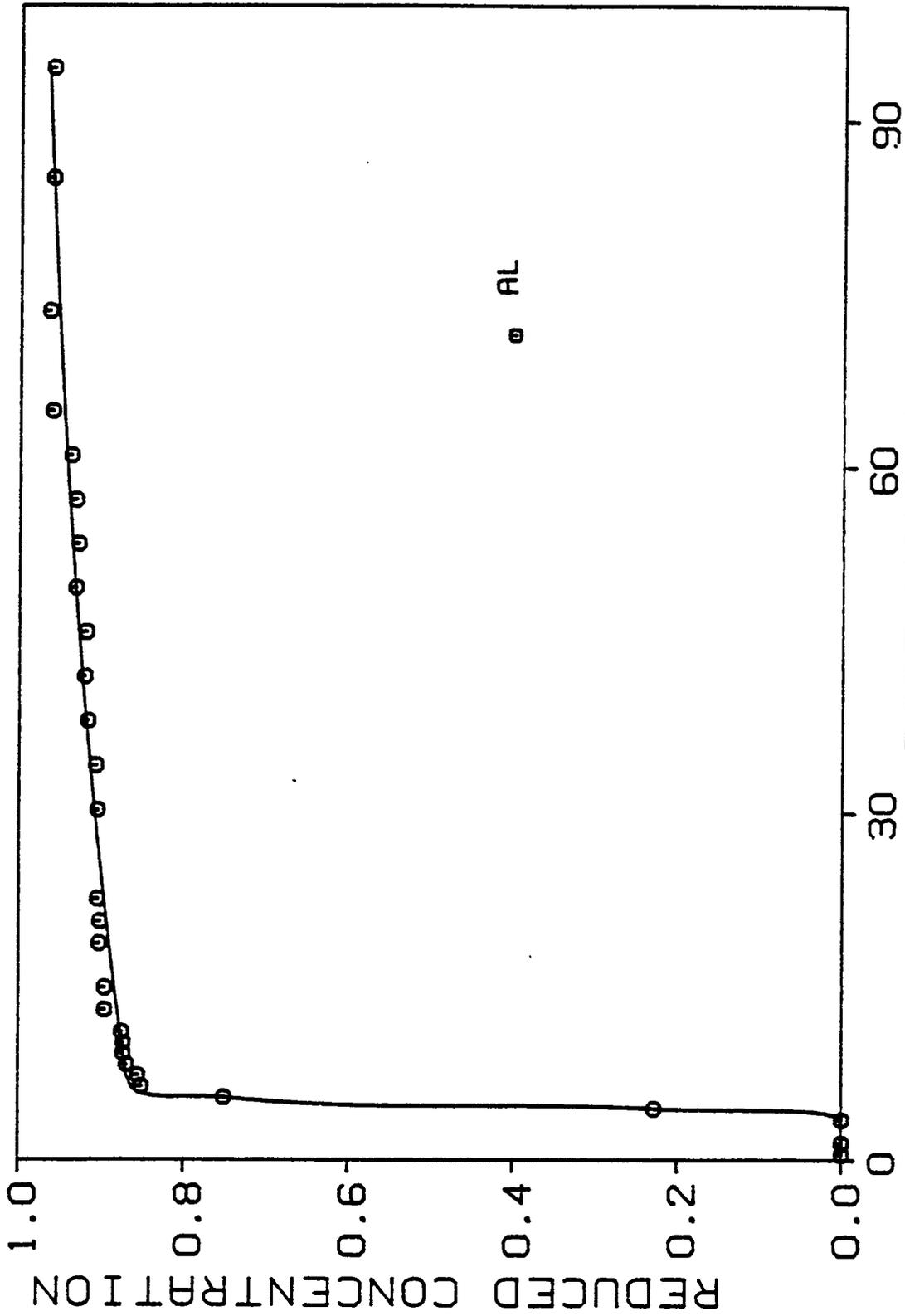


Figure 11. Breakthrough curve for $5.18 \mu\text{g mL}^{-1}$ Al at pH 4.29 on kaolinite with a column length of 64.3 mm. Solid line is the fitted curve from the nonequilibrium model.

increased (Table 5). By assuming σ^k constant in Eqn. 17, fewer pore volumes of higher concentration influent would be required to saturate the CEC of kaolinite thus reflecting smaller R_1 values. A similar argument may be used for the decreasing values of R with increased concentration of influent Al (Table 5). The high R^{fit} value for experiment 7 and low R^{fit} value for experiment 8 may reflect the higher and lower influent pH values, respectively (Table 3).

Effects of influent Al solution pH on the reaction of Al with kaolinite were investigated for constant influent Al concentration of $1.50 \mu\text{g mL}^{-1}$ and a column length of ≈ 3.9 mm (Table 6, Figs. 12, 15, and 16). Adjusting the pH from 4.28 to 4.08 resulted in a substantial loss of the slower kinetic reaction as noted by larger predicted values of β and smaller predicted values of R (Table 6, Figs. 12 and 15). Lowering the influent pH to 3.97 completely eliminated the slower kinetic reaction and the observed Al BTC was well-predicted by a one-site equilibrium model (Table 6, Fig. 16). This latter model is a degenerate form of the two-site model which considers type-1 sites only. The simultaneous termination of Ca desorption and Al adsorption evident from the BTC at pH 3.97 confirms that the negatively charged exchange sites of kaolinite are in local equilibrium with the solution phase. The predicted R , obtained for Al adsorption at

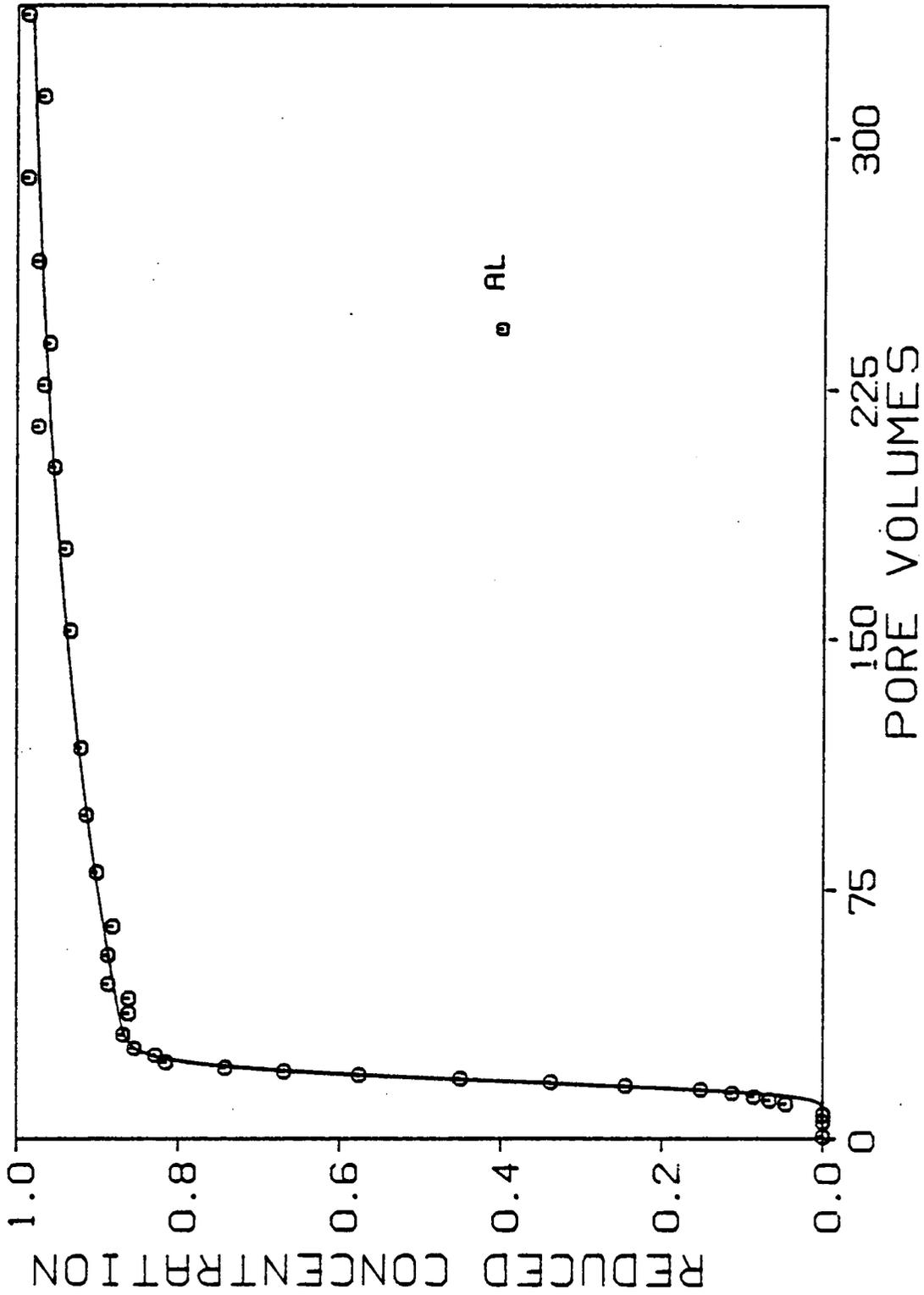


Figure 12. Breakthrough curve for $1.51 \mu\text{g mL}^{-1}$ Al at pH 4.28 on kaolinite. Solid line is the fitted curve from the nonequilibrium model.

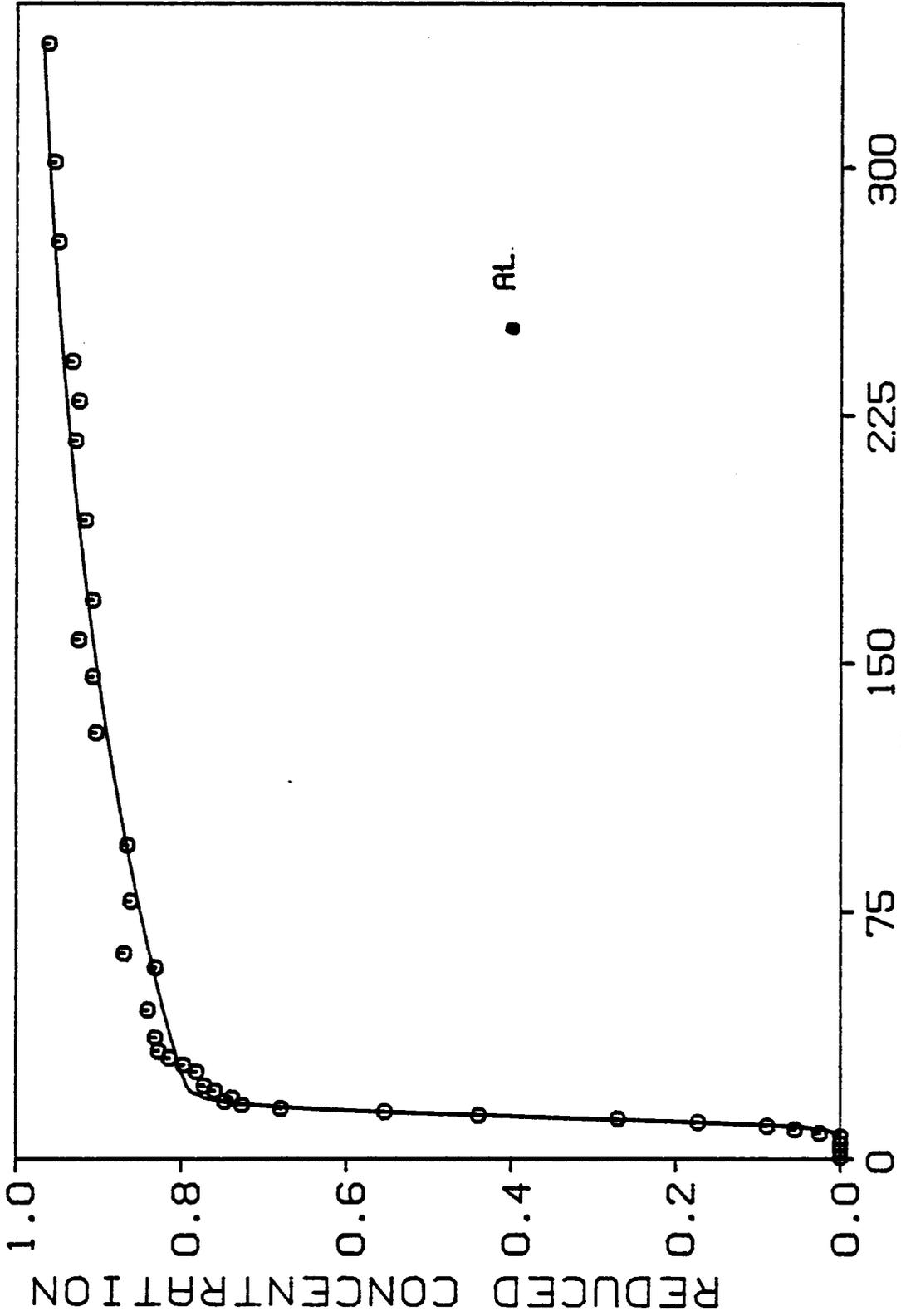


Figure 13. Breakthrough curve for 2.37 $\mu\text{g mL}^{-1}$ Al at pH 4.38 on kaolinite. Solid line is the fitted curve from the nonequilibrium model.

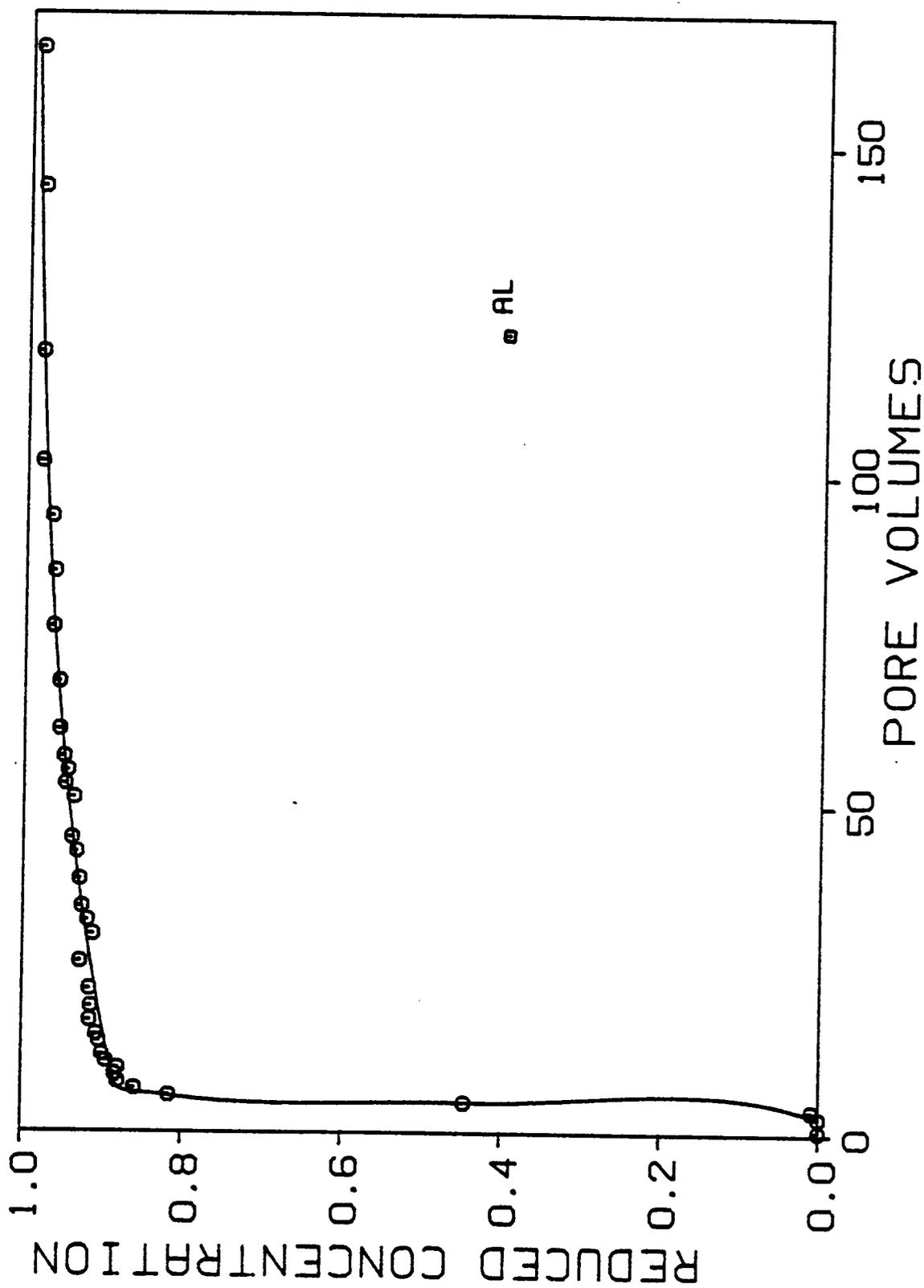


Figure 14. Breakthrough curve for $7.75 \mu\text{g mL}^{-1}$ Al at pH 4.20 on kaolinite. Solid line is the fitted curve from the nonequilibrium model.

pH 3.97 was found to be 14.7. This value compares well with the R_1 values obtained for Al adsorption at the same influent concentration but of pH 4.28 and 4.08 which were 16.7 and 15.7, respectively. When the pH of the influent Al solution was lowered below pH 3.8, dissolution of the kaolinite structure occurred and Al was released from the octahedral layer of the clay. Theoretical calculations assuming kaolinite in equilibrium with gibbsite and soil-silica confirmed that kaolinite dissolution does not occur until a pH of 3.8 or below is obtained.

4.5 SUMMARY AND CONCLUSIONS

The present study has indicated the existence of at least two mechanisms for Al adsorption on Ca-kaolinite. It has been shown that equilibrium (type-1) reactions on kaolinite involve Ca-Al exchange. Diffusive mass transfer limitations across Nernst films apparently do not occur for surface charge sites as long as the velocity of the influent is relatively rapid. Kinetic reactions on kaolinite are inferred to involve Al polymerization. Potentiometric titration performed on effluent Al indicated an increase in the H^+ concentration as Al reacts with kaolinite. The titration curves exhibited a small H^+ inflection which suggests en-

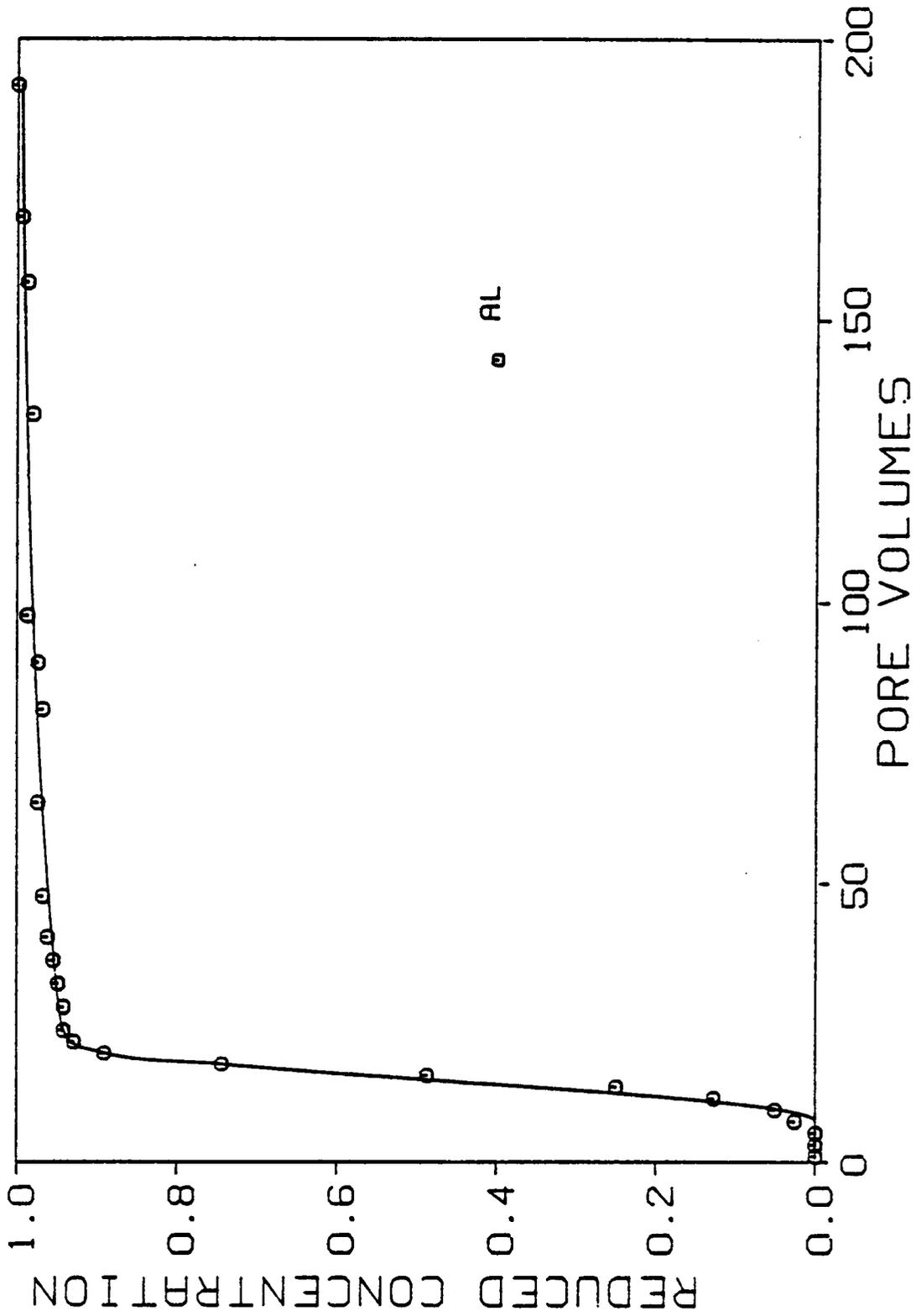


Figure 15. Breakthrough curve for $1.56 \mu\text{g mL}^{-1}$ Al at pH 4.08 on kaolinite. Solid line is the fitted curve from the nonequilibrium model.

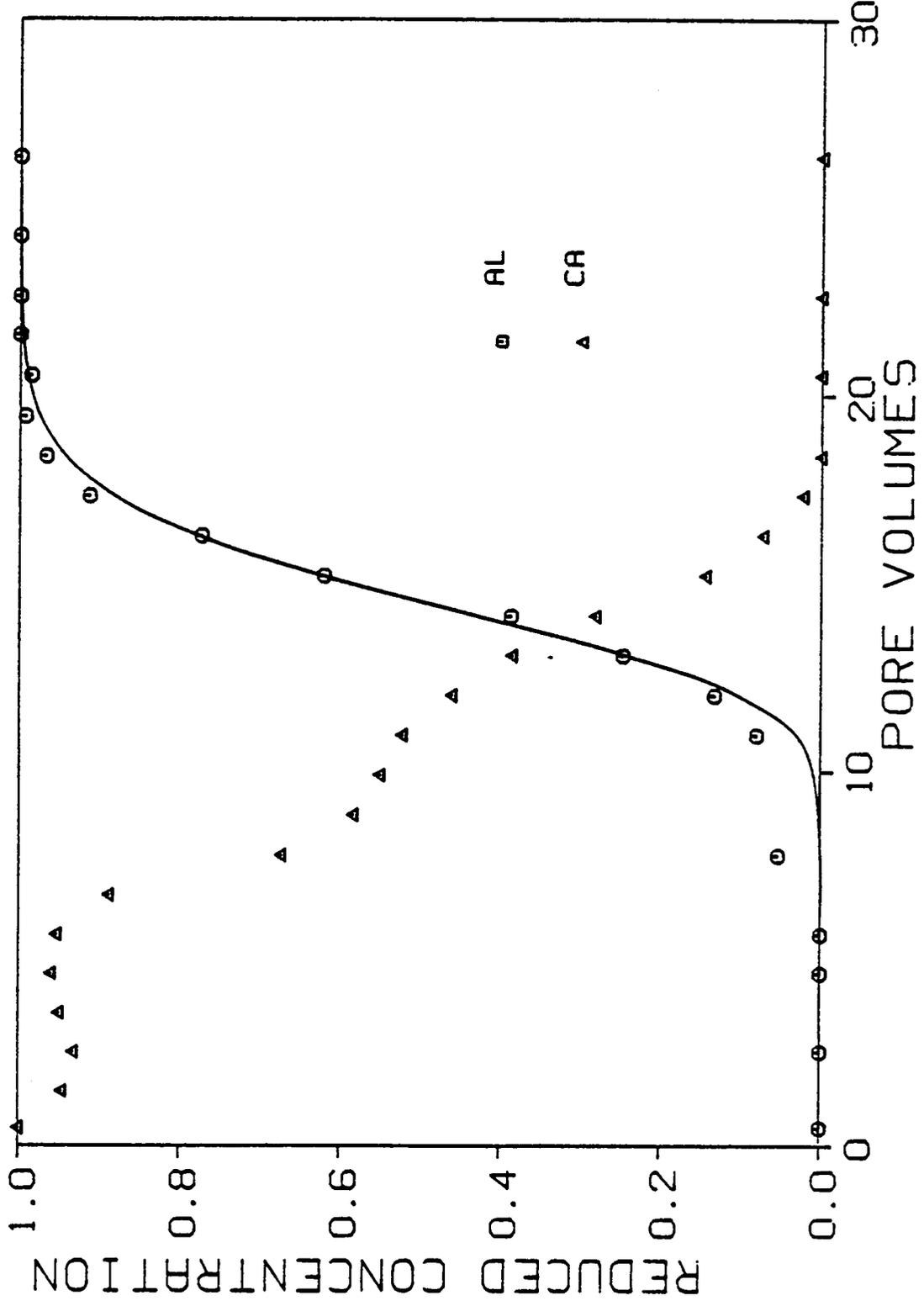


Figure 16. Breakthrough curve for 1.50 $\mu\text{g mL}^{-1}$ Al at pH 3.97 on kaolinite with corresponding desorbed Ca. Solid line is the fitted curve from the equilibrium model.

hanced hydrolysis of Al in the presence of kaolinite. Loss of the kinetic reaction as influent pH was lowered also supports the hypotheses that these reactions are related to the enhanced hydrolysis of Al on kaolinite. A higher concentration of H_3O^+ in the influent would limit the potential hydrolysis of surface-bound Al. Independent investigations of Al adsorption on $< 2 \mu m$ gibbsite and quartz from partially neutralized Al solutions, revealed negligible adsorption of Al (Jardine et al., 1985). These minerals were used to mimic Al reactions on exposed octahedral and tetrahedral surfaces of kaolinite, respectively. The negligible adsorption on these minerals indicates that Al most likely is not binding to the uncharged octahedral and tetrahedral surfaces of kaolinite, but rather electrostatically-bound Al on kaolinite serves as a template for sorption of more Al. Since there were minimal diffusive mass transfer limitations, it seems that the α value is a measure of the chemical kinetics of Al polymerization on the solid phase. This process, however, does not include surface polymerization of Al which could occur without additional adsorption from the solution phase.

Chapter V

MONONUCLEAR AND POLYNUCLEAR ALUMINUM SPECIATION THROUGH DIFFERENTIAL KINETIC REACTIONS WITH FERRON

5.1 ABSTRACT

The kinetic reaction of ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid) with partially neutralized Al solutions of varying basicity and age were investigated with the intent of separating mononuclear and polynuclear Al. Ferron solutions buffered with varying quantities of NaOAc, $\text{NH}_2\text{OH}\cdot\text{HCl}$, and acetic acid suggested that reduction of ferron by $\text{NH}_2\text{OH}\cdot\text{HCl}$ may be essential before monotonically increasing absorbance vs. time functions occur for Al reactions with ferron. When the latter reagent is buffered with appropriate quantities of NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$ it must be aged for ≈ 5 days at room temperature until ferron reduction has slowed. This solution remains stable for ≈ 25 days and exhibits consistent kinetic reactions with Al during this time period. A large portion of ferron interactions with partially neutralized Al of varying basicity and age was described by a binary species first-order rate function which predicted the rates of monomer and

small polymer reactions with ferron as well as the mole fraction of monomeric species present (f_a). Predicted f_a are based on the differential kinetic reactions of ferron with Al, thus arbitrary separation times for determining mononuclear and polynuclear Al are avoided. Rate parameters established for mononuclear Al solutions using a single specie first-order equation compared well with those determined for mononuclear Al from partially neutralized solutions using the binary species model. Ferron reactions at longer times were related to the decomposition of large Al polymers which were well described by psuedo-first-order kinetics.

5.2 INTRODUCTION

The chemical partitioning and speciation of aqueous Al into its various organic and inorganic forms has received much attention in recent years resulting from the complexities imparted by acid deposition on soil and the need for analytical control of water treatment processes (Johnson et al., 1981; Akitt and Farthing, 1981 a,b; Buffle et al., 1985). Several colorimetric techniques have been employed

in an effort to partition mononuclear from polynuclear Al species (Okura et al. 1962; Hem and Roberson, 1967; Blamey et al., 1983; Seip et al., 1984). Based on the kinetic reaction of Al with 8-hydroxyquinoline, Turner (1969) distinguished three forms of Al in partially neutralized solutions. Mononuclear Al was assumed to react instantaneously with the reagent, polynuclear Al was believed to be consumed by a pseudo-first order reaction, and an initial solid phase reacted by an apparent $2/3$ order process. As the partially neutralized Al solutions aged, the quantity of polynuclear Al species decreased to form a second type of polynuclear hydroxy-Al cation which was much less reactive with 8-hydroxyquinoline than its precursor (Turner, 1976). Distinction of mononuclear from polynuclear and organic Al, assuming a 15 min and 15 sec reaction duration between the former Al type and 8-hydroxyquinoline, has also been proposed by Bloom et al. (1978) and James et al. (1983), respectively.

The kinetic reaction of Al with ferron (7-iodo-8-hydroxy-quinoline-5-sulphonic acid) has also been utilized to partition mononuclear from polynuclear Al species (Smith and Hem, 1972; Schwan et al, 1981; Buffle et al., 1985). Smith (1971) assumed that mononuclear Al reacted instantaneously with ferron, intermediate polymers react-

ed by psuedo-first-order kinetics, and large polymers or initial solid phases reacted with ferron extremely slow or were totally inert. Bersillion et al. (1980) suggested that at least four categories of soluble Al species exist in partially neutralized solutions with mononuclear Al distinguished from the others by assuming a 30 sec reaction with ferron. Distinction of monomeric from polymeric and organic Al assuming a 30 sec reaction duration between the former Al type and ferron has also been suggested by others (Hodges and Zelazny, 1983a; Snodgrass et al., 1984; Jardine et al., 1985). In agreement with the findings of Smith (1971), several researchers have noted the reaction of ferron with polymeric Al conformed to psuedo-first-order kinetics (Tsai and Hsu, 1984; Parthasarathy and Buffle, 1985), with rapidly reacting polymers gradually developing into another polymeric species whose reaction with ferron was much slower (Tsai and Hsu, 1985).

The following study evaluates the interaction of ferron with Al under well defined experimental conditions which eliminate arbitrary separation of mononuclear and polynuclear Al by using the differential kinetic reactions of ferron with partially neutralized Al solutions.

5.3 MATERIALS AND METHODS

5.3.1 Experimental

5.3.1.1 Aluminum Detecting Reagent

The buffered ferron mixture used in the present study to evaluate the forms of Al in partially neutralized solutions was similar to that proposed by Bersillion et al. (1980). The Al detecting reagent consisted of 55.6%, by volume, 2.85×10^{-3} M ferron and 2.52×10^{-4} M 1-10 phenanthroline buffered at pH 5.2 with 22.2% 4.3 M NaOAc, and 22.2% 0.48 M HCl and 1.44 M $\text{NH}_2\text{OH}\cdot\text{HCl}$. The individual solutions were initially filtered through prewashed Gelman GA-6 0.45 μm membranes (see appendix A) and the latter two buffer solutions were combined prior to the addition of ferron. The reagent was stored at room temperature in the dark. The concentration of ferron in the final solution was $\approx 1 \times 10^{-3}$ M which assured that the ferron⁻¹ molecule was the only significant species (Goto et al., 1974). As suggested by Bersillion et al. (1980), the background color of the buffered ferron mixture was found to decrease rapidly with age. The mechanism of color loss was investigated by preparing three

additional ferron mixtures; one which was buffered at pH 5.1 with buffering reagents described above but diluted 100X, another which was buffered at pH 4.9 with glacial acetic acid and ≈ 4 M NaOAc, and a third which was not buffered but diluted with an equivalent portion of distilled H₂O. The final concentration of ferron in these solutions was again $\approx 1 \times 10^{-3}$ M and all solutions were stored at room temperature in the dark. The absorbance spectra of the four different ferron solutions were monitored for several months using a Beckman DU-7 UV-VIS spectrophotometer. The samples were scanned at a rate of 600 nm min⁻¹ from a wavelength of 350 to 650 nm using distilled water as a blank.

5.3.1.2 Al-Ferron Kinetics

Partially neutralized 1×10^{-4} M AlCl₃ and preacidified mononuclear Al solutions were made using methods described by Jardine et al. (1985). The former solutions were prepared by very slow addition of dilute NaOH (eg. 0.086 mL min⁻¹) to preacidified AlCl₃ solutions until basicities (OH/Al) 0.22, 0.84, 1.88, and 2.31 were attained. One mL aliquots of the mononuclear or partially neutralized Al solutions were placed in narrow bottomed polypropylene vessels and 10 mL of the buffered ferron mixture was rapidly inject-

ed into the sample using a repipet. Mixing was complete upon injection and the sample was immediately aspirated into a Hitachi spectrophotometer using a peristaltic pump. Absorbance changes were monitored at 370 nm as a function of time on an automatic chart recorder. Injection and aspiration of the sample into the cell of the spectrophotometer utilized $\approx 2-3$ sec. Mononuclear Al-ferron interactions were monitored continuously for at least 90 sec at which time no further increase in absorbance was detected. Partially neutralized Al-ferron interactions were monitored continuously for ≈ 300 sec until absorbance increases became slow. Fresh samples of the aging mixture were then manually monitored at known times for ≈ 2 hrs until absorbance increases were undetectable. All kinetic studies were conducted at 298-300K.

5.3.2 Theoretical

Partially neutralized Al solutions have been shown to exist as a binary mixture of mononuclear and polynuclear Al (Smith and Hem, 1972). The interaction of these species with the common reagent ferron results in an irreversible bimolecular reaction expressed as,



where A and B are concentrations in moles L⁻¹ of mononuclear and polynuclear Al, R is the concentration of the reagent, k_a and k_b are the forward rate constants for monomers and polymers, respectively, and C is a common product. Although it has been suggested that polynuclear Al initially breaks down to form mononuclear Al before reaction with ferron (Hem and Roberson, 1967), the use of Eqn. 21 is justified since the rate limiting step of the process is the degradation of polymers to monomers if k_a >> k_b (Tables 8 and 9). If conditions for the bimolecular reaction are adjusted so that a 50-fold or greater excess of reagent to reactant is imparted, the two competing irreversible reactions can be described by psuedo-first-order kinetic expressions with respect to the reactant (Frost and Pearson, 1961; Mark and Rechnitz, 1968):

$$A_t = A_0 e^{-k_a t} \quad (22)$$

$$B_t = B_0 e^{-k_b t} \quad (23)$$

where A₀ and B₀ refer to the initial mononuclear and polynuclear Al concentrations in solution, and A_t and B_t refer to their concentrations at any time t. Since A and B react with ferron to form a common product, than

$$C_t = A_0 - A + B_0 - B \quad (24)$$

$$C_{\infty} - C_t = A_0 e^{-k_a t} + B_0 e^{-k_b t} \quad (25)$$

where $C_{\infty} = A_0 + B_0$ is the concentration of product at equilibrium and C_t is the concentration at any time t . Dividing Eqn. 25 by the total concentration, C_{∞} , and rearranging terms, one obtains

$$\frac{(C_{\infty} - C_t)}{C_{\infty}} = (e^{-k_a t} - e^{-k_b t}) \frac{A_0}{(A_0 + B_0)} + e^{-k_b t} \quad (26)$$

where $A_0/(A_0 + B_0) = f_a$ which is the mole fraction of mononuclear Al in the initial solution. A plot of observed $(C_{\infty} - C_t)/C_{\infty}$ vs. t (0-250 sec) was fit to Eqn. 26 using a non-linear least-square inversion technique which provided predicted values of k_a , k_b , and f_a .

The two species rate equation (eg. Eqn. 26) was unable to describe observed $(C_{\infty} - C_t)/C_{\infty}$ data at longer times, which accounted for 7-22% of the entire reaction depending on the basicity of the Al solution. Using a time delay analysis technique (see Appendix B), this portion of the $(C_{\infty} - C_t)/C_{\infty}$ data was confirmed to exist as a separate Al-ferron reaction with different rate kinetics relative to the two reactions which preceded it. Tsai and Hsu (1984, 1985) have also suggested the existence of this ternary reaction while investigating the interaction of ferron with hydrolyzed Al. Allowing ≈ 150 sec transition between the secondary and ternary reaction to assure completion of the former process,

the observed data during the ternary reaction was described by simple pseudo-first-order kinetics.

The reaction of ferron with mononuclear Al solutions were described by a degenerate form of the model which considered only one specie (eg. pseudo-first-order kinetics).

5.4 RESULTS AND DISCUSSION

5.4.1 Chemical Properties of the Aluminum Detecting Reagent

The buffering of ferron solutions with NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$ resulted in diminishing background color of the mixture upon age. To investigate the mechanism of color loss, absorbance scans were performed on several types of ferron solutions which were either diluted with distilled H_2O (D- H_2O) or buffered with varying quantities of NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$ or acetic acid (Fig. 17a). The absorbance spectra of the freshly buffered ferron solutions were similar to each other but differed markedly from the D- H_2O diluted ferron solution. The former solutions all contain NaOAc, with two containing $\text{NH}_2\text{OH}\cdot\text{HCl}$ (scans A and B) and a third containing acetic acid (scan C). Thus OAc^- is the only constituent common to all three solutions and its interaction with ferron probably causes the observed shifts in the ab-

sorbance spectra (Fig 17a). The interaction of acetate with 8-hydroxyquinoline, which is similar in composition to ferron, has also been suggested by Turner and Sulaiman (1971). As the unbuffered and buffered ferron solutions aged, no changes in the observed absorbance spectra were detected for the unbuffered or NaOAc-acetic acid buffered ferron solutions for several months (Fig 17a, scans C,D). Ferron which was buffered with NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$ revealed significant decreases in absorbance peaks with time (Figs 17b,c). Since the presence of acetate and water had no effect on ferron absorbance with time, the observed absorbance decreases, thus color loss, are the result of ferron reduction by $\text{NH}_2\text{OH}\cdot\text{HCl}$. Higher concentrations of $\text{NH}_2\text{OH}\cdot\text{HCl}$ resulted in more rapid absorbance decreases which slowed considerably after 7 days aging (Fig 17b). Lower concentrations of $\text{NH}_2\text{OH}\cdot\text{HCl}$ with ferron resulted in significant, but slower absorbance decreases for periods longer than one month (Fig 17c). Ferron reduction by $\text{NH}_2\text{OH}\cdot\text{HCl}$ also resulted in a shift of λ_{max} with age when Al was added to the system. The ferron-Al mixture buffered with high concentrations of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NaOAc initially had a $\lambda_{\text{max}} = 370 \text{ nm}$, which decreased to 364 and 359 nm as the ferron was aged 35 and 365 days, respectively.

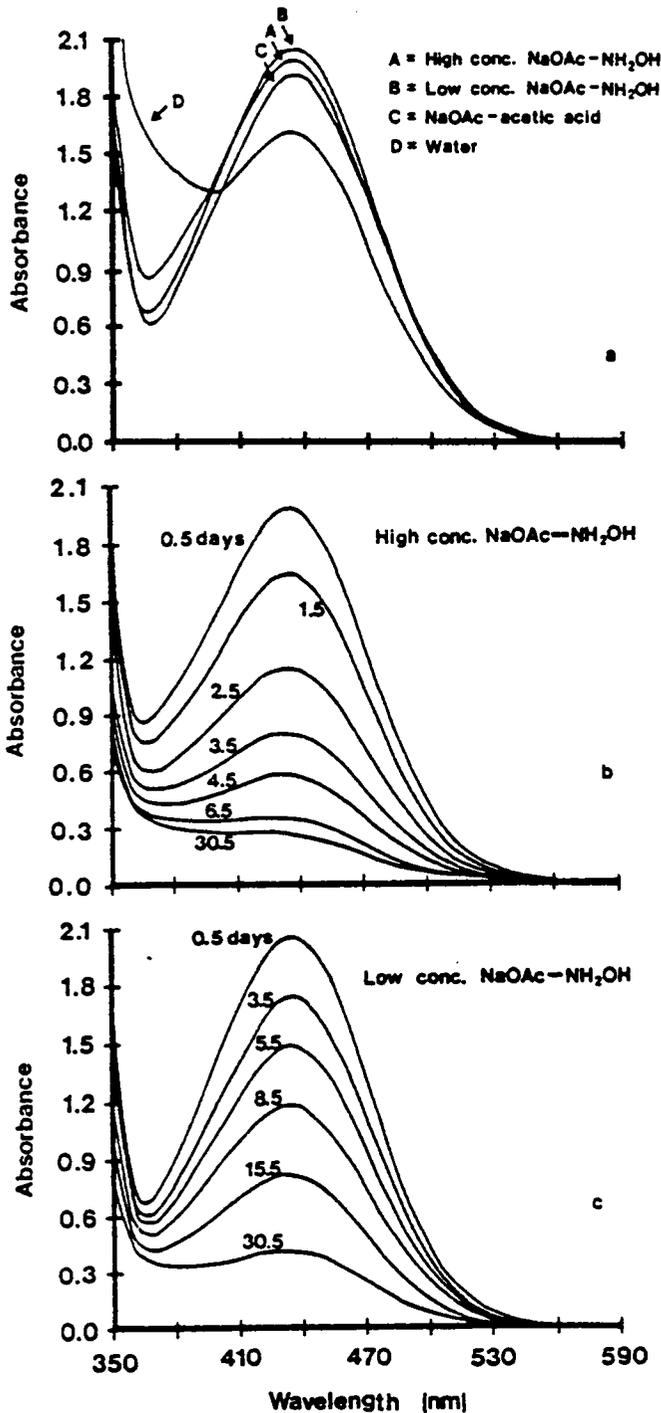


Figure 17. Absorbance spectra of $\approx 1 \times 10^{-3}$ M ferron diluted with D-H₂O or buffered with selected quantities of NaOAc and NH₂OH·HCl or acetic acid. Effect of age on the absorbance spectra of $\approx 1 \times 10^{-3}$ M ferron buffered with b) high concentrations of NaOAc and NH₂OH·HCl and c) low concentrations of NaOAc and NH₂OH·HCl.

The kinetics of Al with each of the three buffered ferron solutions (aged 6 days) revealed that the system buffered with high concentrations of NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$ gave the only monotonically increasing absorbance vs. time function (Fig 18). Ferron buffered with low concentrations of NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$ and with glacial acetic acid produced obscure kinetic reactions with Al where the maximum absorbance was reached early in the reaction and began to decrease as changes in absorbance slowed (Fig 18). The maximum absorbance values differ for the various ferron solutions since they are buffered at slightly different pH values (see Materials and Methods). It is possible that ferron reduction must occur before continuous absorbance vs. time functions result. The well behaved functions for mononuclear Al concentrations of $0.5\text{-}5.0\ \mu\text{g mL}^{-1}$ provide maximum absorbance values which have excellent conformity to Beers law ($r^2=0.999$), with typical slope and intercept values of 0.035 and 0.0002, respectively. Thus the kinetics of Al were investigated using buffered ferron mixtures which contained the high concentrations of NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$.

If conditions for a bimolecular reaction are adjusted so that a 50-fold or greater excess of reagent to reactant is used, second-order rate expressions reduce to pseudo-first-order expressions (Mark and Rechnitz, 1968). When in-

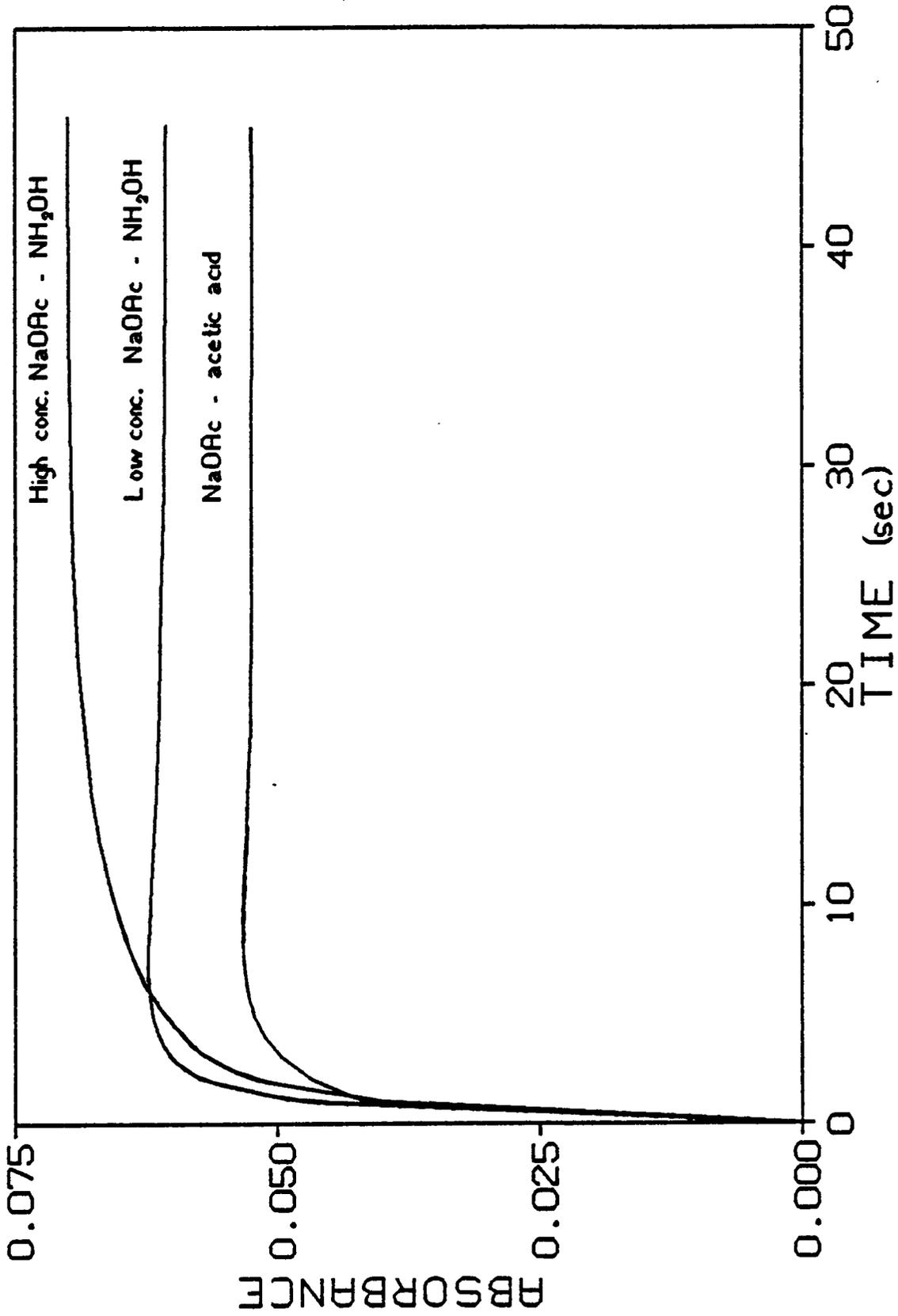


Figure 18. Absorbance vs. time functions for the interaction of 2.0 $\mu\text{g mL}^{-1}$ Al with selected buffered ferron solutions.

investigating the kinetics of Al with ferron, the latter reagent always had a 100-fold greater concentration than the Al. Under such conditions, the kinetics of Al monomers with ferron are very rapid (Fig 18), with the reaction being 75% complete within 3-5 sec. To verify that the concentration difference was sufficient to assume psuedo-first-order kinetics, ferron aged 10-days was diluted 20X and 33X with D-H₂O and their interaction with Al investigated (Fig. 19). The various concentrations were found to have no effect on the kinetics of Al with ferron and suggest the rate of reaction is psuedo-first-order with respect to Al. The results also suggest minimal complexation of the acetate anion, OAc⁻, with solution Al. Diluted concentrations of ferron, thus OAc⁻, were all found to react similarly with Al as mentioned. The chemical speciation model GEOCHEM (Mattigod and Sposito, 1979) also suggested that Al bound with OAc⁻ in the undiluted ferron solution was at most 0.5%. Akitt and Farthing (1984) however, suggest that the acetate anion enhances the polymerization of Al⁺³. Their results should be viewed with caution since the OAc⁻ - Al mixtures studied had initial pH values close to 8.0. High pH values such as these tend to induce rapid Al polymerization.

The reaction of various concentrations of mononuclear Al with several aged ferron solutions suggested that the

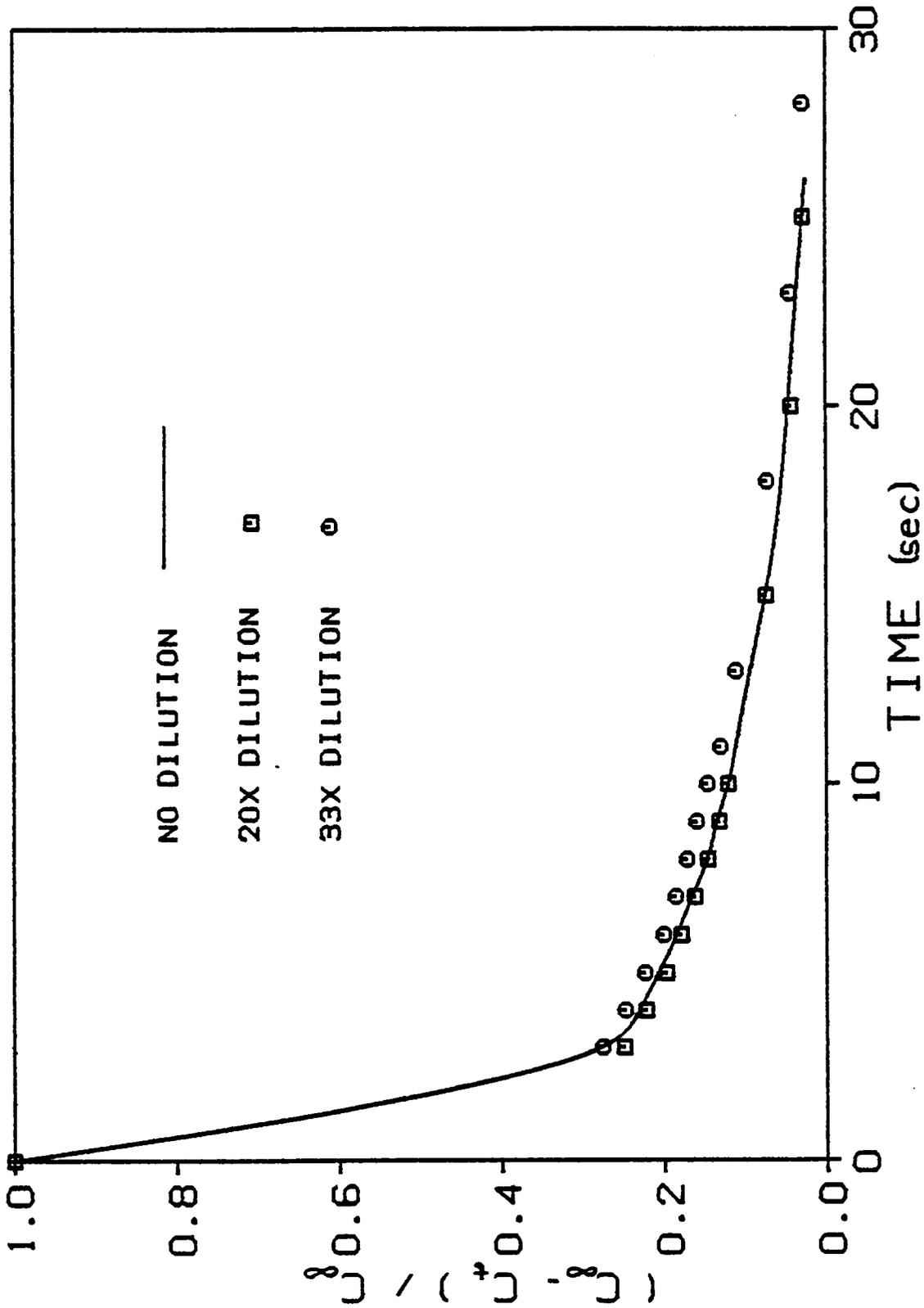


Figure 19. Observed reduced concentration-time plots for the reaction of 5.0 $\mu\text{g mL}^{-1}$ Al and various concentrations of ferron buffered with high concentrations of NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$.

latter reagents provided consistent kinetic reactions during the aging period of ≈5-25 days (Table 7). Premature use of ferron which was undergoing rapid reduction and use of ferron after ≈25 days resulted in slightly different rates of reaction with Al.

5.4.2 Interaction of Partially Neutralized Al with Ferron

Continuous absorbance vs. time functions for various partially neutralized Al solutions with ferron revealed an initial rapid absorbance increase which became slow at longer times (Fig 20). The ferron-Al interactions were monitored continuously for ≈300 sec and manually for ≈2 hrs until absorbance increases became undetectable. Initial rapid increases of absorbance should be related to mononuclear Al interactions with ferron and slower absorbance increases at longer times should reflect Al polymers of varying size, with small polymers reacting more rapidly with ferron than large polymers (Smith, 1971; Tsai and Hsu, 1984). The initial 250 sec of the reaction were expressed as reduced concentration-time functions $((C_{\infty}-C_t)/C_{\infty})$ vs. t , and the observed data was fit to the two species first-order rate function (Eqn. 26, Fig 21). The binary reaction model described the data reasonably well and provided predicted rate constants for ferron interactions with Al monomers and small

Table 7. Rate constants for the reaction of aged ferron with various mononuclear Al concentrations.

Ferron age (days)	Mononuclear Al $\mu\text{g mL}^{-1}$					
	1.0	1.5	2.0	2.5	3.0	5.0
	----- k_a in min^{-1} -----					
5	19.8 \pm 3.0 [†]	19.2 \pm 3.6	19.8 \pm 3.6	19.2 \pm 3.6	21.0 \pm 3.6	21.6 \pm 3.6
7	18.6 \pm 2.4	23.4 \pm 3.6	24.0 \pm 3.6	21.6 \pm 2.4	24.6 \pm 3.6	23.4 \pm 2.4
13	20.4 \pm 4.2	21.0 \pm 3.6	21.0 \pm 3.6	21.6 \pm 3.6	22.8 \pm 4.2	24.6 \pm 5.4
20	18.6 \pm 3.0	21.0 \pm 2.4	18.6 \pm 3.6	22.2 \pm 3.6	*	21.6 \pm 4.2
26	19.2 \pm 3.0	19.2 \pm 3.6	19.2 \pm 3.6	*	*	*

[†] C.I. = 0.95

* No data available.

polymers, k_a and k_b , respectively, and values for the fraction of monomeric Al in solution, f_a (Table 8). Using time-delay analysis (Appendix B), absorbance increases at times longer than 300 sec were shown to correspond to a ternary reaction which was well described by pseudo-first-order kinetics (Fig 22). Most likely this portion of the reaction is related to the interaction of ferron with large polymers which have a rate constant k_c .

The reaction of ferron with mononuclear Al solutions was described by a degenerate form of the two species rate equation (Fig 21) which considers only one species. Predicted k_a values for mononuclear Al were similar over the concentration range studied and confirm that Al in these solutions are of a similar form (Table 7). The values compare well with k_a values established for partially neutralized Al solutions using the binary species model (Table 8) suggesting accurate distinction between mononuclear and polynuclear Al interactions with ferron. As the initial basicity and the pH of the Al solutions (n_0 and pH_0 , respectively) became greater, the predicted fraction of monomer, f_a , became less and the fraction of the total reaction attributable to the ternary reaction increased (Table 8). Thus as n_0 increases large Al polymers become more significant.

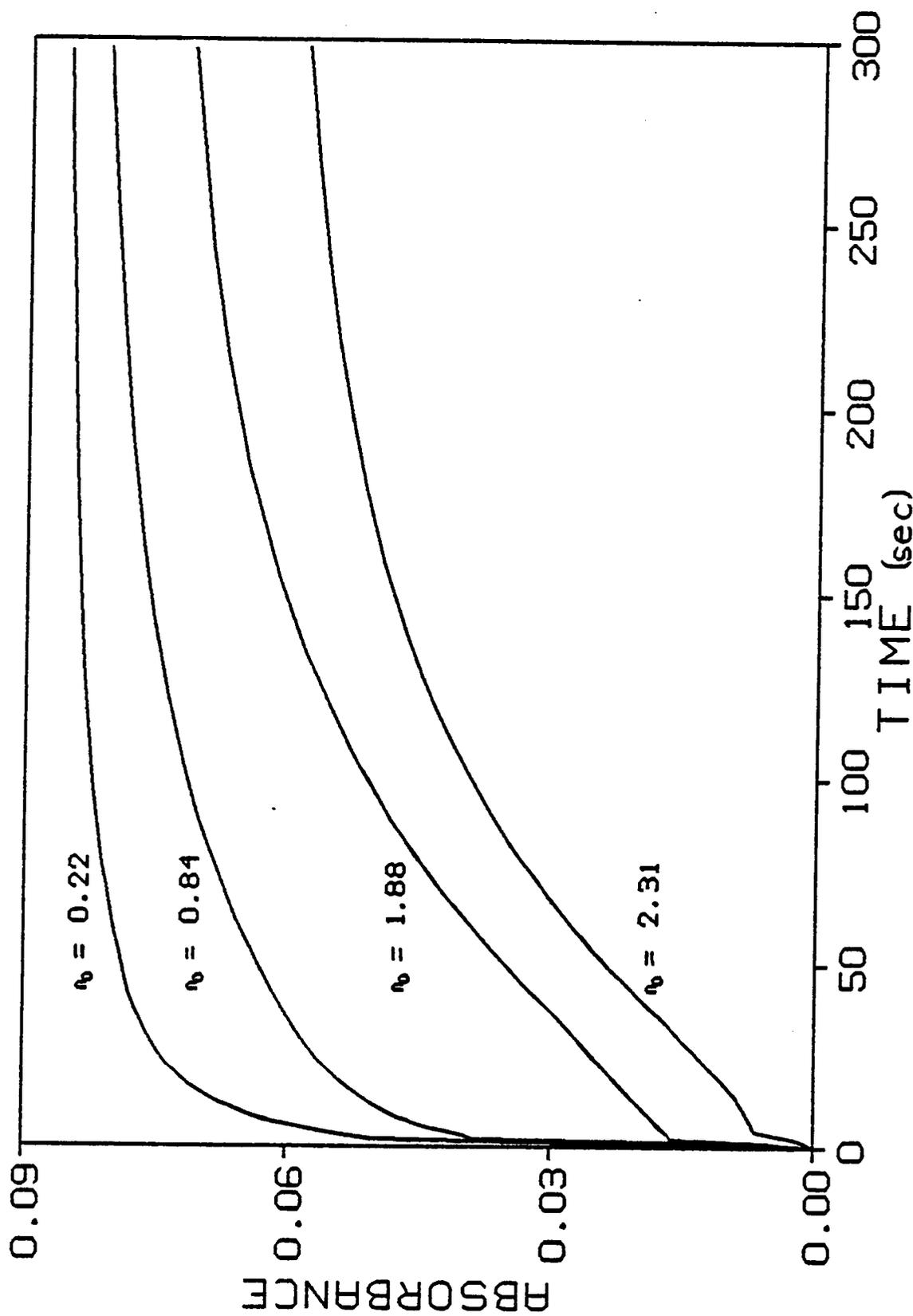


Figure 20. Absorbance vs. time functions for the interaction of partially neutralized Al with ferron buffered with high concentrations of NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$.

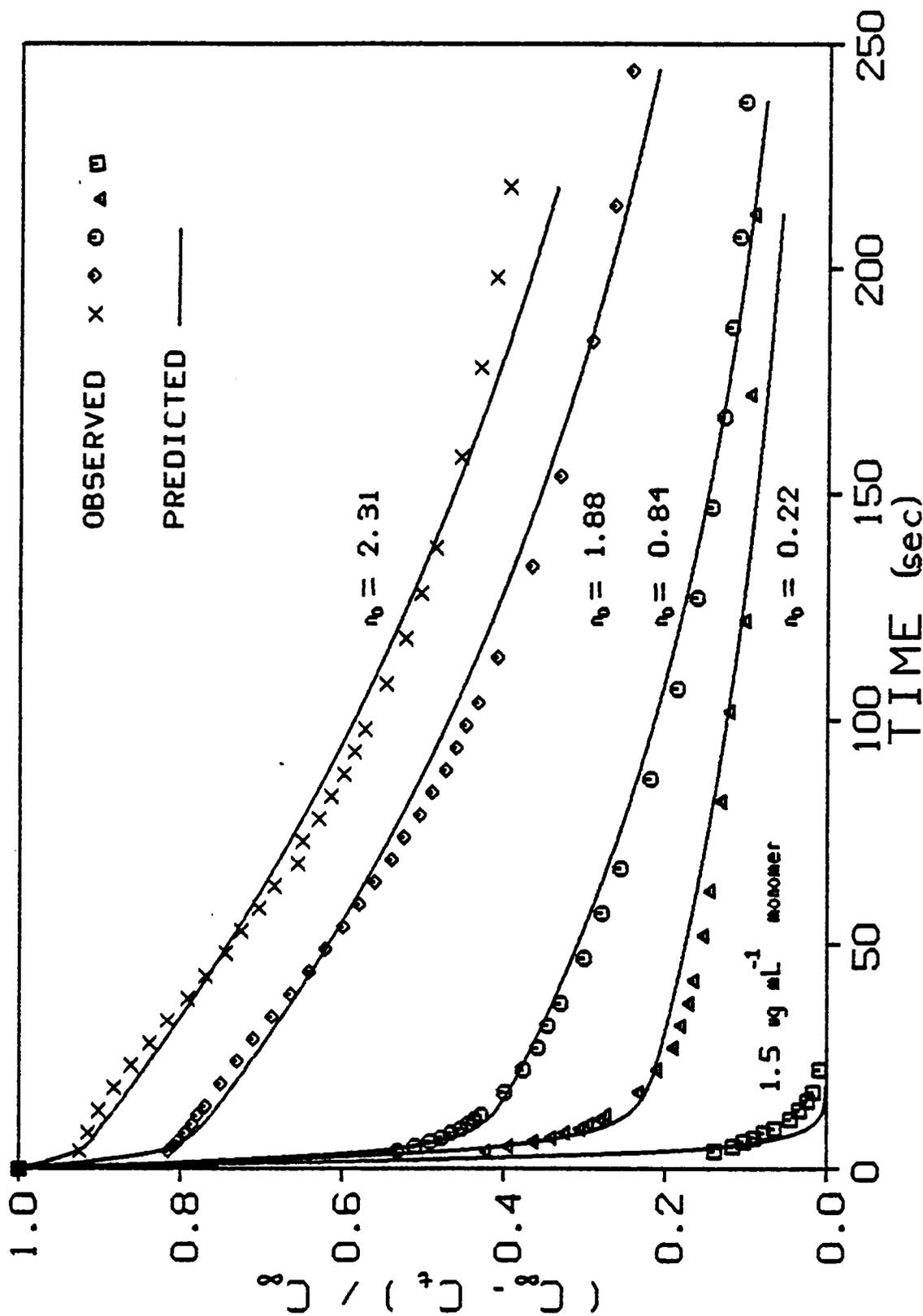


Figure 21. Observed reduced concentration-time plots and model predicted curves using Eqn. 26 for selected partially neutralized and monomeric Al solutions.

Table 8. Rate constants and chemical characteristics for the reaction of ferron with freshly prepared partially neutralized Al.

OH/Al (n_0)	pH ₀	age of partially neutralized Al		k_a	k_b	k_c	f_a	fraction of tertiary reaction	fraction of Al precipitated X 100
		--- days ---	----- min ⁻¹ -----						
0.22	4.57	4	21.6±3.6†	0.546±0.120	0.0069±0.0001	0.75±0.03	0.06	0.0	
0.84	4.74	4	22.2±3.6	0.462±0.036	0.0077±0.0027	0.55±0.01	0.08	0.0	
1.88	4.96	2	23.4±6.6	0.318±0.024	0.0071±0.0012	0.20±0.03	0.13	0.0	
2.31	5.27	0.2	33*	0.282±0.018	0.0043±0.0012	0.061±0.020	0.22	10.5	

† C.I. = 0.95

* Error greater than 100% for this estimate.

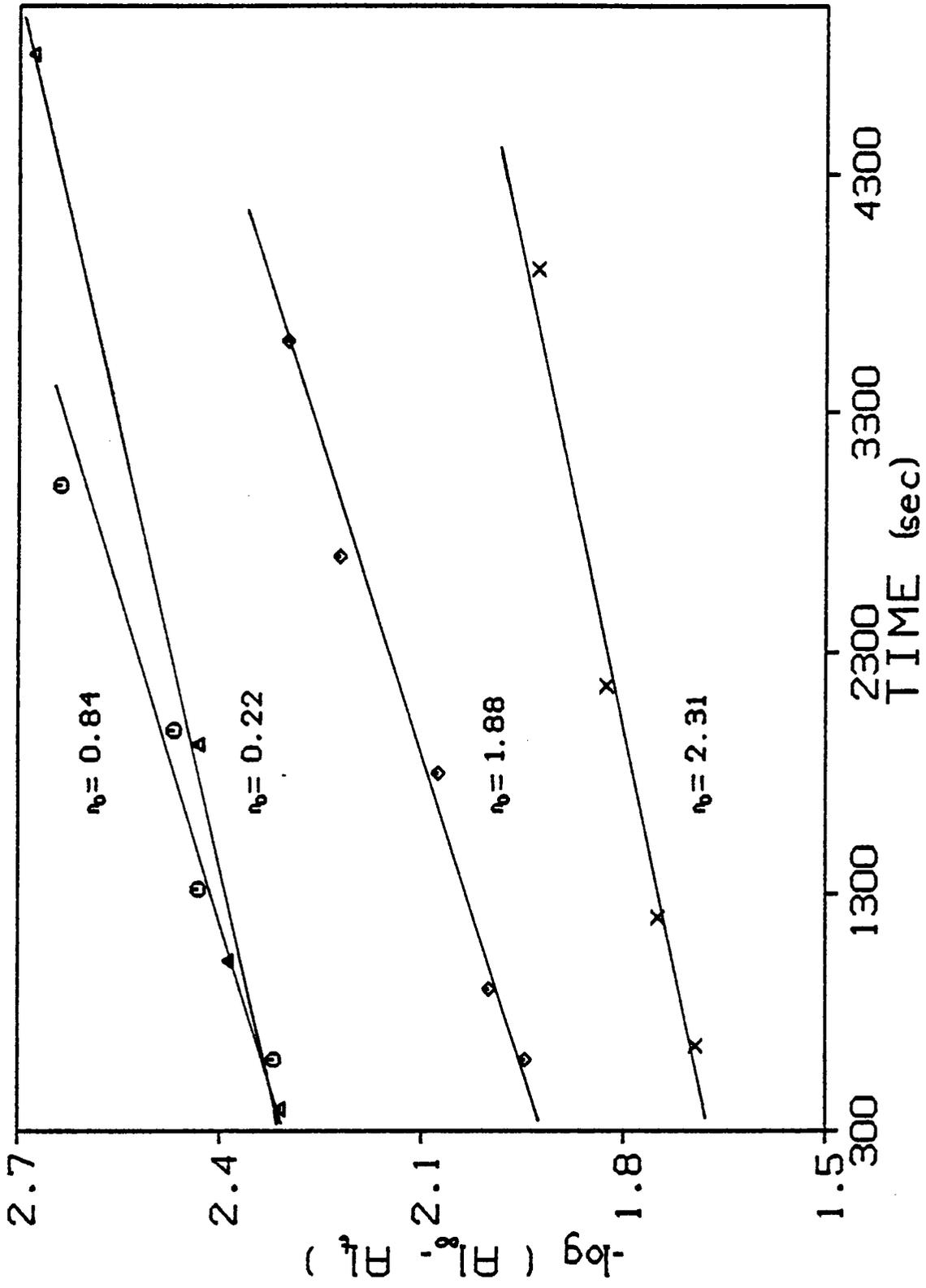


Figure 22. Pseudo-first-order plots for the ternary reaction of partially neutralized Al with ferron.

Predicted f_a values are slightly lower than those proposed by Bersillion et al. (1980) for various partially neutralized Al solutions using ferron. These authors may have slightly overestimated mononuclear Al by assuming polymer reactions with ferron were not significant for the initial 30 sec of the reaction. Smith and Hem (1972) assumed ferron interactions with mononuclear Al were essentially instantaneous. Predicted f_a values from the present study are still significantly lower than those proposed by these authors since they preacidified their Al solutions with $\text{NH}_2\text{OH}\cdot\text{HCl}$ prior to ferron analysis. Polynuclear Al exposed to the lower pH would most likely denature into monomeric units which would account for the overpredicted monomer concentrations in their solutions. Predicted f_a values from the present study are based on the differential kinetic reactions of mononuclear and polynuclear Al with ferron and do not assume arbitrary reaction times for separation. Employing a constant separation time may be erroneous since the duration of monomer interactions with ferron depend on n_0 (eg. for $n_0=0.22$ and 2.31 , the duration of monomer reactions was ≈ 15 sec and ≈ 4 sec, respectively). Interestingly enough, however, plots of f_a vs n_0 for each of these authors and the present study provide essentially the same slope (Fig. 23). This suggest the change in monomer concentration

from one hydrolyzed solution to another is well predicted by each study. Discrepancies between estimated f_a at any value n_0 , still persist however.

As f_a decreases the error associated with k_a increases since the reaction duration of mononuclear Al is very short and observed data is limited (Fig 21, Table 8). The reaction rate of ferron with small and large polymers, k_b and k_c , respectively, are significantly lower than k_a , with k_c being appreciable lower than k_b . The magnitude of k_b decreased with increasing n_0 , suggesting that small polymers at higher n_0 values may have a larger molecular size than those at lower n_0 values. Observed k_c values did not decrease significantly with increasing n_0 , except for the case of $n_0=2.31$ which also had 10.5% precipitated Al (ferron undetectable Al). The slight sigmodal curvature at the beginning of the high basicity solutions (eg. $n_0=1.88, 2.31$) is most likely related to a condition where the kinetics of polymer degradation has not yet reached a steady state since the duration of monomer reactions are short (Figs. 20 and 21). Once a steady state is reached, well behaved, monotonically continuous functions result.

Partially neutralized Al solutions with $n_0=0.84$ and 1.88 were monitored with age using ferron kinetics (Figs. 24 and 25, respectively). As solutions aged, precipitated Al

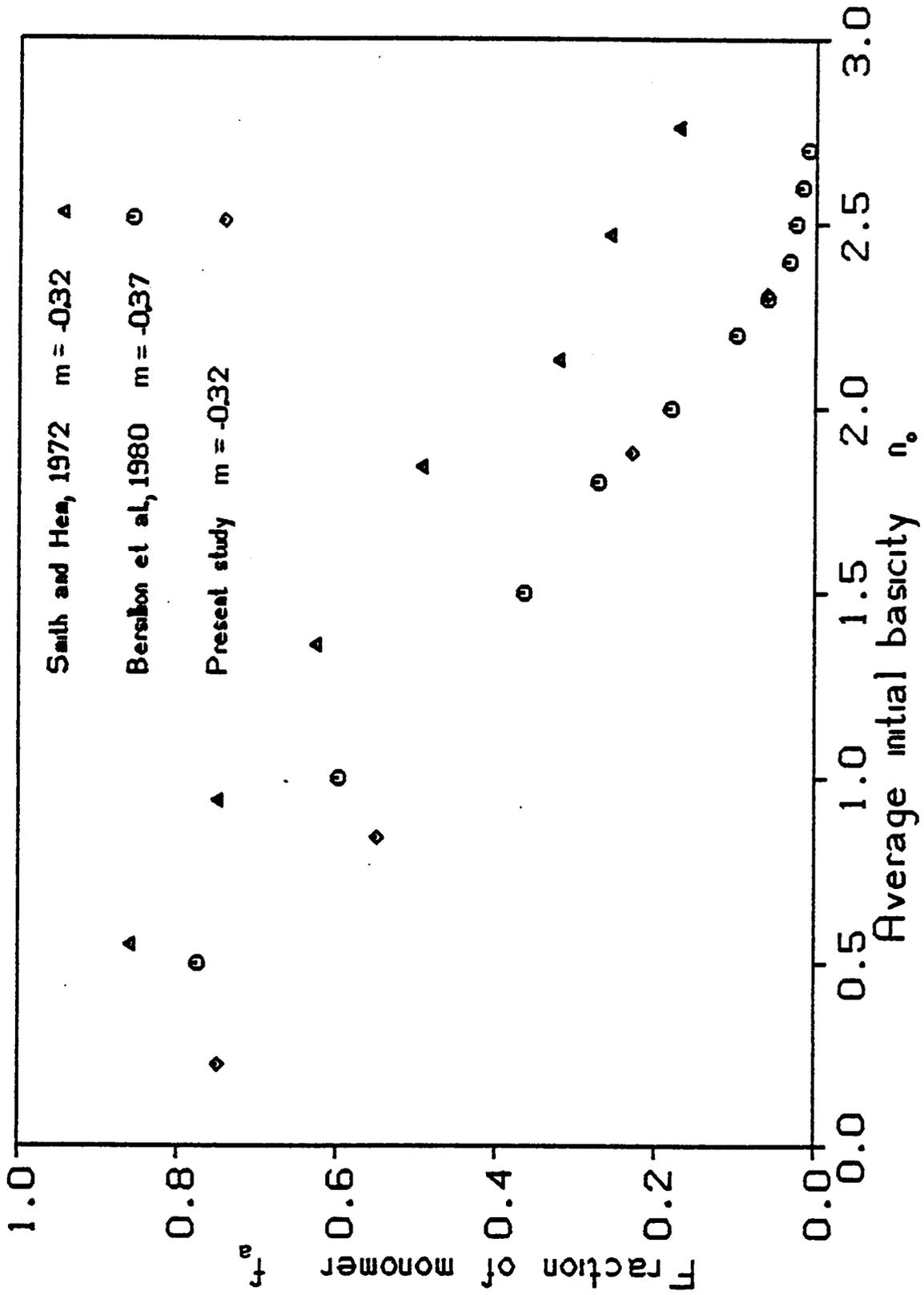


Figure 23. Estimated fraction of mononuclear Al (f_a) in partially neutralized Al solutions as a function of the initial solution basicity (n_0).

occurred which is undetectable to ferron. The maximum concentration of Al in the aging solutions is still C_m ($\approx 2.5 \mu\text{g mL}^{-1}$ Al) even though it is not completely detectable. Predicted k_a values for mononuclear Al (Table 7) again compare well with k_a values established for aging partially neutralized Al solutions using the binary species model (Table 9). Slight variations of predicted k_a for $n_0=1.88$ also persist. Predicted f_a values remained essentially constant as the partially neutralized Al solutions are aged. Constant mononuclear Al concentrations in aging partially neutralized solutions have also been suggested by others (Hem and Robertson, 1967; Tsai and Hsu, 1984). Rate constants k_b and k_c decreased significantly with age suggesting small and large Al polymers were most likely increasing in size or rearranging their Al-OH structure to form a more stable phase, thus reacting slower with ferron (Table 9). Increasing polymerization or enhanced stability of preexisting Al polymers is also supported by decreasing OH/Al ratios and pH values as well as increasing precipitated Al with age (Table 9). Equilibrium stability diagrams for solution Al as a function of pH suggested that the aging partially neutralized Al solutions were indeed approaching a more stable phase since they approached the theoretical gibbsite solubility curve with increasing age (Fig. 26). Such trends for aging par-

tially neutralized Al solutions have also been shown by others (Smith and Hem, 1972; Turner, 1976; Hodges and Zelazny, 1983a).

5.5 SUMMARY

The kinetics of ferron with partially neutralized Al of varying basicity and age were well described by three parallel psuedo-first-order reactions. Arbitrary separation of mononuclear and polynuclear Al was avoided using a binary species rate function which accurately seperates the two forms of Al based on differential kinetic reactions with ferron. The ferron solution should be well buffered with NaOAc and $\text{NH}_2\text{OH}\cdot\text{HCl}$ and aged at least 5 days but not longer than =25 days so that kinetic functions increase monotonically to a maximum and are comparable from day to day. The kinetics of ferron with 1N KCl extractable Al are also applicable to the presented model since the presence of KCl was found not to effect the rate of Al reaction with ferron.

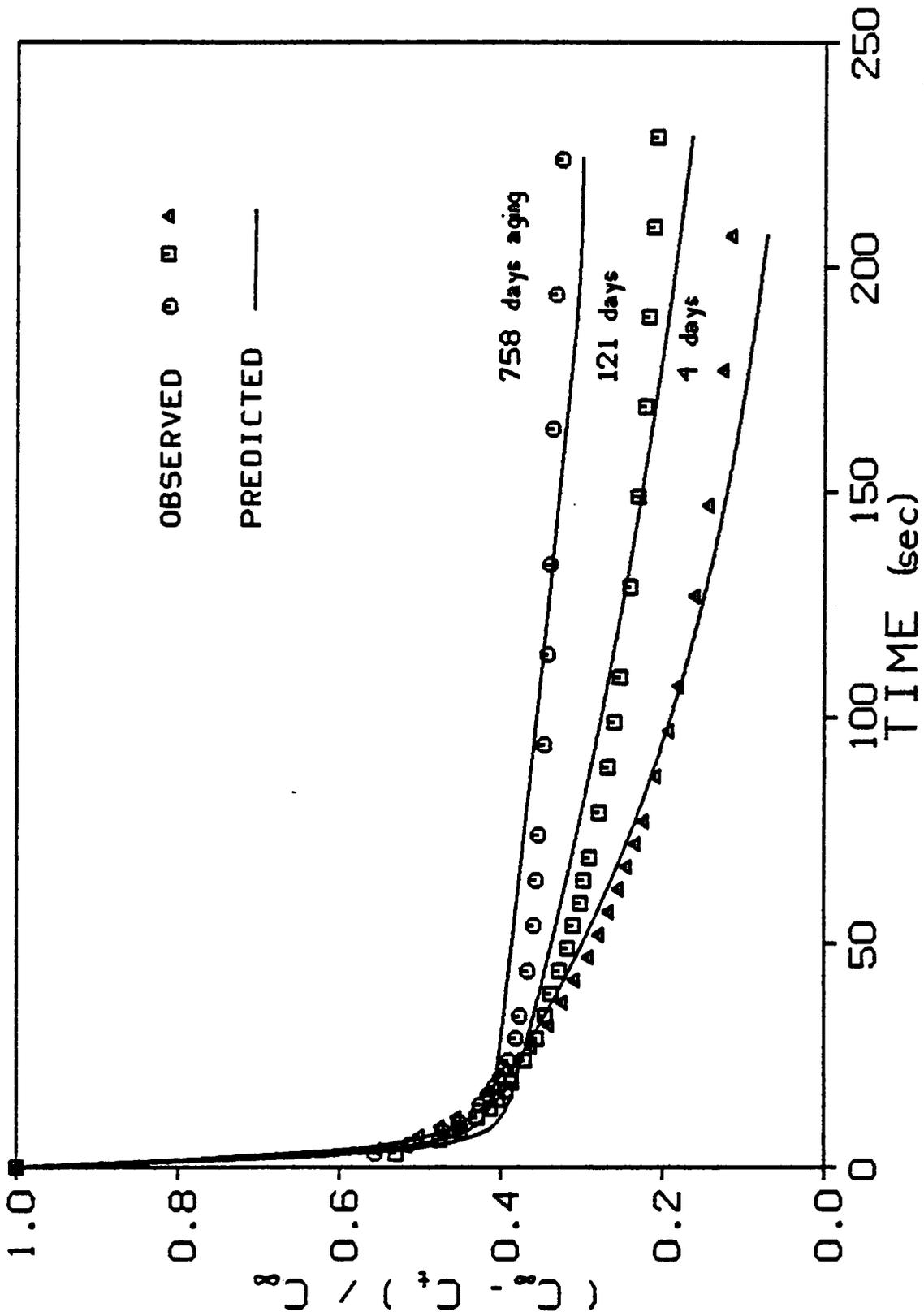


Figure 24. Observed reduced concentration-time plots and model predicted curves using Eqn. 26 for Al solutions with $n_0=0.84$ and subsequently aged.

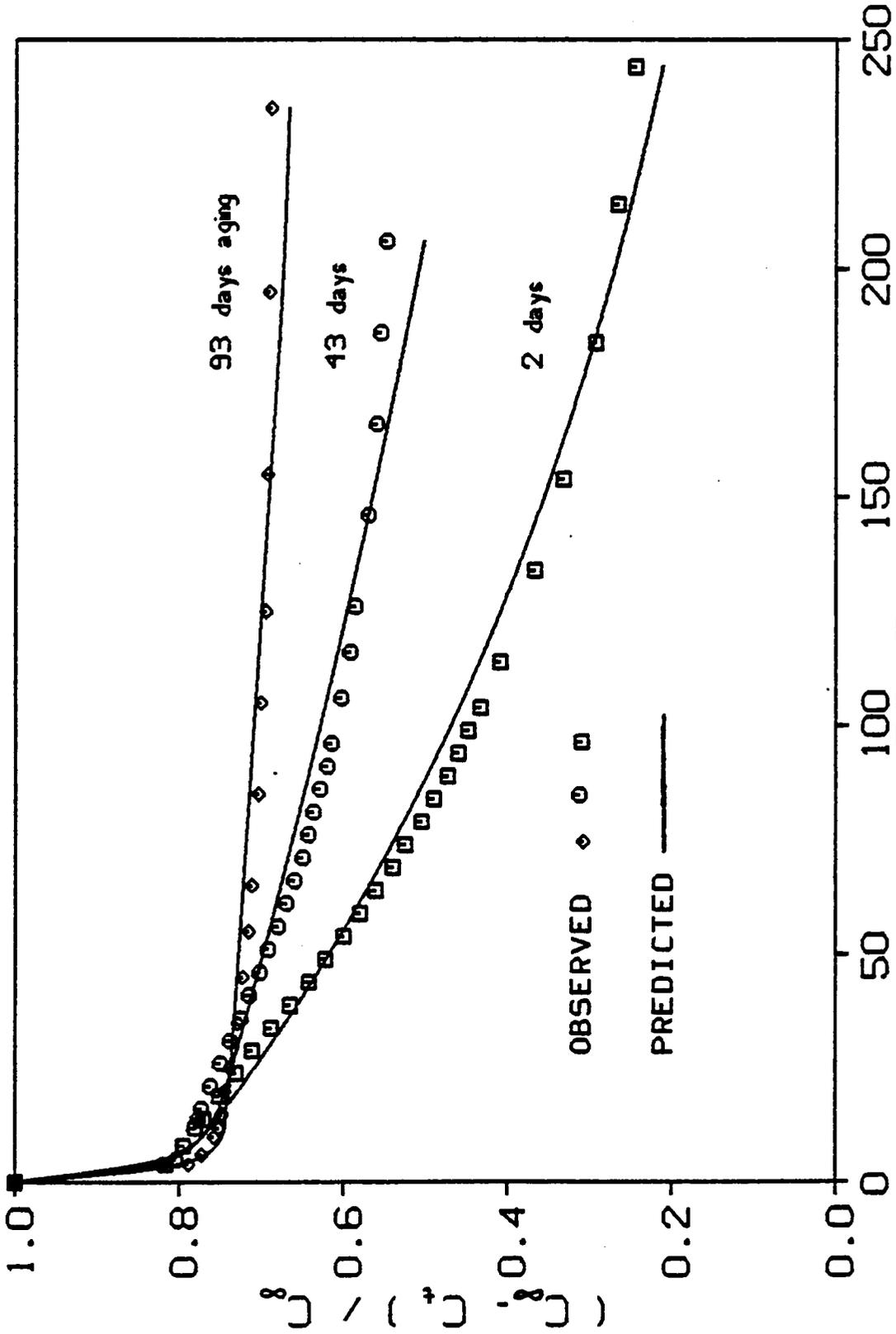


Figure 25. Observed reduced concentration-time plots and model predicted curves using Eqn. 26 for Al solutions with $n_0=1.88$ and subsequently aged.

Table 9. Rate constants and chemical characteristics for the reaction of ferron with aged partially neutralized Al.

age of partially neutralized Al (days)	k_a	k_b	k_c	f_a	OH/Al	pH	fraction of Al precipitated X 100
	----- min ⁻¹ -----						
	$n_o = 0.84$						
4	22.2±3.6†	0.462±0.036	0.0077±0.0027	0.55±0.01	0.84	4.74	0.0
121	24.6±3.6	0.240±0.036	0.0031±0.0004	0.59±0.02	0.59	4.70	7.8
758	22.2±3.0	0.096±0.030	0.0010±0.0003	0.58±0.02	0.38	4.56	21.0
	$n_o = 1.88$						
2	23.4±6.6†	0.318±0.024	0.00713±0.00122	0.20±0.03	1.88	4.96	0.0
14	6.6±3.0	0.288±0.042	0.00137±0.00076	0.25±0.04	1.56	4.91	20.8
29	15.6±8.4	0.228±0.030	*	0.28±0.03	1.45	4.81	26.9
43	16.8±6.0	0.126±0.012	0.00061±0.00001	0.22±0.01	1.05	4.63	42.3
63	13.8±3.0	0.078±0.012	0.00035±0.00001	0.25±0.01	0.75	4.59	55.8
93	23.4±4.2	0.031±0.007	0.00042±0.00001	0.25±0.01	0.40	4.59	60.1

† C.I. = 0.95

* No data available.

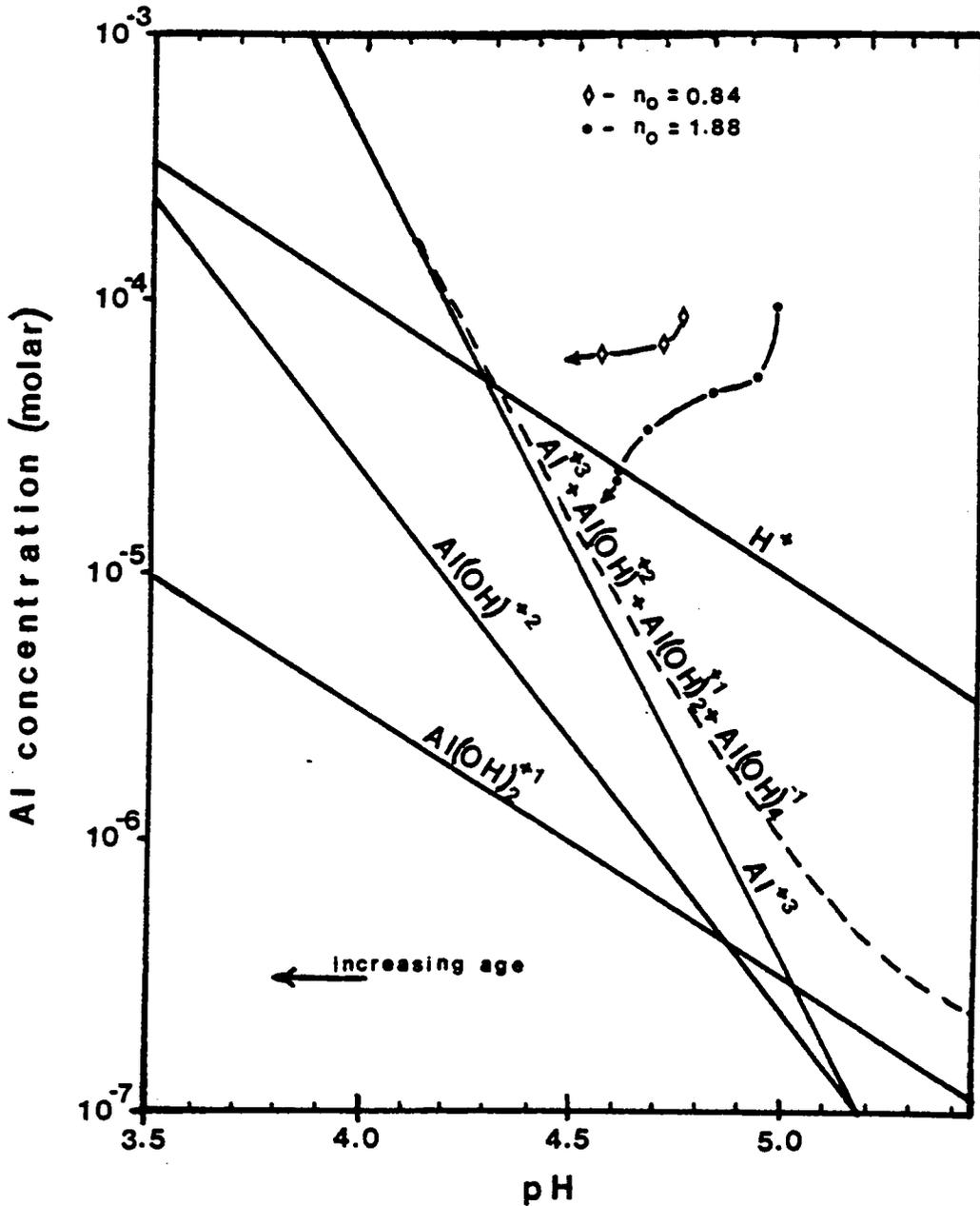


Figure 26. Equilibrium stability diagram of solution Al as a function of pH with observed data from aging partially neutralized Al solutions with $n_0 = 0.84$ and 1.88 . The observed data illustrates an aging time of 758 and 93 days for the Al solutions with $n_0 = 0.84$ and 1.88 , respectively.

Chapter VI

CONCLUSION

The present study has indicated the existence of at least two mechanisms for Al adsorption on Ca-kaolinite, montmorillonite, and peat. An initial rapid interaction of Al involved Al-Ca exchange while further Al adsorption reflected Al polymerization on the solid phase. Transition between rapid and slow Al concentration increases corroborated with the termination of desorbed Ca elution and supports the former mechanism of Al adsorption on these soil constituents. The mechanism was further supported by independent estimates of model predicted parameters used to analyze the transient displacement experiments. The slow reaction involving Al polymerization on the adsorbents was supported by the enhanced production of H^+ as Al transport occurred, the loss of this secondary reaction as the influent pH was lowered, and the high average basicity values for adsorbed, exchangeable, and nonexchangeable Al. Negligible adsorption of Al on $<2 \mu m$ gibbsite and quartz indicated that Al most likely was not binding to the uncharged octahedral and tetrahedral surfaces of kaolinite and montmorillonite, but rather electrostatically-bound Al on the adsorbents serves as a template for sorption of more Al.

The chemical partitioning of aqueous Al in partially neutralized Al solutions was accomplished through modeled reactions with ferron. Arbitrary separation of monomeric and polymeric Al was avoided using a binary species rate function which accurately separates these Al forms based on differential kinetic reactions with ferron. Analysis of effluent Al from transient displacement experiments using this method will provide accurate speciation of both solid and solution phase Al.

Chapter VII

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APPENDIX A

SOLUTION ALUMINUM ANOMOLIES RESULTING FROM VARIOUS FILTERING MATERIAL

A.1 ABSTRACT

Commercially available filter paper and membranes of varying composition were examined for their effect on solution Al. The loss of solution Al from unneutralized and partially neutralized AlCl_3 samples in equilibrium with the filter disc resulted from the negative charge and/or residual anion content of the filter material. Potentiometric titration analysis of the equilibrium Al solutions indicated marked titration curve distortions for several filter material which was related to their residual contaminants. Removal of residual salts from uncharged membrane filters essentially eliminated any loss of Al from solution.

A.2 INTRODUCTION

Filtration of liquids for the removal of particulates or collection of precipitates and solid phases is performed routinely in soil and environmental research. Filters used for these separations are either fibrous, composed of cellulose or synthetic organic fibers, or membrane types which feature pores of a reproducible diameter. The latter filter types commonly contain a nonionic detergent as a wetting agent, a humectant to prevent membrane drying, and a small amount of inorganic electrolyte (Zief and Mitchell, 1976; Cooney, 1980; Kosta, 1982). Significant cation and anion concentrations have been reported in a variety of filter material (Dams et al., 1972; Robertson, 1972; Muneta, 1980; Habib and Minski, 1981; Jay, 1985) as well as numerous UV-adsorbing contaminants (Cooney, 1980). Filter membranes composed of cellulose nitrate have been shown by Schneider and Guranowski (1975) to adsorb significant quantities of purines and pyrimidines. Fibrous cellulotic filters have also been noted to adsorb significant quantities of Cd^{2+} (John and VanLaerhoven, 1976) and Al (Frink and Peech, 1962). Standard EPA regulations on water quality require that environmental water samples, including those effected by acid deposition, be filtered prior to analysis (Envir. Prot. Agency, 1973). Potential adsorption of influent ma-

terial on filters and failure to consider contamination of effluent by residual filter electrolytes, limits reliable aqueous solubility values and the quality of environmental water samples (Liu et al., 1977). This work investigates the effects of various filter material on solution Al, a common aqueous component in environments affected by acid rain; and also evaluates the leacheable anions and charge properties of the filter material.

A.3 MATERIALS AND METHODS

Twenty three different filter papers and membranes (Table 10) commonly used in soil research were tested for their effect on solution Al, their glass-distilled water (GD-H₂O) extractable anion concentrations, and their potential cation and anion exchange capacities (CEC and AEC, respectively). Filter disc were used from newly purchased stocks with the exception of M1, M4, G5, N2, N3, and N4, and selected at random within a box avoiding those disc located near the top and bottom of the stack (McDonald and Duncan, 1978). Filters were transferred to polymethylpentene (PMP) beakers of 6.5 cm diameter using clean, dry teflon forceps. Filters were never folded, handled, or damaged in anyway with the exception of Whatman 50 whose ends were slightly crimped because of its larger size.

Table 10. Select chemical and physical properties of filter disc.†

Filter disc type	Code	Diameter	Membrane Composition
		--- mm ---	
Whatman WCN 0.20 μm	W1	47.0	Cellulose nitrate
Whatman WCN 0.45 μm	W2	47.0	Cellulose nitrate
Whatman WCN 1.0 μm	W3	47.0	Cellulose nitrate
Whatman No. 42	W4	42.5	Cellulose with organic binder
Whatman No. 50	W5	55.0	Cellulose with organic binder
Millipore VSWP 0.025 μm	M1	47.0	Mixed cellulose acetate and cellulose nitrate
Millipore GSWP 0.22 μm	M2	47.0	Mixed cellulose acetate and cellulose nitrate
Millipore HAWP 0.45 μm	M3	47.0	Mixed cellulose acetate and cellulose nitrate
Millipore HAWP 0.45 μm	M4	25.0	Mixed cellulose acetate and cellulose nitrate
Sterile Gelman Acrodisc 0.20 μm	G1	25.0	Polysulfone
Sterile Gelman Acrodisc 0.45 μm	G2	25.0	Polysulfone
Gelman GA-8 0.20 μm	G3	47.0	Cellulose triacetate
Gelman GA-6 0.45 μm	G4	47.0	Cellulose triacetate
Old Gelman GA-6 0.45 μm^*	G5	47.0	Cellulose triacetate
Gelman GA-3 1.2 μm	G6	47.0	Cellulose triacetate
Nuclepore 0.20 μm	N1	25.0	Polycarbonate
Nuclepore 1.0 μm	N2	47.0	Polycarbonate
Nuclepore 3.0 μm	N3	47.0	Polycarbonate
Nuclepore 5.0 μm	N4	47.0	Polycarbonate
Nuclepore MF 0.22 μm	N5	47.0	Mixed cellulose nitrate - cellulose diacetate
Nuclepore MF 0.45 μm	N6	47.0	Mixed cellulose nitrate - cellulose diacetate
Nalgene 0.20 μm	Na1	47.0	Cellulose nitrate
Nalgene 0.45 μm	Na2	47.0	Cellulose nitrate

†Product name is indicated for benefit of the reader and does not infer official endorsement nor condemnation.

*G5 had Lot No. = 2.5 million and other Gellman GA discs had Lot No. = 4.1 million.

The effect of the filter disc on solution Al was investigated by equilibrating 5 ml of $\approx 2.45 \mu\text{g mL}^{-1}$ AlCl_3 , either unneutralized or partially neutralized ($\text{OH}/\text{Al} = 0.5$), with a single 47mm disc or two 25mm disc for ≈ 12 hrs. The mixture was sealed and periodically gently agitated. Equilibrium solutions were analyzed for total acidity using potentiometric titrations and for total Al using ferron (Jardine et al., 1985).

Inherent anion concentrations of the filter disc were studied by equilibrating 5 ml GD- H_2O with fresh filters using methods described above. Anion concentrations were determined using a Dionex ion chromatograph (IC).

The potential CEC and AEC of the filter disc were evaluated by washing the disc three times, over a 3 hr period with 5 ml aliquots of gold label 1×10^{-3} M MgCl_2 (pH 8.4) and 1×10^{-3} M $\text{Mg}(\text{NO}_3)_2$ (pH 6.0), respectively. Filter disc were washed 7 times with ≈ 50 ml aliquots of GD- H_2O and dried at 308 K. Five mL $\approx 9 \times 10^{-5}$ M AlCl_3 (pH 4.4) and 5×10^{-4} M gold label CaCl_2 (pH 5.7) were added to the MgCl_2 and MgNO_3 saturated disc, respectively. The former equilibrium solutions were analyzed for desorbed Mg using atomic adsorption spectrophotometry and for the loss of solution Al using ferron. The MgNO_3 saturated disc were analyzed for desorbed NO_3^- utilizing IC. During all studies the PMP beakers were

found to have no effect on the dilute electrolyte solutions or GD-H₂O added. Experiments using Gelman Acrodisc, which have membrane filters encased in modified acrylic, were treated exactly as described above except solutions were syringe injected through single 25 mm disc. All studies were performed in duplicate or triplicate except the AEC experiment which was not repeated.

A.4 RESULTS AND DISCUSSION

Several filter disc in equilibrium with unneutralized and partially neutralized 2.45 $\mu\text{g mL}^{-1}$ AlCl₃ removed a significant portion of Al from solution (Table 11). The latter solution consistently removed more Al than the unneutralized solution due to the presence of \approx 25% polymeric Al (Jardine et al., 1985). Solution Al losses were also apparent from potentiometric titration analysis of the unneutralized Al solution (Fig. 27) and the partially neutralized sample (Fig. 28 and Table 12) which were equilibrated with the filter material. Titration data for all filters exposed to unneutralized Al are not presented since trends are identical to those presented for the partially neutralized solution (Table 12). The equilibrium solution in contact with filter disc generally contained a lower pH relative to the control which was not exposed to any filter material (negative ΔpH),

with several solutions revealing pronounced H^+ inflections during titration analysis. The increase of solution H^+ may be the result of enhanced Al hydrolysis or polymerization in the presence of the filter disc (Jardine et al., 1985). Marked titration curve distortions were apparent in many filter solutions because of pH decreases and Al losses (Figs. 27,28). All Whatman, Nalgene, and M1 and M4 disc were observed to have skewed titration tails, at higher pH values. Such distortions may be related to organic contaminants or altered forms of Al and may account for the obscure results obtained for filter G5 (Fig 27, Table 12). Filters G1, G2, G3, and N1, N2, N3 in equilibrium with the various Al solutions had no effect on potentiometric titration analysis which is consistent with their very small removal of solution Al (Tables 11 and 12).

Filter disc which resulted in large losses of solution Al generally had high levels of F^- , PO_4^{3-} , and/or SO_4^{2-} (Table 13). These anions tend to complex Al which may become undetectable to ferron. Significant quantities of F^- , PO_4^{3-} , and/or SO_4^{2-} were present in filter disc W1, M2, M3, G5, N5, N6, Na1, and Na2; all of which removed appreciable quantities of Al from solution with exception to G5. This latter membrane has been shown to contain significant residual Al (Dams et al., 1972). Several filter material were

Table 11. Unneutralized and partially neutralized Al solutions in equilibrium with filter disc.

Filter Code	≈ 12.26 μg Al unneutralized pH 4.4		≈ 12.26 μg Al OH/Al = 0.5 pH 4.7	
	μg Al removed by filter	Fraction of Al removed X 100	μg Al removed by filter	Fraction of Al removed X 100
W1	1.33	10.9	2.22	19.7
W2	0.48	5.9	1.77	14.5
W3	1.19	9.7	3.12	25.6
W4	4.15	33.7	6.95	57.1
W5	4.53	36.8	7.34	60.3
M1	0.58	4.7	2.27	18.6
M2	0.85	6.9	2.71	22.2
M3	1.55	12.6	2.24	18.4
M4	0.05	0.4	0.45	3.7
G1	0.27	2.2	0.25	2.1
G2	0.27	2.2	0.37	3.0
G3	0.57	4.6	0.42	3.5
G4	0.17	1.4	0.44	3.6
G5	0.00	0.0	0.00	0.0
G6	0.57	4.6	0.65	5.4
N1	0.12	1.0	0.25	2.0
N2	0.00	0.0	0.54	4.4
N3	0.66	5.4	0.25	2.1
N4	0.80	6.5	0.13	1.1
N5	1.06	8.7	2.72	24.0
N6	1.94	15.9	5.97	52.7
Na1	9.62	78.2	10.30	84.6
Na2	8.95	72.7	10.60	87.0

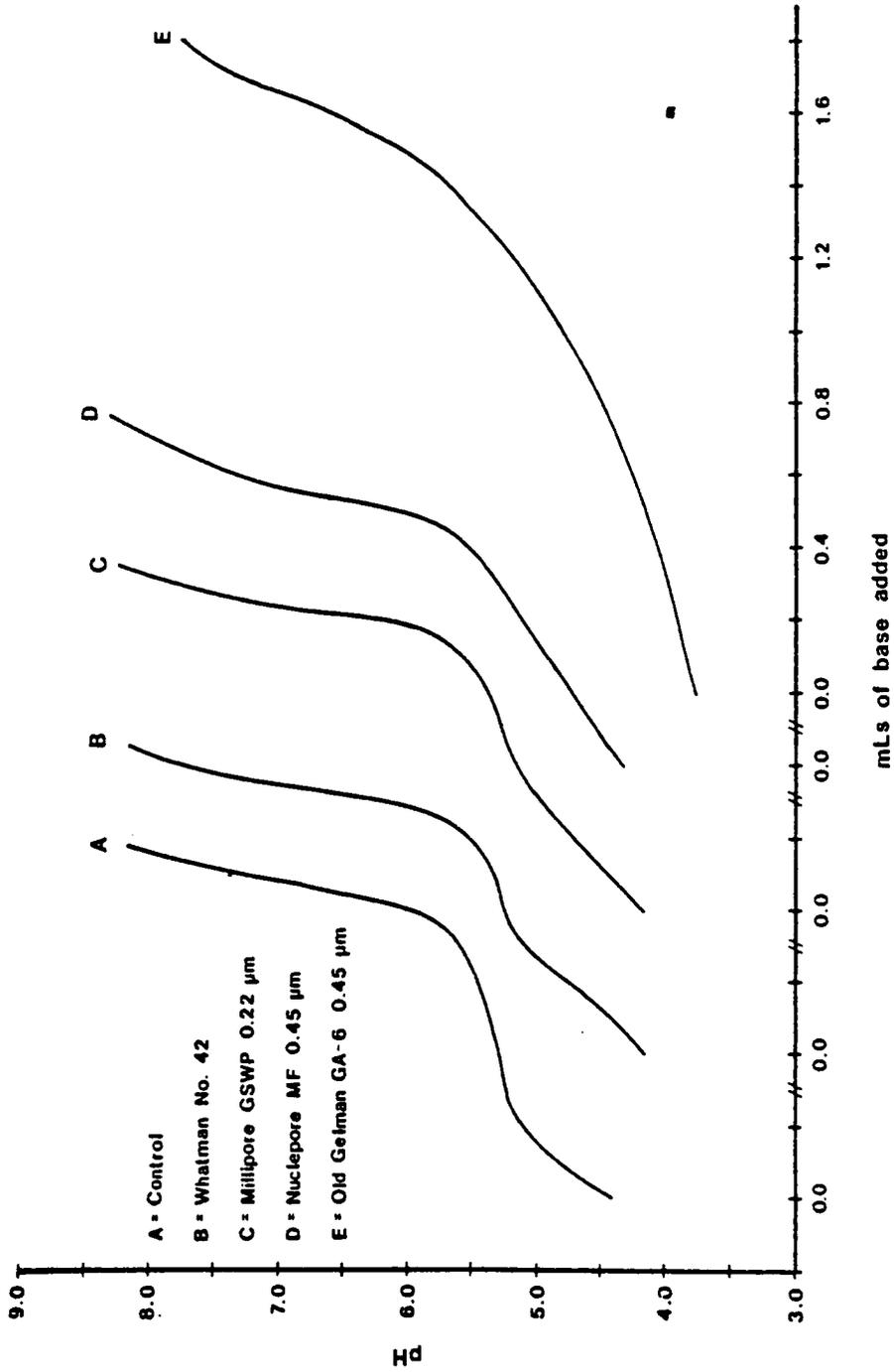


Figure 27. Potentiometric titrations of 2.45 $\mu\text{g mL}^{-1}$ unneutralized Al for unfiltered controls and solutions in equilibrium with several filter disc.

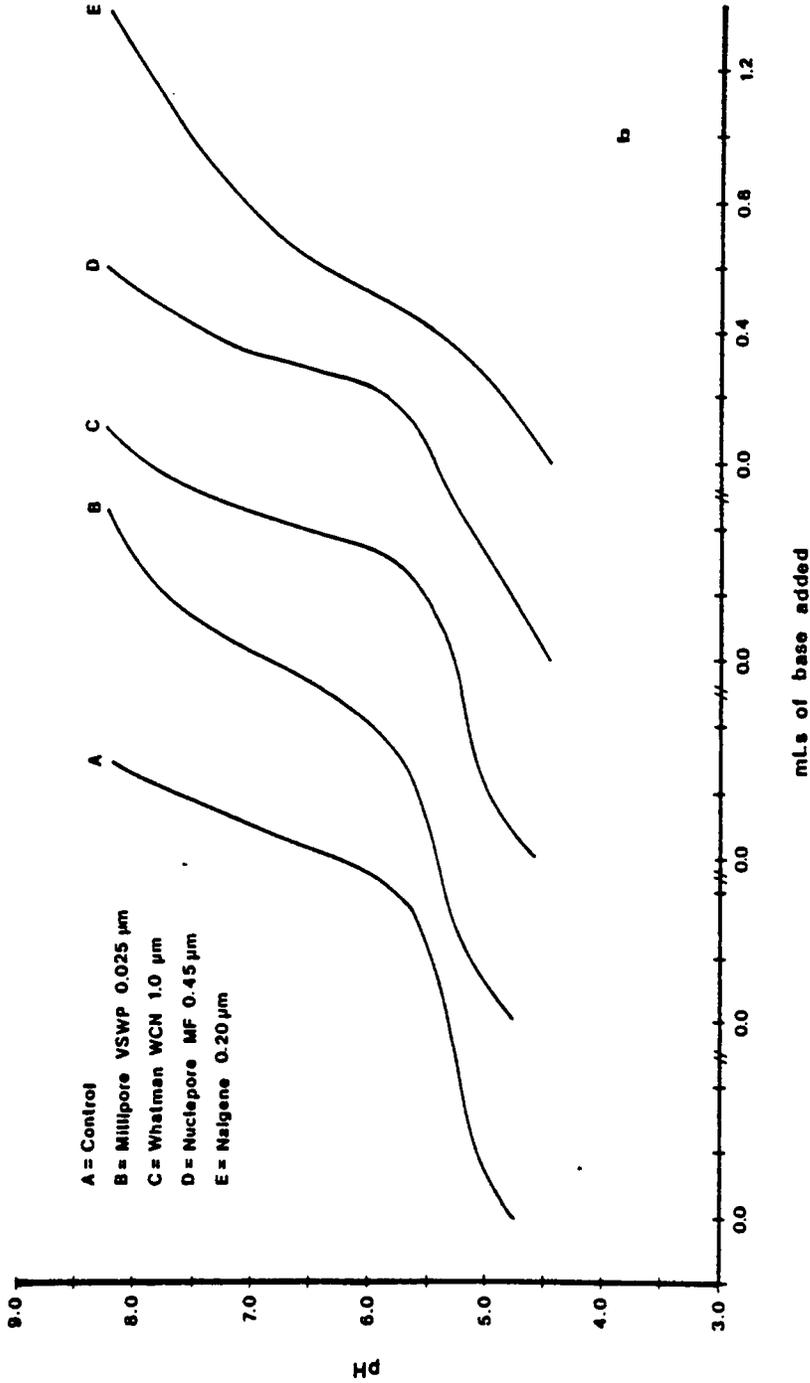


Figure 28. Potentiometric titrations of 2.45 $\mu\text{g mL}^{-1}$ partially neutralized Al (OH/Al = 0.5) for unfiltered controls and solutions in equilibrium with several filter disc.

Table 12. Potentiometric titration analysis of the partially neutralized Al solution in equilibrium with filter disc.

Filter Code	meq Al mL ⁻¹	meq H mL ⁻¹	ΔpH^\ddagger
Control	0.228	0.000	----
W1	0.164	0.013	-0.14
W2	0.200	0.000	-0.10
W3	0.193	0.000	-0.33
W4	0.123	0.030	-0.40
W5	0.120	0.036	-0.37
M1	0.207	0.000	-0.01
M2	0.219	0.000	-0.39
M3	0.218	0.000	-0.15
M4	0.222	0.000	-0.09
G1	0.224	0.000	-0.05
G2	0.224	0.000	0.00
G3	0.222	0.000	-0.07
G4	0.239	0.000	-0.19
G5	*	0.476	-0.97
G6	0.236	0.000	-0.15
N1	0.228	0.000	-0.04
N2	0.228	0.000	-0.05
N3	0.231	0.000	-0.06
N4	0.232	0.000	-0.19
N5	0.171	0.000	+0.02
N6	0.086	0.073	-0.39
Na1	*	0.100	-0.34
Na2	*	0.078	-0.29

‡ $\Delta\text{pH} = (\text{Disc equilibrium pH} - \text{control pH})$

* Characteristic Al titration curve not present.

also noted to contain high concentrations of Cl^- (eg. Millipore) and NO_3^- (eg. W5, M1, G5). Although these anions are serious contaminants of the filter disc, their effect on solution Al is minimal. The membrane filters N1, N2, N3, and N4 contained no detectable anions which is consistent with their very small removal of solution Al (Table 11). Jay (1985) also found very low or no detectable anions in similar polycarbonate membranes.

The residual anions of the filter material did not entirely account for the loss of Al from solution. Many of the filter disc were found to have a significant negative charge (Table 14). The filter disc used in determining negative charge were free of all residual anions except Cl^- which accompanied the saturating and exchanging salts. All Whatman disc were found to have an appreciable CEC as noted by the release of Mg by Al from the Mg-sat filter disc. Filters W4 and W5 had the largest negative charge which is consistent with the finding of others using similar cellulosic material (John and VanLaerhoven, 1976). Other filter material which exhibited a significant CEC were M1, G5, N5, N6, Na1 and Na2. Comparison of the fraction of Al removed from solution at pH 4.4 when the filter disc were "cleaned" of their residual anions (Table 14), to the fraction of Al removed when residual anions were present (Table 11, Column

Table 13. Anions released by filter disc in equilibrium with 5 ml GD-H₂O.

Filter Code	F ⁻	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
	----- μg -----				
W1	0.6	4.2	1.2	<0.2	4.6
W2	0.5	1.2	1.9	<0.2	1.9
W3	0.9	6.0	1.8	<0.2	0.8
W4	0.4	10.4	0.4	<0.2	<0.5
W5	0.7	2.2	7.1	<0.2	<0.5
M1	1.7	29.6	14.8	<0.2	2.0
M2	0.5	18.4	2.3	5.7	0.4
M3	0.4	12.4	1.5	3.9	0.5
M4	0.6	12.0	6.9	0.3	2.2
G1	2.0	0.7	<0.2	<0.2	0.9
G2	2.2	0.9	<0.2	<0.2	1.0
G3	1.1	7.5	1.6	<0.2	0.2
G4	0.9	25.4	2.9	0.2	2.7
G5	6.8	18.2	10.0	<0.2	7.0
G6	0.9	6.1	1.4	1.5	<0.5
N1	<0.02	<0.1	<0.2	<0.2	<0.5
N2	<0.02	<0.1	<0.2	<0.2	<0.5
N3	<0.02	<0.1	<0.2	<0.2	<0.5
N4	<0.02	<0.1	<0.2	<0.2	<0.5
N5	0.8	6.7	3.5	6.7	<0.5
N6	1.4	6.9	2.9	10.5	0.6
Na1	0.7	0.8	3.7	7.3	13.3
Na2	0.9	0.7	2.4	9.9	5.2
GD-H ₂ O	<0.02	<0.1	<0.2	<0.2	<0.5

1 and 2), suggest the primary loss of Al by Whatman filter disc resulted from their negative charge. The removal of solution Al by N5, N6, Na1, and Na2 is related to their residual anion content and negative charge. The removal of residual salts from the uncharged Gelman filters essentially eliminated any loss of Al from solution (Tables 11 and 14). The filter disc were also tested for the possibility of positive charge. Filters M2, M3, and M4 were the only disc to exhibit a very small but measureable AEC as noted by the release of NO_3^- by Cl^- from NO_3^- -sat filter disc (Table 14). The relatively small AEC may be the result of the high saturating pH used (eg pH 6.0). Saturating solutions of lower pH may induce additional positive charge if this charge is pH dependent. Potential positive charge may exist on Na1 and Na2 filters also, since residual SO_4^{2-} of the filter disc was found to be exchangeable to CaCl_2 (pH 5.7) but not to $\text{Mg}(\text{NO}_3)_2$ (pH 6.0) or $\text{GD-H}_2\text{O}$.

The present study confirms that much of the commonly used filter papers and membranes have significant inorganic electrolyte contaminants and may be negatively or positively charged. Of the filter material investigated we prefer using filters N1, N2, N3, and N4 (Nuclepore polycarbonate) which are not likely to alter the Al chemistry of environmental water samples which pass through them. With appro-

Table 14. Analysis of filter disc for potential negative and positive charge.

Filter Code	Test for negative charge			Test for positive charge
	$\mu\text{g Mg}$ desorbed	$\mu\text{g Al}$ adsorbed	Fraction of Al removed X 100	$\mu\text{g NO}_3^-$ desorbed
W1	2.6	1.19	9.8	0.0
W2	1.1	0.73	6.1	0.0
W3	2.3	0.74	6.1	0.0
W4	12.8	4.35	35.8	0.0
W5	12.2	4.76	39.2	0.0
M1	2.3	0.87	7.1	0.0
M2	0.6	1.32	10.9	0.8
M3	0.5	0.44	3.6	0.9
M4	0.0	0.00	0.0	1.3
G1	0.0	0.00	0.0	0.0
G2	0.0	0.00	0.0	0.0
G3	0.0	0.00	0.0	0.0
G4	0.0	0.12	1.0	0.0
G5	2.5	0.63	5.2	0.0
G6	0.0	0.15	1.1	0.0
N1	0.0	0.00	0.0	0.0
N2	0.0	0.00	0.0	0.0
N3	0.0	0.00	0.0	0.0
N4	0.0	0.00	0.0	0.0
N5	0.9	0.23	1.9	0.0
N6	1.0	0.54	4.4	0.0
Na1	2.9	2.19	18.1	0.0*
Na2	1.8	2.38	19.6	0.0*

*Study complicated by the presence of SO_4^{2-} in the extract which was exchangeable to CaCl_2 (pH 5.7) but not MgNO_3 (pH 6.0) or $\text{GD-H}_2\text{O}$.

priate cleaning (Wallace et al., 1977; Jay, 1985), the Gelman series (eg. G1, G2, G3, G4, G6) should also be satisfactory. The values for the quantity of leachable anions and fraction of Al loss from solution are by no means absolute and should not be used as correction factors for another's work. McDonald and Duncan (1978) have clearly shown that although a single box of filter disc provide reproducible contaminants, large discrepancies exist from the box to box. Comparing G4 to G5 in the present study, which differ only in stock number, illustrates this point as well.

APPENDIX B

A TIME DELAY ANALYSIS TECHNIQUE FOR DISTINGUISHING COMPLEX REACTIONS OF ALUMINUM WITH FERRON

Monotonically increasing absorbance-time functions are common for the colorimetric determination of Al in solution (Turner, 1969; Smith and Hem, 1972; Blamey et al., 1983). In general, the curves have an initial rapid increase in absorbance which slows and continues to long times (Fig. 29). Usually the curves are simple exponential functions which are described by first-order kinetic expressions. Many times, however, simple exponential expressions will not fully describe the curves. It may be that the complex function is composed of several parallel reactions or that experimental error has become large at longer times. Distinction between the two possibilities is achieved by employing a time-delay analysis technique (Espenson, 1981; Mason, personal communication). Assuming a major portion of the absorbance-time function is described by first-order kinetics (self-verification of this assumption is implicit in the final results), one may write:

$$\ln (A_{\infty} - A_t) = \ln (A_{\infty} - A_0) - kt \quad (27)$$

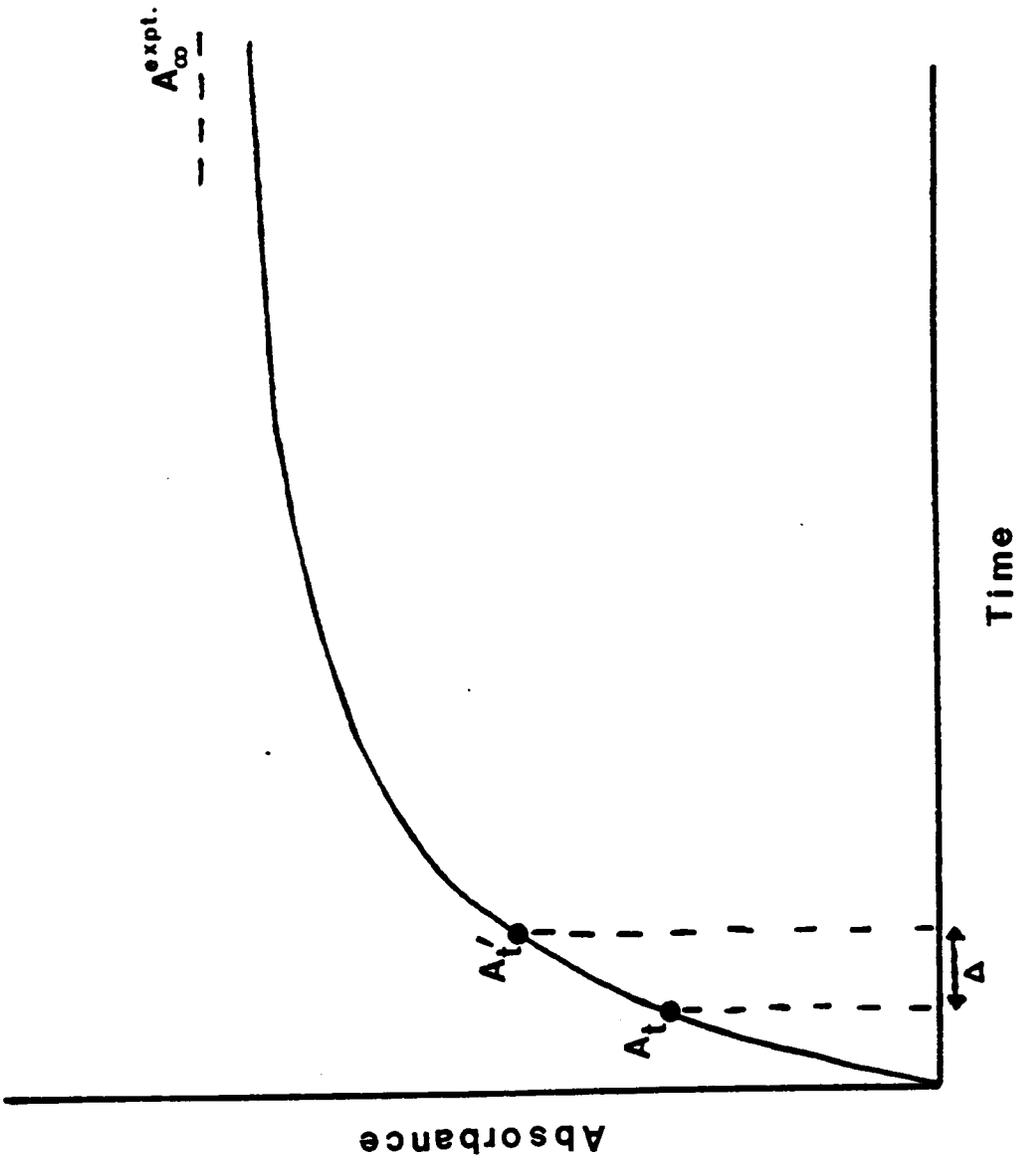


Figure 29. Typical absorbance-time function for the colorimetric detection of Al in solution.

where A_0 , A_t , and A_∞ are absorbance values at time zero, at time t , and the value at equilibrium, respectively, and k is the first-order rate constant. Since the rate of Al reaction with ferron is dependent on the amount of reactant remaining in solution (uncomplexed Al), the difference between A_∞ and A_t and A_0 is required in Eqn. 27. Rearranging Eqn. 27, one obtains:

$$\frac{(A_\infty - A_t)}{(A_\infty - A_0)} = e^{-kt} \quad (28)$$

$$(A_\infty - A_t) = (A_\infty - A_0) e^{-kt} \quad (29)$$

A tangent of slope k at point A_t on the absorbance-time function is represented by Eqn. 29 (Fig. 29). Considering another point on the function, $A_{t'}$, which is distance Δ from point A_t , we can similarly express the rate of reaction at this point by:

$$(A_\infty - A_{t'}) = (A_\infty - A_0) e^{-k(t + \Delta)} \quad (30)$$

where $t' = t + \Delta$. Dividing Eqn. 29 by Eqn. 30 and rearranging terms, one obtains:

$$\frac{(A_\infty - A_t)}{(A_\infty - A_{t'})} = e^{k\Delta} \quad (31)$$

$$(A_\infty - A_t) = A_\infty e^{k\Delta} - A_{t'} e^{k\Delta} \quad (32)$$

$$A_t = A_\infty - A_\infty e^{k\Delta} + A_{t'} e^{k\Delta} \quad (33)$$

$$A_t = A_{\infty} (1 - e^{-k\Delta}) + A_{t'} e^{-k\Delta} \quad (34)$$

A plot of A_t vs $A_{t'}$ will be linear for that portion of the reaction which conforms to first-order kinetics. The slope, $e^{-k\Delta}$, and the intercept, $A_{\infty}(1 - e^{-k\Delta})$, can be used to find the predicted value of A_{∞} . If the predicted A_{∞} value is significantly different from the experimental A_{∞} value, the extended tailing at long times for absorbance-time functions, which is not predicted by simple expressions, is the result of complex parallel reactions occurring in the system. If the predicted and experimental A_{∞} are similar, tailing of the absorbance-time function is the result of experimental error and cannot be considered a separate reaction in the system.

Investigating the reaction of partially neutralized Al with ferron (Chapter V), it was noted that a two species rate equation was unable to describe observed $(C_{\infty} - C_t)/C_{\infty}$ data at longer times, which accounted for 7-22% of the entire reaction depending on the basicity of the Al solution. Using the time delay analysis technique, predicted A_{∞} values were determined from linear A_t vs $A_{t'}$ plots of the secondary reacton of Al with ferron. Predicted A_{∞} were significantly less than experimental A_{∞} values suggesting this portion of the $(C_{\infty} - C_t)/C_{\infty}$ data was a separate Al-ferron reaction (Figs.

30, 31; example plots for Al solutions with $n_0=0.84$ and 1.88, respectively). Thus the extended tailing of the absorbance-time functions at long times was indeed a ternary reaction of Al with ferron and it was found to be well described by pseudo-first-order kinetics.

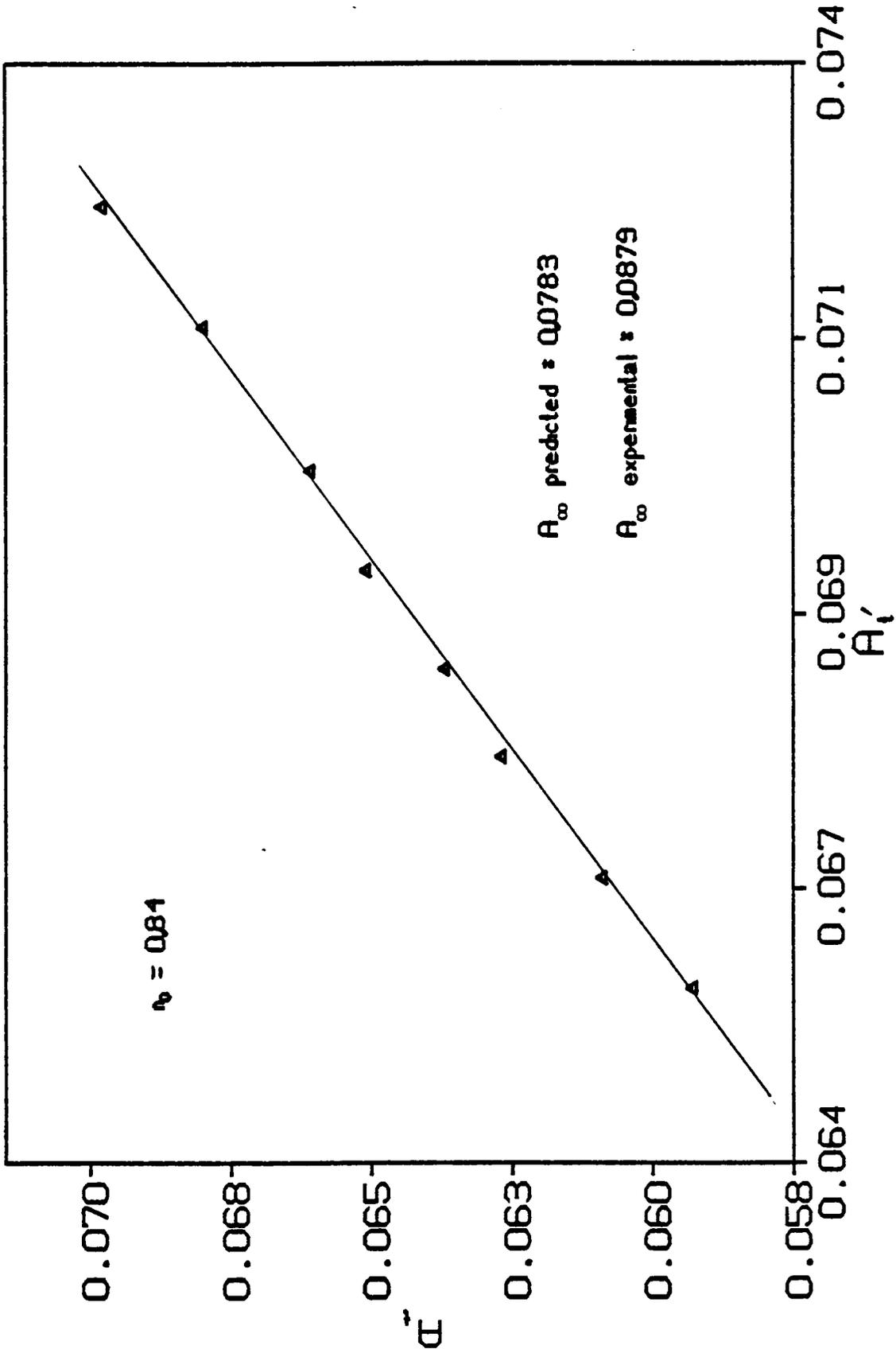


Figure 30. A_t vs. A_t' function using time delay analysis theory to predict A_∞ for the reaction of ferron with partially neutralized Al, $n_0=0.84$.

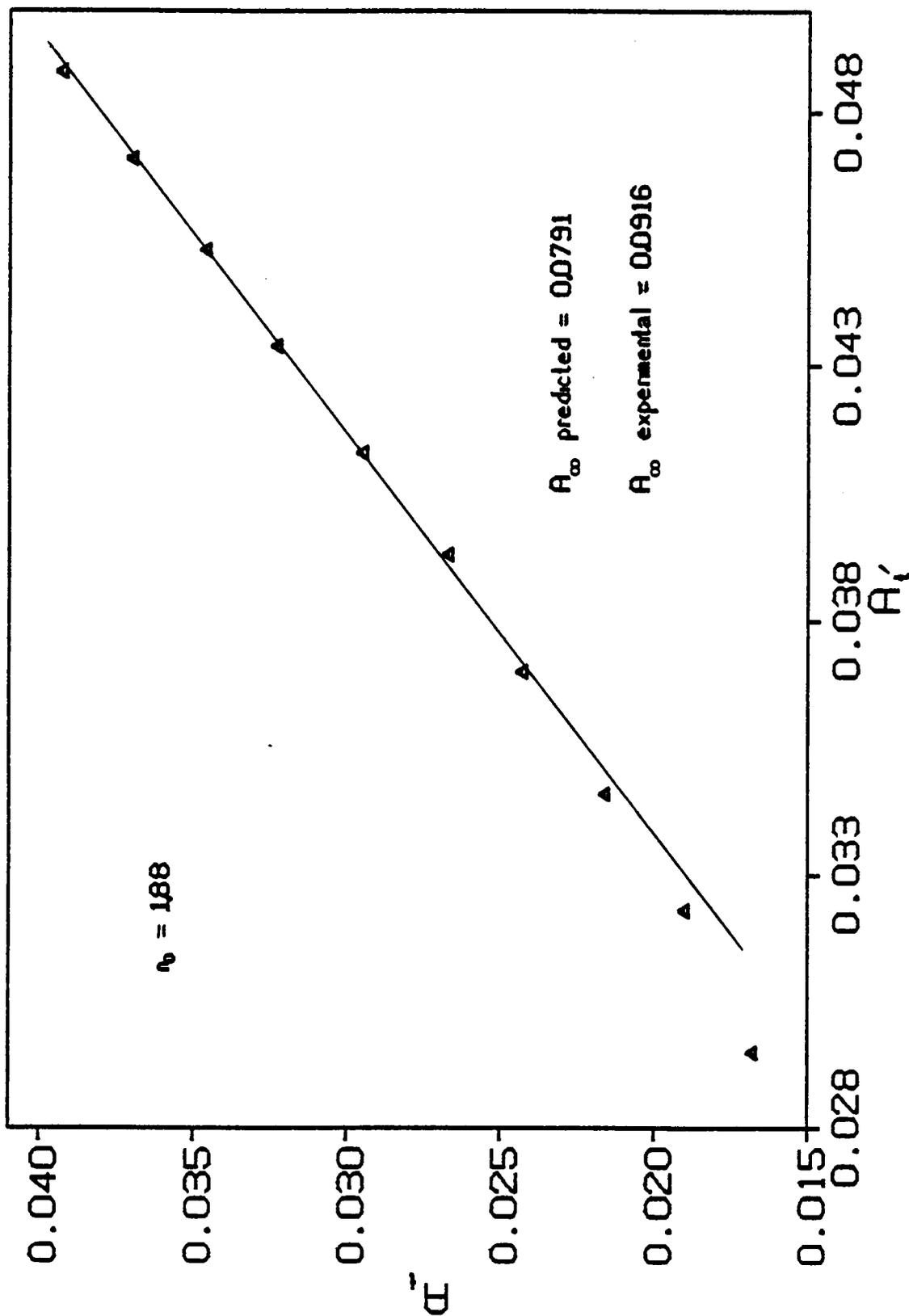


Figure 31. A_t vs. A_t' function using time delay analysis theory to predict A_{∞} for the reaction of ferron with partially neutralized Al, $n_0=1.88$.

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