ADSORPTION OF SULFATE AND PHOSPHATE AT THE MINERAL-WATER INTERFACE: ISOTHERM, STOICHIOMETRY, AND MODELS

by

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Adsorption of Sulfate and Phosphate at Mineral-Water Interface:

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(ABSTRACT)

Processes occurring at mineral-water interfaces play critical roles for regulating the composition of surface and groundwater, for soil development, and for the availability of plant nutrients. Sulfate adsorption at three pH levels was conducted on γ-Al₂O₃ and kaolinite. The adsorption isotherms were described well by the simple Langmuir, two-site Langmuir, Freundlich, and Temkin equations. The capacity of SO₄²⁻ adsorption for γ-Al₂O₃ was five times greater than for kaolinite, indicating the difference in reactive site density between γ-Al₂O₃ and kaolinite. Mathematical analyses for the adsorption isotherms demonstrated that SO₄²⁻ may not be adsorbed on the d-plane, i.e., in the diffuse layer, whereas both outer- and inner-sphere complexation mechanisms predicted SO₄²⁻ adsorption equally well.

There is a release of OH⁻ from soil colloids with the addition of SO₄²⁻. The ratio of moles of OH⁻ released per mole of SO₄²⁻ adsorbed is referred to as the OH/SO₄ exchange stoichiometry. The OH/SO₄ stoichiometry not only provides an important constraint on surface complexation models, but also is a critical area of research to explain the effects on soil pH from the application of SO₄²⁻ amendments such as gypsum. The OH/SO₄ stoichiometry on γ-Al₂O₃ and kaolinite was determined by a back-titration method with a pH-stat autotitrator as well as calculated from SO₄²⁻ adsorption edges at various SO₄²⁻ concentrations by the thermodynamic approach. The stoichiometry depended upon
suspension pH, $\text{SO}_4^{2-}$ equilibrium concentration, and source of adsorbents. It increased with increasing solution pH and $\text{SO}_4^{2-}$ adsorption density. At a low pH the stoichiometry was low and was similar for $\gamma$-Al$_2$O$_3$ and kaolinite. At higher pH levels it was higher for $\gamma$-Al$_2$O$_3$ than for kaolinite. The average values of the stoichiometry calculated by the thermodynamic approach were in agreement with those measured by back titration for both $\gamma$-Al$_2$O$_3$ and kaolinite. The thermodynamic approach provides an easier experimental method to evaluate the OH/anion stoichiometry as a function of pH and adsorption density. It also indicated that at low pH levels (< 5) the stoichiometry might be overestimated due to dissolution of adsorbents; whereas at higher pH levels (5-8) it might be underestimated due to precipitation of Al hydroxy sulfates and gibbsite.

It is known that PO$_4^{3-}$ is retained by soils through ligand exchange, i.e., inner-sphere complexation, but the mechanism for $\text{SO}_4^{2-}$ adsorption at the mineral-water interface has been in debate. By studying the effects of ionic strength on ion adsorption, it is possible to distinguish between inner- and outer-sphere ion surface complexes. This study was conducted to evaluate ionic strength effects on $\text{SO}_4^{2-}$ and PO$_4^{3-}$ adsorption on $\gamma$-Al$_2$O$_3$ and kaolinite at varying solution pH (3-11), and to infer $\text{SO}_4^{2-}$ and PO$_4^{3-}$ adsorption mechanisms at the mineral-water interface. The adsorption of $\text{SO}_4^{2-}$ on $\gamma$-Al$_2$O$_3$ and kaolinite decreased monotonically with increasing solution pH and was markedly decreased by increasing the concentration of background electrolyte. On the contrary, PO$_4^{3-}$ adsorption on $\gamma$-Al$_2$O$_3$ and kaolinite increased from pH 3-4 and decreased from pH 6 to 11, with an adsorption plateau between pH 4 and 6. Phosphate adsorption was little affected by changes in ionic strength. At low pH, PO$_4^{3-}$ adsorption showed a slight decrease with increasing ionic strength; whereas, at high pH, PO$_4^{3-}$ adsorption increased slightly with increasing ionic strength, resulting in a cross-over point where there was no ionic strength effect. The triple layer model (TLM) was applied to model the adsorption of $\text{SO}_4^{2-}$ and PO$_4^{3-}$ with both inner- and outer-sphere complexes using the FITEQ 3.1 computer program. The $\text{SO}_4^{2-}$ adsorption was better modeled by assuming outer-sphere complex formation, while PO$_4^{3-}$ adsorption was better modeled by assuming inner-sphere complex formation.
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# TABLE OF CONTENTS

ABSTRACT ..................................................................................................................... ii  
ACKNOWLEDGMENTS ............................................................................................. iv  
TABLE OF CONTENTS ............................................................................................ vii  
LIST OF TABLES ....................................................................................................... x  
LIST OF FIGURES ..................................................................................................... xi  

I. INTRODUCTION ........................................................................................................ 1  
1-1 Background ......................................................................................................... 1  
1-1.1 Sulfur ............................................................................................................. 1  
1-1.2 Phosphorus .................................................................................................... 3  
1-1.3 Surface Complexation Models ....................................................................... 4  
1-2 Research Objectives .......................................................................................... 5  
1-3 Organization ....................................................................................................... 6  
1-4 References .......................................................................................................... 6  

II. MODELS FOR EQUILIBRIUM ADSORPTION ......................................................... 9  
2-1 Introduction ......................................................................................................... 9  
2-2 Empirical Adsorption Models ........................................................................... 10  
2-2.1 Langmuir Equation ....................................................................................... 10  
2-2.2 Freundlich Equation ..................................................................................... 13  
2-2.3 Temkin Equation ......................................................................................... 15  
2-2.4 Brunauer-Emmett-Teller (BET) Equation ..................................................... 15  
2-3 Surface Complexation Models ........................................................................... 17  
2-3.1 Introduction ................................................................................................... 17  
2-3.2 Constant Capacitance Model ....................................................................... 19  
2-3.3 Diffuse Layer Model .................................................................................... 24  
2-3.4 Triple Layer Model ...................................................................................... 27  
2-3.5 Four Layer Model ......................................................................................... 31
2-3.6 One-pK Model .................................................................................. 34
2-7 References .......................................................................................... 37

III. QUANTITATIVE AND MECHANISTIC ANALYSIS OF SULFATE
ADSORPTION ON γ-Al₂O₃ AND KAOLINITE DETERMINED BY
ISOTHERMS ............................................................................................. 46
Abstract ................................................................................................... 46
3-1 Introduction ......................................................................................... 47
3-2 Materials and Methods ..................................................................... 48
   3-2.1 Adsorbents .................................................................................. 48
   3-2.2 Adsorption Experiments ............................................................... 49
   3-2.3 Adsorption Isotherm Equations .................................................... 51
3-3 Results and Discussion .................................................................... 52
   3-3.1 Adsorption Isotherms ................................................................. 52
   3-3.2 Quantitative Analysis for SO₄²⁻ Adsorption Mechanisms .......... 57
3-4 References ......................................................................................... 68
3-5 Appendix ........................................................................................... 71

IV. HYDROXYL-SULFATE EXCHANGE STOICHIOMETRY ON γ-Al₂O₃
AND KAOLINITE .................................................................................. 72
Abstract ................................................................................................... 72
4-1 Introduction ......................................................................................... 73
4-2 Theory of Thermodynamic Approach .............................................. 76
4-3 Materials and Methods ...................................................................... 81
   4-3.1 Pretreatment on γ-Al₂O₃ ............................................................... 81
   4-3.2 Preparation of <2 mm Kaolinite Clay Suspension ....................... 81
   4-3.3 Experimental Procedure and Analysis ....................................... 82
4-4 Results and Discussion .................................................................... 84
   4-4.1 Aluminum Dissolving from γ-Al₂O₃ and Kaolinite ...................... 84
   4-4.2 Back-titration and Measured χ .................................................... 89
   4-4.3 Adsorption Edges and Calculated χ ........................................... 92
LIST OF TABLES

Table 3-1. Sulfate adsorption maximum and free energy on γ-Al₂O₃ and kaolinite ............... 52
Table 3-2. Comparison of r² for SO₄²⁻ adsorption on different planes ........................................ 65

Table 4-1. Mean values of χ obtained from measurement and calculation at
selected pH levels for γ-Al₂O₃ and kaolinite ........................................................................ 96

Table 5-1. Solid and suspension properties used in TLM modeling for SO₄ and
PO₄ adsorption on γ-Al₂O₃ and kaolinite ............................................................................ 134
Table 5-2. Reactions and equilibrium constants used in TLM modeling for SO₄
and PO₄ adsorption on γ-Al₂O₃ and kaolinite ........................................................................ 137
Table 5-3. Sulfate surface complexation reactions and complexation constants
optimized with FITEQL ........................................................................................................ 138
Table 5-4. Phosphate surface complexation reactions and complexation constants
optimized with FITEQL ........................................................................................................ 138
Table 5-5. Values of the goodness of fit for modeling SO₄ and PO₄ adsorption on
γ-Al₂O₃ and kaolinite ........................................................................................................ 140
Table 5-6. Species, components, and stoichiometry for SO₄ adsorption on γ—
Al₂O₃ (A matrix) ................................................................................................................... 141
Table 5-7. Species, components, and stoichiometry for SO₄ adsorption on γ—
Al₂O₃ (B matrix) ................................................................................................................... 142
Table 5-8. Solution conditions for SO₄ and PO₄ adsorption on γ-Al₂O₃ and
kaolinite .................................................................................................................................... 145
LIST OF FIGURES

Fig. 2-1. Constant capacitance model ................................................. 20
Fig. 2-2. Diffuse layer model ............................................................. 25
Fig. 2-3. Basic Stern model ............................................................... 28
Fig. 2-4. Original triple layer model .................................................... 29
Fig. 2-5. Four layer model ............................................................... 32

Fig. 3-1. Sulfate equilibrium adsorption on (a) γ-Al₂O₃ and (b) kaolinite in 0.01 M KCl ........................................................................................................ 53
Fig. 3-2. Comparison of isotherms for SO₄²⁻ adsorption on γ-Al₂O₃ in 0.01 M KCl .......... 55
Fig. 3-3. Comparison of isotherms for SO₄²⁻ adsorption on kaolinite in 0.01 M KCl .......... 56
Fig. 3-4. Plots for SO₄²⁻ adsorption on the d-plane for γ-Al₂O₃ in 0.01 M KCl ............... 59
Fig. 3-5. Plots for SO₄²⁻ adsorption on the d-plane for kaolinite in 0.01 M KCl ............... 60
Fig. 3-6. Plots for SO₄²⁻ adsorption on the β-plane for γ-Al₂O₃ in 0.01 M KCl ............... 62
Fig. 3-7. Plots for SO₄²⁻ adsorption on the β-plane for kaolinite in 0.01 M KCl ............... 63
Fig. 3-8. Plots for SO₄²⁻ adsorption on the o-plane for γ-Al₂O₃ in 0.01 M KCl. A capacitance value of 1 F m⁻² was used in calculation ................................................. 66
Fig. 3-9. Plots for SO₄²⁻ adsorption on the o-plane for kaolinite in 0.01 M KCl. A capacitance value of 1 F m⁻² was used in the calculation ................................. 67

Fig. 4-1. Dissolution of γ-Al₂O₃ and kaolinite as a function of pH at various concentrations of SO₄²⁻ .............................................................................. 86
Fig. 4-2. Solubility diagrams for jurbaneite, alunite, basaluminite, and gibbsite with sulfate activities of 10⁻³ M for γ-Al₂O₃ and 10⁻⁴ M for kaolinite. Symbols represent the data points in this study ........................................................................... 88
Fig. 4-3. Consumption of HCl (V₁HCl) (a, b) and the OH⁻/SO₄²⁻ exchange stoichiometry (χ) (c, d) as a function of the total SO₄²⁻ concentration for γ-Al₂O₃ and kaolinite at three pH levels ........................................................... 91
Fig. 4-4. Adsorption edges for $\text{SO}_4^{2-}$ on $\gamma-\text{Al}_2\text{O}_3$ and kaolinite. ............................................................ 93

Fig. 4-5. Adsorption isotherms of $\text{SO}_4^{2-}$ on $\gamma-\text{Al}_2\text{O}_3$ and kaolinite at various pH levels. .................................................................................................................. 94

Fig. 4-6. Variation of the sulfate exchange stoichiometry ($\chi$) with pH and adsorption density ($\Gamma$) for $\gamma-\text{Al}_2\text{O}_3$ and kaolinite. ................................................................. 97

Fig. 5-1. Triple layer model. (a) Assume that (i) $\text{PO}_4$ is adsorbed on the o-plane with inner-sphere complexes, and $\text{PO}_4$ ions are directly linked to the metal ions in the solid, forming covalent bonds; (ii) $\text{SO}_4$ ions are attracted by the positive charges from the surface groups. (b) Illustration for the distribution of potentials, charges, and capacitances with distances............. 125

Fig. 5-2. Sulfate adsorption edge on $\gamma-\text{Al}_2\text{O}_3$ as a function of pH and ionic strength. .................................................................................................................. 148

Fig. 5-3. Sulfate adsorption edge on kaolinite as a function of pH and ionic strength. .................................................................................................................. 149

Fig. 5-4. Phosphate adsorption edge on $\gamma-\text{Al}_2\text{O}_3$ as a function of pH and ionic strength .................................................................................................................. 150

Fig. 5-5. Phosphate adsorption edge on kaolinite as a function of pH and ionic strength .................................................................................................................. 151

Fig. 5-6. TLM outer- and inner-sphere modeling of sulfate adsorption on $\gamma-\text{Al}_2\text{O}_3$ in 0.01 M KCl. The outer-sphere modeling curve is the sum of the two surface species of $\text{AlO}_2^-(\text{HSO}_4^\cdot)$ and $\text{AlO}_2^+=(\text{SO}_4^\cdot)^2$. The inner-sphere modeling curve represents the $\text{AlSO}_4^-$ surface species. .............................................. 155

Fig. 5-7. TLM outer- and inner-sphere modeling of sulfate adsorption on $\gamma-\text{Al}_2\text{O}_3$ in 0.1 M KCl. The outer-sphere modeling curve is the sum of the two surface species of $\text{AlO}_2^-(\text{HSO}_4^\cdot)$ and $\text{AlO}_2^+(\text{SO}_4^\cdot)^2$. The inner-sphere modeling curve represents the $\text{AlSO}_4^-$ surface species. .............................................. 156

Fig. 5-8. TLM outer- and inner-sphere modeling of sulfate adsorption on $\gamma-\text{Al}_2\text{O}_3$ in 1.0 M KCl. The outer-sphere modeling curve is the sum of the two
surface species of $\text{AlOH}_2^+-(\text{HSO}_4)_-^-$ and $\text{AlOH}_2^+-(\text{SO}_4)_2^-$. The inner-
sphere modeling curve represents the $\text{AlSO}_4^-$ surface species. ............................... 157

Fig. 5-9. TLM outer- and inner-sphere modeling of phosphate adsorption on $\gamma$-
$\text{Al}_2\text{O}_3$ in 0.01 M KCl. The inner-sphere modeling curve is the sum of the
$\text{AlPO}_4^{2-}$ and $\text{AlHPO}_4^-$ surface species. The outer-sphere modeling curve
represents the $\text{AlOH}_2^+-(\text{HPO}_4)_2^-$ surface species ........................................... 159

Fig. 5-10. TLM outer- and inner-sphere modeling of phosphate adsorption on $\gamma$-
$\text{Al}_2\text{O}_3$ in 0.1 M KCl. The inner-sphere modeling curve is the sum of the
$\text{AlPO}_4^{2-}$ and $\text{AlHPO}_4^-$ surface species. The outer-sphere modeling curve
represents the $\text{AlOH}_2^+-(\text{HPO}_4)_2^-$ surface species ........................................... 160

Fig. 5-11. TLM outer- and inner-sphere modeling of phosphate adsorption on $\gamma$-
$\text{Al}_2\text{O}_3$ in 1 M KCl. The inner-sphere modeling curve is the sum of the
$\text{AlPO}_4^{2-}$ and $\text{AlHPO}_4^-$ surface species. The outer-sphere modeling curve
represents the $\text{AlOH}_2^+-(\text{HPO}_4)_2^-$ surface species ........................................... 161

Fig. 5-12. TLM outer- and inner-sphere modeling of sulfate adsorption on
kaolinite in 0.001 M KCl, with the outer-sphere surface species $\text{AlOH}_2^+-(\text{SO}_4)_2^-$
and the inner-sphere surface species $\text{AlSO}_4^-$ ......................................................... 163

Fig. 5-13. TLM outer- and inner-sphere modeling of sulfate adsorption on
kaolinite in 0.01 M KCl, with the outer-sphere surface species $\text{AlOH}_2^+-(\text{SO}_4)_2^-$
and the inner-sphere surface species $\text{AlSO}_4^-$ ......................................................... 164

Fig. 5-14. TLM outer- and inner-sphere modeling of sulfate adsorption on
kaolinite in 0.1 M KCl, with two outer-sphere surface species $\text{AlOH}_2^+-(\text{HSO}_4)_-^-$
and $\text{AlOH}_2^+-(\text{SO}_4)_2^-$, and the inner-sphere surface species $\text{AlSO}_4^-$
................................................................. ............................... 165

Fig. 5-15. TLM outer- and inner-sphere modeling of phosphate adsorption on
kaolinite in 0.01 M KCl, with the inner-sphere surface species $\text{AlPO}_4^{2-}$
and the outer-sphere surface species $\text{SiOH}_2^+-(\text{PO}_4)_3^-$. ............................... 166
Fig. 5-16. TLM outer- and inner-sphere modeling of phosphate adsorption on kaolinite in 0.1 M KCl, with two inner-sphere surface species \( \text{AlHPO}_4^- \) and \( \text{AlPO}_4^{2-} \), and one outer-sphere surface species \( \text{SiOH}_2^--(\text{PO}_4)^{3-} \). .......... 167

Fig. 5-17. TLM outer- and inner-sphere modeling of phosphate adsorption on kaolinite in 1 M KCl, with two inner-sphere surface species \( \text{AlHPO}_4^- \) and \( \text{AlPO}_4^{2-} \), and one outer-sphere surface species \( \text{SiOH}_2^--(\text{PO}_4)^{3-} \). .......... 168
Chapter 1

INTRODUCTION

Processes occurring at mineral-water interfaces play critical roles in regulating the composition of surface and groundwater, in the development of soils and in the availability of plant nutrients (Stumm, 1992). These processes are typically subdivided into adsorption and precipitation based on the molecular level structure of surface complexes at the mineral-water interface. Because the mobility and availability of nutrients or pollutants is a strong function of the type of sorption complex formed, our ability to distinguish between different sorption mechanisms is essential in predicting the fate of these ions in soils and waters. This research was undertaken to investigate the adsorption of SO$_4$ and PO$_4$ onto Al oxide and kaolinite.

1.1 Background

1.1.1 Sulfur

Plant needs for sulfur (S) have been recognized for over 200 years (Duke and Reisenauer, 1986). Plants contain as much S as P, the usual range being from 0.2 to 0.5% on a dry weight basis. Sulfur ranks in importance with N as a constituent of amino acids in proteins that account for 90% of S in plants. In the past three decades, S deficiencies have been reported with increasing frequencies throughout the world (Pasricha and Fox, 1993). Mined gypsum (CaSO$_4$.2H$_2$O) has long been used as a nutrient source to correct S deficiencies (Alcendo and Rechcigal, 1993).
In recent years Clean Air legislation has resulted in the production of industrial gypsum by-products from the capture of SO₂ from the flue gases in fossil fuel powered generators. It was estimated that by the year 2000 over 150 million tons of these materials will be produced annually in US. At present, many of these high-Ca and high-S by-products are being stockpiled in lagoons or mixed with fly ash for storage in landfills at considerable expense to power plants and consumers. A beneficial alternative to disposal would be utilization as an amendment for acid soils.

Much research has showed that the utility of gypsum can be extended to acid, infertile soils as an ameliorant for subsoil acidity, surface crusting, and subsurface hard layers, and as a source of Ca for developing peanut pods (Sumner, 1993). Subsurface acidity is a major constraint to the successful production of many important crops and there is an urgent need for practical methods of ameliorating acid subsoils, particularly in those parts of the world struggling to achieve self-sufficiency in food production. The use of gypsum (mined and by-product) is an effective approach to overcome the limitations in acid soils.

Sulfate has also received great attention due to its role in acid deposition impacts on natural ecosystems. Acid rain accelerates leaching of nutrient cations, acidification of soils and waters, and decline of forests (Alewell and Martzner, 1993; Back et al., 1995; Edwards et al., 1995; Lange and Hauhs, 1995; Prenzel and Meiwes, 1994; Reuss and Johnson, 1986; Robarge and Johnson, 1992; Sjostrom, 1994). Cation leaching is decreased as long as SO₄ is retained since the absence of anion movement through the soil would restrict cation movement. Thus, SO₄ retention is a mechanism that delays the
response of watershed systems to input of acid deposition. Weakly-bonded $\text{SO}_4$, however, as proposed in Chapter V, seems to be leached relatively readily.

Finally, $\text{SO}_4$ is a major anion in acid mine drainage. Although commonly associated with coal mines, acid mine drainage also occurs in areas where pyrite or marcasite becomes exposed during land disturbances (such as metallic sulfide mines, highway road cuts, subway tunnels, etc.). In the process, sulfide minerals oxidize to form a series of soluble hydrous iron sulfates. Natural waters readily dissolve the salts which hydrolyze to form acidic drainage having high concentrations of $\text{SO}_4$ and $\text{Fe}^{2+}$ (Caruccio and Geidel, 1994). Acid mine drainage contaminates surface and groundwater in the mining districts of the Rocky mountains (Kimball et al., 1995).

1-1.2 Phosphorus

Phosphorus is one of the essential nutrients for plants. In most soils, 50 to 90% of P is inorganic, consisting of Fe and Al phosphates in acidic soils and Ca phosphates in alkaline soils. Adsorption of P by soils occurs rapidly and because of the high binding energy between soil and P, adsorption tends to dominate desorption. Phosphorus deficiency in plants is believed to constitute the second most important soil fertility problem throughout the world (Lookman et al., 1995). Phosphorus is supplied to crops through application of both commercial fertilizer and animal manure. As a result, P from agricultural non-point sources has been identified as the main cause of cultural eutrophication in surface waters. A concentration of 0.01 mg L$^{-1}$ for inorganic P has
been proposed as a critical level expected to promote noxious aquatic plant growth in lake water. Phosphorus is the single most important nutrient to manage for controlling accelerated eutrophication in freshwater lakes (Daniel et al., 1994).

1-1.3 Surface Complexation Models

During the last two decades, surface complexation models (SCMs) have been developed to model the adsorption of inorganic ions and organic chemicals at mineral-water interfaces (Davis and Kent, 1990; Goldberg, 1992, 1995). The SCMs assume that minerals have surface functional groups, which can form complexes with the adsorbing species playing a role similar to ligands in aqueous solution chemistry. The surface of a mineral is considered to be composed of amphoteric surface hydroxyl groups. A number of different SCMs have been proposed with differences in their respective molecular hypotheses. Each model assumes a particular interfacial structure, resulting in the consideration of various kinds of surface reactions and electrostatic correction factors to mass law equations. These models are a primary tool for interpreting ion adsorption observation in single mineral suspensions, with applications ranging from computing surface equilibrium constants to testing hypotheses regarding the interfacial structure of surface complexes. However, applications of SCMs to soils have met with difficulty, in part because of the heterogeneous chemical and mineralogical nature of soil materials.
1-2 Research Objectives

Mechanisms for $\text{SO}_4$ retention by minerals and soils have been in debate although $\text{SO}_4$ adsorption has extensively investigated. The primary objective of this research was to examine the $\text{SO}_4$ adsorption behavior, to evaluate its adsorption mechanism, and to compare with $\text{PO}_4$ adsorption which is known as inner-sphere complexation. The specific objectives were to:

1) measure the adsorption capacity of $\text{SO}_4$ by $\gamma-\text{Al}_2\text{O}_3$ and kaolinite;

2) determine the $\text{SO}_4/\text{OH}$ exchange stoichiometry on $\gamma-\text{Al}_2\text{O}_3$ and kaolinite by a back titration method;

3) develop the thermodynamic approach to measure the anion exchange stoichiometry based on adsorption edge experiments;

4) evaluate the effect of adsorption density, suspension pH, and source of mineral on the exchange stoichiometry;

5) investigate the ionic strength effects on $\text{SO}_4$ and $\text{PO}_4$ adsorption by $\gamma-\text{Al}_2\text{O}_3$ and kaolinite;

6) model the adsorption behavior of $\text{SO}_4$ and $\text{PO}_4$ at different ionic strengths using the triple layer surface complexation model; and

7) assess the nature of $\text{SO}_4$ and $\text{PO}_4$ surface complexation at mineral-water interface.
1-3 Organization

This dissertation is divided into 5 chapters which follow this introduction. In chapter II, background information is provided on empirical and surface complexation models. Chapter III provides mathematical analyses for the SO$_4$ adsorption isotherms and comparison of different adsorption equations. Chapter IV presents the results of macroscopic SO$_4$/OH exchange stoichiometry by Al oxide and kaolinite. The experimental and modeling results of the ionic strength dependence of SO$_4$ and PO$_4$ adsorption are given in chapter V. Chapter VI provides a summary and recommendations for future work.

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Chapter II

MODELS FOR EQUILIBRIUM ADSORPTION

2-1 Introduction

Several equilibrium-based models have been advanced to describe ion adsorption by soils and soil constituents. They can be classified as (1) empirical models or (2) surface complexation models. Because of the complexity of natural systems, the empirical approach has been widely used in describing the partitioning of solutes between solid and aqueous phases in soil chemistry and geochemistry. Surface complexation models, on the other hand, have been used primarily by aquatic scientists interested in developing a thermodynamic understanding of the coordinative properties of mineral surface functional groups via laboratory investigations. The development of chemical equilibrium and reaction models and their more recent availability for personal computers has eliminated the drudgery of manually solving dozens of simultaneous thermodynamic equations and has opened new research opportunities for soil chemists (Leoppert et al., 1995).
2-2 Empirical Adsorption Models

2-2.1 Langmuir Equation

The Langmuir equation is perhaps the best known adsorption equation. There have been many attempts to fit the results of ion adsorption studies on soils, sediments, and minerals to the Langmuir equation. The Langmuir equation is expressed as

\[ \Gamma = \frac{K \Gamma_m C_{eq}}{1 + KC_{eq}} \]  \hspace{1cm} (2-1)

where \( \Gamma \) is the amount of \( \text{SO}_4^{2-} \) adsorbed (\( \mu \text{mol m}^{-2} \)); \( \Gamma_m \) is the adsorption maximum (\( \text{mmol m}^{-2} \)); \( C_{eq} \) is the equilibrium concentration of \( \text{SO}_4^{2-} \); and \( K \) is a coefficient related to the adsorption energy. The \( \Gamma_m \) and \( K \) values can be obtained by nonlinear regression. The adsorption energy may be calculated by the equation (Adamson, 1990)

\[ K = \frac{N_o \sigma^0 \tau_o}{(2 \pi M \Delta T)^{1/2}} \exp \left( \frac{Q}{RT} \right) \]  \hspace{1cm} (2-2)

where \( N_o \) is the Avogadro number equal to \( 6.02 \times 10^{23} \) ions mol\(^{-1} \), \( \sigma^0 \) is the area of an adsorptive site, i.e., the area of adsorbed ion in cm\(^2\), \( \tau_o \) is the time the ion could stay on the surface, ranging from \( 10^{-12} \) to \( 10^{-13} \) sec, \( M \) is the weight of adsorbed ion in gram, \( R \) is the gas constant equal to \( 8.314 \times 10^7 \) ergs deg\(^{-1}\) mol\(^{-1}\), \( T \) is the absolute temperature, and \( Q \) is the adsorption energy in erg mol\(^{-1}\).

Rearrangement of Eq. (2-1) yields

\[ \frac{C_{eq}}{\Gamma} = \frac{1}{\Gamma_m K} + \frac{C_{eq}}{\Gamma_m} \]  \hspace{1cm} (2-3)
Thus, the $\Gamma_m$ and K values are easily determined by plotting $C_{eq}/\Gamma$ versus $C_{eq}$, and the intercept equals $1/\Gamma_m K$ and the slope equals $1/\Gamma_m$.

The Langmuir equation assumes that the adsorption occurs as a monomolecular layer, the adsorption energy remains constant during the entire adsorption process and the surfaces are homogeneous with no lateral interaction. Although a close fit to the Langmuir equation is generally obtained at low concentrations over a limited range, a curved relationship between $C_{eq}/\Gamma$ and $C_{eq}$ over a wide range of concentrations is often observed, implying that the adsorption energy is not a constant but rather a function of adsorption, and that there is no well-defined maximum (Sanyal and De Datta, 1991).

To account for such nonlinearity of the simple Langmuir plots, researchers have proposed several modifications to the simple Langmuir equation. Syers et al. (1973), Ram et al. (1987), and Mehadi and Taylor (1988) used a two-site Langmuir equation, and obtained satisfactory agreement with experimental data. They proposed that the two surfaces are characterized by different adsorption energy and adsorption maximum. The two-site Langmuir equation can be written as

$$
\Gamma = \frac{K_1 \Gamma_{m1} C_{eq}}{1 + K_1 C_{eq}} + \frac{K_2 \Gamma_{m2} C_{eq}}{1 + K_2 C_{eq}}
$$

(2-4)

This variation of the Langmuir equation overcomes the problem of heterogeneous sites but still does not overcome the problem of lateral interactions, assumed constant adsorption energy, and coupled adsorption-desorption (White and Zelazny, 1986). Furthermore, Posner and Bowden (1980) criticized this two-site adsorption equation and attributed the phenomena to the variable energy of adsorption of aqueous ions by soils. They further stated that splitting
an adsorption isotherm into a series of traditional Langmuir equations is erroneous unless
there is some *a priori* reasoning for doing so.

Sibbesen (1981) proposed an extended Langmuir equation, wherein the adsorption
energy term was replaced by a term, the value of which decreased with increasing ion
concentration. The extended Langmuir equation is expressed as

\[
\Gamma = \frac{\Gamma_m K C_{eq}^D C_{eq}}{1 + K C_{eq}^D C_{eq}}
\]

(2-5)

where D is a coefficient. Equation 5 is more suited to explain ion adsorption data in the
experimental soils than the simple, or the two-site, Langmuir equations.

To improve the applicability of the simple Langmuir equation for ion adsorption
studies in soils, Kuo (1988) used a modified version developed through statistical mechanics
(Adamson, 1990; p. 605). The modified equation takes into account the lateral interactions
among the surface-sorbed ion species. The equation used by Kuo (1988) is

\[
\frac{\theta}{1 - \theta} = \alpha C_{eq} \exp\left(\frac{Q - z \sigma \theta}{RT}\right)
\]

(2-6)

where \(\theta\) is equal to \(\Gamma/\Gamma_m\), \(Q\) is the energy derived from the chemical component, and \(\sigma\) is the
interaction energy of which the net contribution to the total energy of adsorption can increase
or decrease depending on the number of nearest neighbors \((z)\) surrounding a central ion
surface species, and on the fraction of sites covered; \(\alpha\) is a coefficient.
Equation (2-6) contains only three adjustable parameters if the actual determination of $z$ is not necessary, considering that $z \omega$ is the interaction energy for all neighbors surrounding a central adsorbed ion species. Introducing $\beta = z \omega$, and $K = \alpha \exp(Q/RT)$, Eq. (2-6) yields

$$\frac{\theta}{1 - \theta} = KC_{eq} \exp\left(-\beta \theta / RT\right)$$

(2-7)

Solution for $\Gamma_m$, $K$, and $\beta$ in Eq. (2-7) was made using a nonlinear least square program (Kuo, 1988), and the accuracy of the estimated parameters $\Gamma_m$ and $K$ by this model, compared with the same parameters estimated by the simple Langmuir isotherm, has been evaluated based on the goodness of fit of the experimental results. It was demonstrated that the simple Langmuir equation underestimated considerably the adsorption capacity of the soils, particularly at higher concentrations.

### 2-2.2 Freundlich Equation

The Freundlich equation was also widely used to describe ion adsorption in soils (Torrent, 1987; Shaviv and Shachar, 1989; Buchter et al., 1989). It can be expressed as (Schulthess and Sparks, 1991; White and Zelazny, 1986):

$$\Gamma = \alpha C_{eq}^\frac{1}{n}$$

(2-8)

where $\alpha$ and $A$ are coefficients. Some authors tend to attach less significance to the Freundlich equation because it does not provide any measure of an adsorption maximum in which soil scientists may primarily be interested. Nevertheless, the Freundlich coefficient, $\alpha$, may be regarded as a hypothetical index of ions adsorbed from a solution having unit equilibrium
concentration. A high degree of correlation was found between the Freundlich $\alpha$ and the
Langmuir $\Gamma_m$ or the Temkin adsorption parameter.

One difficulty of using the simple Freundlich equation is how best to overcome the
difficulties of distinguishing the adsorption by soils of added ion from that already present.
Denoting the native ion as $Q_N$, the Freundlich equation may be written as (Barrow, 1978):

$$\Gamma = \alpha C_{eq}^{1/b} - Q_N \tag{2-9}$$

Deviations that one may expect in the plot of the simple Freundlich equation (e.g., plot of $\log\Gamma$
vs. $\log C_{eq}$) due to a neglect of $Q_N$, especially if the latter is relatively large, were demonstrated
by Barrow (1978) using data from an experiment that studied the effect of previous ion
addition on adsorption of an added ion by soils.

Sibbesen (1981) proposed a modified version of the Freundlich equation, namely

$$\Gamma = \alpha C_{eq}^{(C_{eq}^{-D})/D} \tag{2-10}$$

in which the original shape governing parameter $1/A$ of the Freundlich equation (Eq. 2-8) was
replaced by $C_{eq}^{D/A}$, $D$ being a coefficient. Out of several adsorption equations used (e.g., the
simple and two-site Langmuir equations, extended Freundlich and Langmuir equations,
Gunary equation, and Fitter-Sutton equation), Eq. (2-10) was found to yield the best fit to the
experimental data on P adsorption by soils. Moreover, coefficients of Eq. (2-10) were also
found to be the least correlated.
2-2.3 Temkin Equation

The Temkin equation is based on the assumption that the bonding energy of adsorption decreases linearly with increasing surface coverage. The resulting concentration dependence is quite complex, but for the middle range of surface coverage, the equation reads (White and Zelazny, 1986):

\[
\frac{\Gamma}{\Gamma_m} = \frac{RT}{b} \ln (AC_{eq})
\]  

(2-11)

where A and b are coefficients. The simple form of Eq. (2-11) is

\[
\Gamma = \beta \ln C_{eq} + B
\]  

(2-12)

where \( \beta \) and B are coefficients. According to Eq. (2-12), a plot of \( \Gamma \) versus \( \log C_{eq} \) should yield a straight line. Such plots for soils in many cases, however, yielded gentle curves, rather than straight lines (Fox and Kamprath, 1970; Roy and De Datta, 1985; Russell et al., 1988). But the agreement with the experimental data was, in general, better over a wider range of concentrations than that with Langmuir plots.

2-2.4 Brunauer-Emmett-Teller (BET) Equation

Another equation sometimes used to describe adsorption processes is the BET equation. The BET equation reduces to the Langmuir equation under restricted conditions. Unlike the other equations, monolayer adsorption is not assumed. Instead, each adsorbed species acts as a site for further adsorption in multilayer. The BET equation is expressed as (Adamson, 1990; p. 611):
\[ \Gamma = \frac{\Gamma_m K' C_{eq}/C_0}{\left(1 - \frac{C_{eq}}{C_0}\right) \left(1 + (K' - 1) \frac{C_{eq}}{C_0}\right)} \] (2-13)

where \(C_0\) is unique to the BET equation and limits its usage in soils. \(C_0\) is the concentration of the adsorbed species required to precipitate the most likely solid form of the adsorbed species. Choice of a value for \(C_0\) presents a problem when many solid forms can precipitate. The coefficient \(K'\) is related to the adsorption energy which can be expressed as (Adamson, 1990; p. 611)

\[ K' = \frac{a_i b_i}{b_i a_i} \exp \left(\frac{Q_i - Q_v}{RT}\right) \] (2-14)

where \(a\) and \(b\) are coefficients, \(i\) denotes the first layer of adsorption, \(i\) denotes all the succeeding layers of adsorption, and \(Q\) is the adsorption energy. Generally, since \(a_i b_i / b_i a_i\) equals 1, Eq. (2-14) becomes

\[ K' = \exp \left(\frac{Q_i - Q_v}{RT}\right) \] (2-15)

Like the Langmuir equation, lateral interactions are ignored and a homogeneous surface is assumed. The BET equation can be plotted as \(C_{eq}/\Gamma(C_0 - C_{eq})\) against \(C_{eq}/C_0\) to determine \(\Gamma_m\) and \(K'\) using the equation

\[ \frac{C_{eq}}{\Gamma(C_0 - C_{eq})} = \frac{1}{\Gamma_m K'} + \frac{K' - 1}{\Gamma_m K'} \frac{C_{eq}}{C_0} \] (2-16)

A problem with the usage of the BET equation (Eq. 16) is that by choosing a highly soluble phase, the \((C_0 - C_{eq})\) term on the left of the equation closely approaches \(C_0\) and the equation becomes:
\[
\left( \frac{C_{eq}}{C_0} \right) \frac{1}{\Gamma} = \frac{1}{\Gamma_m K'} + K' - 1 \left( \frac{C_{eq}}{C_0} \right)
\]

(2-17)

When this form is plotted, a straight line is automatically attained (White and Zelazny, 1986).

The first application of the BET equation to soils was by Griffin and Jurinak (1973) in a study of P adsorption on calcite surfaces. They found that the adsorption maxima calculated by the BET equation were very close to those calculated from the Langmuir equation. Taylor and Eliis (1978) also applied the BET equation to adsorption data initially fitting a two site Langmuir equation. They found a good agreement for the monolayer capacity between the Langmuir and BET equations.

2-3 Surface Complexation Models

2-3.1 Introduction

Surface complexation models (SCMs) extend the ion-association model of aqueous solution chemistry to include chemical species on surfaces. The SCMs assume (Davis and Kent, 1990):

1. The surface is composed of specific functional groups that react with dissolved solutes to form surface complexes (ion pairs or coordinative complexes) in a manner analogous to complexation reactions in homogeneous solution.

2. The equilibria of surface complexation and ionization reactions can be described by mass law equations. Equilibrium constants for the surface reactions (K) differ
from those in aqueous phase, in that they are modified with a correction term for the electrostatic energy of the interface (edl) that effectively represents an activity coefficient ratio for the surface species (Goldberg, 1992):

\[ K = K_c \cdot \text{edl} \]  

(2-18)

where \( K_c \) is a conditional equilibrium constant written in terms of activities of aqueous species and concentrations of surface species, and edl is a model-dependent term involving the surface potential or potential within adsorption planes.

3. Surface charge and surface potential are treated as necessary consequences of chemical reactions of the surface functional groups. The Gouy-Chapman electric double layer theory is appropriate for describing the diffuse layer charge and potential surrounding a particle.

4. The apparent bonding constants determined for the mass action equations are empirical parameters related to thermodynamic constants via the rational activity coefficients of the surface species.

5. Adsorption is limited to specific planes; the average charge of a plane is determined by mass balance equations for each plane and the charge of the species in that plane. The sum of the charge of all adsorption planes and the diffuse layer charge is zero according to the law of electroneutrality.

A number of SCMs have been proposed in the last two decades. The models are distinguished by differences in their respective molecular hypotheses, e.g., in their depiction of interfacial structure, including the number of adsorption planes and types of
surface complexes. Each model has a particular electrostatic relationship and assumes a unique interfacial structure. On the other hand, all the models have a set of chemical constraint equations that can be solved numerically. These equations include:

- mass balance equations,
- mass action equations,
- charge balance equations, and
- charge-potential relationship equations.

This discussion of SCMs includes the following models extensively used in soil chemistry and geochemistry: Constant capacitance (CCM), diffuse layer (DLM), triple layer (TLM), four layer (FLM), and one-pK (OPM) models.

2-3.2 Constant Capacitance Model

The simplest SCM is the constant capacitance model in which only one plane is explicitly specified in the model structure (Fig. 2-1). The original development of the model can be found in Hohl and Stumm (1976), and it has been reviewed by Sposito (1984), Hayes (1987), Davis and Kent (1990), and Goldberg (1992). The CCM is applicable in theory only to systems at high, constant ionic strength. At high ionic strength, the electric double layer, consisting of the coordinative surface charge and dissociated counterion charge, can be approximated as a parallel plate capacitor. The molecular hypotheses of this model are as follows:

1. The surface is composed of amphoteric surface sites.
Fig. 2-1. Constant capacitance model. After Hayes (1987).
2. Only one plane in the interfacial region is considered: a surface plane for adsorption of H⁺ and OH⁻, and all other specifically adsorbed solutes, i.e., only inner-sphere complexes are formed.

3. Ionic strength effects are ignored, i.e., background electrolyte ions do not adsorb and are not directly accounted for in the model structure. Hence, the model is only applicable to systems at constant ionic strength.

4. The charge-potential relationship used in the model is

\[ \sigma_o = C \psi_o \]  \hspace{1cm} (2-19)

where \( \sigma_o \) is the surface charge density, \( C \) is the capacitance of the mineral-water interface, and \( \psi_o \) is the surface potential.

5. The constant ionic medium reference state is used for aqueous species; a zero charge reference state is used for surface species.

The following equations are general surface complexation reactions (Goldberg, 1992):

\[ \text{XOH} + \text{H}^+ \rightarrow \text{XOH}_2^+ \]  \hspace{1cm} (2-20)

\[ \text{XOH} \rightarrow \text{XO}^- + \text{H}^+ \]  \hspace{1cm} (2-21)

\[ \text{XOH} + \text{M}^{m+} \rightarrow \text{XOM}^{(m-1)} + \text{H}^+ \]  \hspace{1cm} (2-22)

\[ 2\text{XOH} + \text{M}^{m+} \rightarrow (\text{XO})_2\text{M}^{(m-2)} + 2\text{H}^+ \]  \hspace{1cm} (2-23)

\[ \text{XOH} + \text{L}^{k} \rightarrow \text{XL}^{(l-1)r} + \text{OH}^- \]  \hspace{1cm} (2-24)

\[ 2\text{XOH} + \text{L}^{k} \rightarrow \text{X}_2\text{L}^{(l-2)r} + 2\text{OH}^- \]  \hspace{1cm} (2-25)
where $XOH$ represents the surface functional group, $M$ is a metal ion, $m^+$ is the charge on the metal ion, $L$ is a ligand, and $l^-$ is the charge on the ligand. The intrinsic equilibrium constants describing these reactions are (Goldberg, 1992):

$$K^+ = \frac{[XOH_2^+]}{[XOH][H^+]} \exp\left(\frac{F\Psi}{RT}\right)$$  \hspace{1cm} (2-26)

$$K^- = \frac{[XO^-][H^+]}{[XOH]} \exp\left(-\frac{F\Psi}{RT}\right)$$  \hspace{1cm} (2-27)

$$K_M^1 = \frac{[XOM^{(m-1)}][H^+]}{[XOH][M^{m^+}]} \exp\left(\frac{(m-1)F\Psi}{RT}\right)$$  \hspace{1cm} (2-28)

$$K_M^2 = \frac{[(XO)_2M^{(m-2)}][H^+]^2}{[XOH]^2[M^{m^+}]} \exp\left(\frac{(m-2)F\Psi}{RT}\right)$$  \hspace{1cm} (2-29)

$$K_L^1 = \frac{[XL^{(l-1)}][OH^-]}{[XOH][L^{l^-}]} \exp\left(-\frac{(l-1)F\Psi}{RT}\right)$$  \hspace{1cm} (2-30)

$$K_L^2 = \frac{[X_2L^{(l-2)}][OH^-]^2}{[XOH]^2[L^{l^-}]} \exp\left(-\frac{(l-2)F\Psi}{RT}\right)$$  \hspace{1cm} (2-31)

where square brackets represents concentration (M). To solve the equilibrium problem, two more equations are needed. The mass balance equation for the surface functional group is:

$$[XOH]_T = [XOH] + [XOH_2^+] + [XO^-] + [XOM^{(m-1)}]$$

$$+ [(XO)_2M^{(m-2)}] + [XL^{(l-1)}] + [X_2L^{(l-2)}],$$  \hspace{1cm} (2-32)

and the charge balance equation is:

$$\sigma = [XOH_2^+] - [XO^-] + (m-1)[XOM^{(m-1)}] + (m-2)[(XO)_2M^{(m-2)}]$$

$$- (l-1)[XL^{(l-1)}] - (l-2)[X_2L^{(l-2)}].$$  \hspace{1cm} (2-33)
This set of equations can be solved with the computer program FIT-EQL (Herbelin and Westall, 1994).

The CCM has been used to describe metal ion adsorption on silica (Schindler et al., 1976; Osaki et al., 1990a, b), Al oxide (Hohl and Stumm, 1976), Fe oxide (Lovgren et al., 1990), and kaolinite (Schindler et al., 1987; Osaki et al., 1990b). Application of the CCM to metal adsorption on kaolinite and sediment samples from natural waters was reported by Osaki et al. (1990b). They used the same modeling approach on these heterogeneous systems as had been used for oxide minerals.

Applications of the CCM to anion adsorption have been carried out on goethite for phosphate (Sigg and Stumm, 1981; Goldberg and Sposito, 1984a) and sulfate (Sigg and Stumm, 1981), on clay minerals for borate (Goldberg and Glaubig, 1986b; Goldberg et al., 1993), selenium (Goldberg and Glaubig, 1986b), arsenic (Goldberg and Glaubig, 1988), and molybdate adsorption (Motta and Miranda, 1989).

The first application of the CCM to adsorption on heterogeneous soil systems was the study of Goldberg and Sposito (1984b) on phosphate adsorption. They used the logK values that were averages obtained from a literature compilation of logK values for Al and Fe oxide minerals. They calculated a phosphate-reactive specific surface area and obtained good fits of the CCM to phosphate adsorption data. To describe borate and selenate adsorption on soils, the logK values were optimized with anion surface complexation constants (Goldberg and Glaubig, 1986a, b).
2-3.3 Diffuse Layer Model

The diffuse layer model (DLM) was first proposed by Stumm and co-workers (1970). Dzombak and Morel (1990) described an improved version of the DLM, which was termed the generalized two-layer model. Like the CCM, the DLM describes surface reactions in terms of amphoteric hydroxyl groups that form ionized sites and only inner-sphere complexes are formed in coordination reactions. However, the molecular hypotheses of the DLM differ in the following ways:

1. There are two planes in the interfacial region (Fig. 2-2): (1) a surface plane for adsorption of $H^+$, $OH^-$, and all specifically adsorbed ions, and (2) a diffuse layer plane representing the closest distance of approach for all counterions.

2. The charge-potential relationship in the diffuse layer is described by the Gouy-Chapman theory:

   \[ \sigma_d = -\left(8RT\varepsilon_0 I \times 10^3\right)^{1/2} \sinh(ZF\Psi_d/2RT) \]  

   where $\sigma_d$ is the net charge density ($C m^{-2}$) in the diffuse layer, $\varepsilon$ is the dielectric constant (dimensionless), $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12} C V^{-1} m^{-1}$), and $I$ is the molar electrolyte concentration, $F$ is the Faraday constant, and $\Psi_d$ (volt) is the mean potential at the start of diffuse layer (Dzombak and Morel, 1990).

3. No capacitance parameters are required in the DLM. The electrical potential at the beginning of the diffuse layer (d-plane) equals to the surface potential (see Fig. 2-2). The DLM has usually been restricted to low ionic strengths (< 0.1 M) (Hayes et al., 1991).
Fig. 2-2. Diffuse layer model. After Hayes (1987).
4. The infinite dilution reference state is used for aqueous species; a zero surface charge reference state is used for surface species.

The DLM has two adjustable parameters, $K^+$ and $K^-$, which are applied uniformly to low ionic strength solutions. The surface complexation reactions, mass law action, mass balance, and charge balance equations for the DLM are similar to those for the CCM described above. In the generalized two-layer model (Dzombak and Morel, 1990), however, metal ion adsorption is considered to occur on two types of sites: a small set of high-affinity “strong” sites and a large set of low-affinity “weak” sites. Adsorption on both types of sites takes place as follows:

$$X^\text{w}OH + M^{m+} \rightarrow X^\text{w}OM^{(m-1)} + H^+ \quad (2-35)$$

$$X^\text{s}OH + M^{m+} \rightarrow X^\text{s}OM^{(m-1)} + H^+ \quad (2-36)$$

where $s$ represents the high-affinity and $w$ represents the low-affinity sites. For anion adsorption, it is not necessary to specify two sets of binding sites.

The DLM was used to model cadmium adsorption on polymeric latex (Harding and Healy, 1985a, b) and ferrihydrite (Dzombak and Morel, 1986). The DLM was also applied to effectively model the adsorption of 2,4-dinitrophenol, 2-pyridinemethanol, and several substituted 2-aminophenols onto TiO$_2$, Al$_2$O$_3$, and FeOOH (Stone et al., 1993), through the choice of a single reaction and a single fitting parameter. Dzombak and Morel (1990) provided a reviewed database for the use of the generalized two-layer model with Fe oxides and compared the model characteristics with other SCMs.
2.3.4 Triple Layer Model

Because the CCM and DLM discussed above have only one adsorption plane built into their structure, they are limited in their ability to distinguish between weakly and strongly binding ions (Hayes, 1987). Stern recognized this limitation and proposed the first three-plane model for the mercury electrode/aqueous interface (Davis and Kent, 1990). This model is now referred to as the basic Stern model (BSM). In the BSM, there are two adsorption planes: (1) a surface plane (α-plane) for potential determining ions, and (2) a specific adsorption plane (β-plane) for counterions which bind more weakly (Fig. 2-3). In this model Stern ignored the capacitance of the “outer layer” (between the β-plane and the diffuse layer plane) (Fig. 2-3). The BSM was improved by incorporating two capacitances (Yates et al., 1974) (Fig. 2-4). This modified model, termed the triple layer model (TLM), was quantitatively applied by Davis et al. (1978).

One of the drawbacks of the Davis et al. (1978) implementation of the TLM was their choice of the structure of adsorbing ions. In their implementation, only the H⁺ and OH⁻ ions were allowed to form surface coordination (inner-sphere) complexes; all other adsorbing ions were assumed to form outer-sphere (ion-pair) surface complexes. However, many metal cations and inorganic anions were recognized to form inner-sphere complexes at mineral-water interface (Hayes and Leckie, 1987; Hayes et al., 1988). Hayes (1987) presented an enhanced version of the TLM which allows either inner- or outer-sphere metal or anion complexes to be considered in model calculations. This modified TLM is described in detail in Chapter V.
Fig. 2-3. Basic Stern model. After Hayes (1987).
Fig. 2-4 Original triple layer model. After Hayes (1987).
The molecular hypotheses of the TLM are as follows:

1. The surface is composed of amphoteric sites as described in Eqs. (2-20 and 2-21).

2. There are three planes in the interfacial region: (1) a surface plane (o-plane) for adsorption of H\(^+\), OH\(^-\), and other strongly-adsorbed ions, (2) a near-surface plane (β-plane) for weakly-adsorbed ions, and (3) a diffuse layer plane (d-plane).

3. The Stern-Graham interfacial model is applied for the charge-potential relationships for the two regions between the three layers. The Gouy-Chapman theory is applied for the relationship in the diffuse layer.

4. Different reference states have been applied in the model. Davis et al. (1978) used the infinite dilution reference state for aqueous species and the zero charge reference state for surface species. But Hayes and co-workers adopted a different approach in defining activity coefficients. The standard state for both solution and surface species are defined as 1 mole L\(^{-1}\) at zero surface charge and no ionic interaction. The reference state was chosen for all species as infinite dilution relative to the aqueous phase and zero surface charge (Hayes, 1987).

The TLM has extensively been used to describe the adsorption of metal ions, inorganic anions and organics on oxides, clay minerals, and soils (Goldberg, 1992). Inter-sphere complexes were used to model phosphate (Hawke et al., 1989), molybdate (Zhang and Sparks, 1989), selenite and sulfate (Hayes et al., 1988; Zhang and Sparks, 1990a, b)
adsorption on goethite; selenite and molybdate adsorption on amorphous Fe and Mn oxides (Balistrieri and Chao, 1990); chromate and sulfate adsorption on kaolinite (Zachara et al., 1988); and boron adsorption on kaolinite (Singh and Mattigod, 1992) and Al oxide (Toner and Sparks, 1995).

The TLM was first applied to a soil system by Charlet and Sposito (1989). They found good fits of the TLM to sulfate adsorption on an oxisol using an inner-sphere surface complexes. More recently, Zachara and Smith (1994) used the TLM to model cadmium adsorption on soil-derived smectites, with an inner-sphere Cd complex on AlOH edge sites and outer-sphere complexes on SiOH edge sites.

2-3.5 Four Layer Model

The four layer model (FLM) was introduced by Bowden, Barrow, and their co-workers (Bowden et al., 1977, 1980; Barrow et al., 1980a, 1981; Barrow, 1989). The FLM assumes that H\(^+\), OH\(^-\), and other “strongly adsorbed” oxyanions and metals form inner-sphere complexes (Fig. 2-5). The H\(^+\) and OH\(^-\) ions reside on the surface plane, the σ-plane. The strongly adsorbed ions are placed on the α-plane. The major cations and anions are assumed to form outer-sphere complexes and are placed on the β-plane. The fourth plane, the d-plane, represents the start of the diffuse layer. Since the FLM is based on empirical constraint equations instead of mass action equilibrium principles, it is an empirical model (Hayes, 1987; Goldberg, 1992). Because this model contains four planes, four charge-potential equations and four charge balance equations are needed (Goldberg, 1992):
Fig. 2-5. Four layer model. After Hayes (1987).
\[ \Psi_\alpha \cdot \Psi_z = \sigma_\alpha / C_1 \]  
(2-37)

\[ \Psi_\alpha \cdot \Psi_\beta = (\sigma_\alpha + \sigma_\beta) / C_2 \]  
(2-38)

\[ \Psi_\beta \cdot \Psi_d = (\sigma_\alpha + \sigma_\alpha + \sigma_\beta) / C_3 = \sigma_d / C_3 \]  
(2-39)

The diffuse layer charge, \( \sigma_d \), is calculated as in the TLM, Eq. (2-17). The remaining charge balance equations are:

\[ \sigma_\alpha + \sigma_\alpha + \sigma_\beta + \sigma_d = 0 \]  
(2-40)

\[ \sigma_\alpha = \frac{N_s \left( K_H [H^+] \exp\left( -F \Psi_\alpha / RT \right) - K_{OH} [OH^-] \exp\left( F \Psi_\alpha / RT \right) \right)}{1 + K_H [H^+] \exp\left( -F \Psi_\alpha / RT \right) + K_{OH} [OH^-] \exp\left( F \Psi_\alpha / RT \right) \} \]  
(2-41)

\[ \sigma_\alpha = \frac{N_T \sum Z_i K_i \alpha_i \exp\left( -Z_i F \Psi_\alpha / RT \right)}{1 + \sum Z_i K_i \alpha_i \exp\left( -Z_i F \Psi_\alpha / RT \right) \} \]  
(2-42)

\[ \sigma_\beta = \frac{N_s \left( K_{cat} [C^+] \exp\left( -F \Psi_\beta / RT \right) - K_{an} [A^-] \exp\left( F \Psi_\beta / RT \right) \right)}{1 + K_{cat} [C^+] \exp\left( -F \Psi_\beta / RT \right) + K_{an} [A^-] \exp\left( F \Psi_\beta / RT \right) \} \]  
(2-43)

where \( N_s \) is the maximum surface charge density, \( N_T \) is the maximum adsorption of specifically adsorbed ions, \( K_i \) is the binding constant, \( \alpha_i \) is the activity, and \( Z_i \) is the charge of the \( i \)th specifically adsorbed ion.

There are no mass balance equations in the FLM. In solving the set of above equations, \( N_s, N_T, K_i, \) and \( C_i \) are chosen to optimize model fit to the adsorption data, and the charge densities \( \sigma_i \) and the potential \( \Psi_i \) subsequently calculated with a computer program.

The FLM has been successfully used to describe adsorption of the inorganic anions phosphate, selenite (Bowden et al., 1980; Barrow et al., 1980b), molybdate (McKenzie, 1983), and borate (Bloesch et al., 1987) on goethite. This model was
extended to describe phosphate adsorption by soils (Barrow, 1983, 1984, 1986a). The FLM was applied to describe the effects of time and temperature on fluoride, molybdate (Barrow, 1986b), selenite, and selenate adsorption by a soil (Barrow and Whelan, 1989a); the effect of pH on fluoride (Barrow and Ellis, 1986), phosphate (Barrow, 1984), selenite and selenate (Barrow and Whelan, 1989a), and borate adsorption by soils (Barrow, 1989); the effect of ionic strength on phosphate, sulfate (Bolan et al., 1986), selenite and selenate (Barrow and Whelan, 1989a), and borate adsorption by soils (Barrow, 1989). This model also has been used to describe the adsorption of metals copper, lead, zinc, nickel, and cadmium on goethite (Barrow et al., 1981, 1989), zinc on soils (Barrow, 1986b). Excellent fits to the adsorption data were obtained.

2-3.6 One-pK Model

The one-pK model (OPM) was first proposed by Bolt and van Riemsdijk (1982) and was developed by van Riemsdijk and co-workers (1986, 1987). In the OPM, the reactive surface of a metal oxide consists of a dense packing of (singly coordinated) oxygen atoms, which at the zero point of charge are equally distributed over the surface sites XOH and XOH₂. The charge of XOH and XOH₂ follows from crystallographic considerations and equals \( \frac{1}{2}^- \) and \( \frac{1}{2}^+ \), respectively (van Riemsdijk et al., 1987). The distribution of protons over the two surface sites is governed by the equilibrium:

\[
\text{XOH}^{1+} + \text{H}^+ \rightarrow \text{XOH}_2^{\frac{1}{2}+}, \tag{2-44}
\]

and the equilibrium constant:
\[ K^H = \frac{[XOH_2^{\frac{1}{2}+}]}{[XOH^{\frac{1}{2}}][H^+]} \exp\left(\frac{FP\Psi_d}{RT}\right) \]  

(2-45)

The CCM, DLM, and TLM could all be written based on the one-pK model concept. The basic Stern model (BSM) (Fig. 2-3) as described in the section 2-3 has been chosen for the one-pK model (van Riemsdijk et al., 1987). This model assumes that H\(^+\) and OH\(^-\) form inner-sphere complexes on the o-plane and other cations and anions form outer-sphere complexes at the Stern plane, the β-plane. The surface complexation reactions with cations and anions may be generalized as follows (Goldberg, 1992):

\[ \text{XOH}^{\frac{1}{2}+} + \text{M}^{m+} \rightarrow \text{XOH}_2^{\frac{1}{2}+} \cdot \text{M}^{m+} \]  

(2-46)

\[ \text{XOH}^{\frac{1}{2}+} + \text{M}^{m+} + \text{H}_2\text{O} \rightarrow \text{XOH}_2^{\frac{1}{2}+} \cdot \text{MOH}^{(m-1)} + \text{H}^+ \]  

(2-47)

\[ \text{XOH}^{\frac{1}{2}+} + \text{L}^{l+} \rightarrow \text{XOH}_2^{\frac{1}{2}+} \cdot \text{L}^{l+} \]  

(2-48)

\[ \text{XOH}^{\frac{1}{2}+} + \text{C}^+ \rightarrow \text{XOH}_2^{\frac{1}{2}+} \cdot \text{C}^+ \]  

(2-49)

\[ \text{XOH}^{\frac{1}{2}+} + \text{A}^- \rightarrow \text{XOH}_2^{\frac{1}{2}+} \cdot \text{A}^- \]  

(2-50)

The mass action equations are written as, respectively:

\[ K_M^{1} = \frac{[\text{XOH}_2^{\frac{1}{2}+} - \text{M}^{m+}]}{[\text{XOH}^{\frac{1}{2}}][\text{M}^{m+}]} \exp\left(\frac{mF\Psi_d}{RT}\right) \]  

(2-51)

\[ K_M^{2} = \frac{[\text{XOH}_2^{\frac{1}{2}+} - \text{MOH}^{(m-1)}][H^+]}{[\text{XOH}^{\frac{1}{2}}][\text{M}^{m+}]} \exp\left(\frac{(m - 1)F\Psi_d}{RT}\right) \]  

(2-52)

\[ K_L = \frac{[\text{XOH}_2^{\frac{1}{2}+} - \text{L}^{l+}]}{[\text{XOH}^{\frac{1}{2}}][\text{L}^{l+}]} \exp\left(-lF\Psi_d\right) \]  

(2-53)

\[ K_{C^+} = \frac{[\text{XOH}_2^{\frac{1}{2}+} - \text{C}^+]}{[\text{XOH}^{\frac{1}{2}}][\text{C}^+]} \exp\left(\frac{F\Psi_d}{RT}\right) \]  

(2-54)
\[ K_{A^-} = \frac{[XOH^{3+}]}{[XOH^{2+}][A^-]} \exp \left( \frac{-P\psi_d}{RT} \right) \]  \hspace{1cm} (2-55)

The mass balance equation is:

\[ [XOH]_T = [XOH^{3+}] + [XOH^{2+}], \]  \hspace{1cm} (2-56)

and the charge balance equation:

\[ \sigma_o = 1/2 \{ [XOH^{3+}] - [XOH^{2+}] \}. \]  \hspace{1cm} (2-57)

Since \( \Psi_o = \Psi_d \) in the BSM, two equations for the charge-potential relation are needed:

\[ \sigma_o = C (\Psi_o - \Psi_d), \]  \hspace{1cm} (2-58)

and the relation between charge and potential in the Stern plane (d-plane) is provided by double layer theory, i.e., Eq. (2-34).

The one-pK model has been used to describe cadmium and phosphate adsorption on Fe oxides (van Riemsdijk et al., 1987; van Riemsdijk and van der Zee, 1991). To model the cadmium adsorption, values for log\( K_{11} \), log\( C^+ \), log\( A^- \), and \( C \) were obtained from potentiometric titration data. In general, the model describes the experimental data quite well. This model was tested for phosphate adsorption (van Riemsdijk and van der Zee, 1991) using data as published by Bowden et al. (1980). Both phosphate and the electrolyte ions (\( K^+ \) and \( Cl^- \)) were assigned to d-plane. This model provided a good description of phosphate adsorption on goethite. Only one phosphate specific adjustable parameter is necessary to obtain these results.
2-7 References


Chapter III

QUANTITATIVE AND MECHANISTIC ANALYSIS OF SULFATE

ADSORPTION ON $\gamma$-Al$_2$O$_3$ AND KAOLINITE DETERMINED BY ISOTHERMS

Abstract

Sulfate adsorption behavior has been paid great attention in the past decades because $SO_4^{2-}$ is a major anion in acid deposits and acid mine drainage; yet in recent years coal combustion by-products with a high content of CaSO$_4$ have been used to ameliorate acid soils, in which $SO_4^{2-}$ ions play an important role. Sulfate adsorption at three pH levels was conducted on $\gamma$-Al$_2$O$_3$ and kaolinite. The adsorption isotherms were described by the simple Langmuir, two-site Langmuir, Freundlich, and Temkin equations. Sulfate adsorption was highly pH-dependent, increasing with a decrease in suspension pH. The capacity of $SO_4^{2-}$ adsorption on $\gamma$-Al$_2$O$_3$ was five times that observed for kaolinite for all three pH levels examined, indicating the difference in reactive site density between $\gamma$-Al$_2$O$_3$ and kaolinite. The free energy of adsorption decreased with increasing pH, with a similar magnitude for the two adsorbents at similar pH levels. Mathematical analyses for the adsorption isotherms demonstrated that $SO_4^{2-}$ may not be adsorbed on the d-plane, i.e., in the diffuse layer, whereas both outer- and inner- sphere complexation mechanisms predicted $SO_4^{2-}$ adsorption equally well.
3-1 Introduction

The determination of adsorption isotherms is one of the most useful experimental procedures in the study of the interactions of anions with minerals or soils. First, an adsorption isotherm can be used to obtain the adsorption maximum of an adsorbent and the free energy of adsorption (Parfitt, 1978). Although the Langmuir equation has been applied to describe SO$_4^{2-}$ adsorption in some soils (Couto et al., 1979; Hasan et al., 1970; Kamprath et al., 1956), the Freundlich equation has generally described SO$_4^{2-}$ adsorption more successfully because these systems often lack a clear adsorption maximum (Bolan et al., 1993; Bornemisza and Llanos, 1967; Chao et al., 1962; Marcano-Martinez and McBride, 1989; Singh, 1984; Weaver et al., 1985). In contrast, Aylmore et al. (1967) and Rajan (1978) found that SO$_4^{2-}$ adsorption on minerals was better described by the Langmuir equation, while Inskeep (1989) described equally well by the Langmuir and Freundlich equations.

Sulfate adsorption by soils is highly pH dependent (Kamprath et al., 1956; Couto et al., 1979). The sulfate adsorption capacity of a soil dramatically decreased with an increase in soil pH. Hence, very little SO$_4^{2-}$ was held in the surface soil when it had been limed to pH 6.0 or higher (Kamprath et al., 1956). However, SO$_4^{2-}$ adsorption capacities of minerals at various pH levels has not been documented.

Adsorption isotherms can also be used to indicate different adsorption mechanisms. Adsorption in a diffuse double layer follows the square-root of
concentration; adsorption on the β-plane (outer-sphere complexes) follows a Langmuir type isotherm; and adsorption on the α-plane (inner-sphere complexes) tends to be semilogarithmic (Lyklema, 1983). Spanos et al. (1990) and Vordenis et al. (1992) developed the above concepts and interpreted the mechanisms for MnO$_4^{2-}$, Co$^{2+}$ and Ni$^{2+}$ adsorption onto γ-Al$_2$O$_3$. They proposed that these ions were adsorbed on the inner Helmholtz plane which is identical to the β-plane described herein.

In this study, SO$_4^{2-}$ adsorption was conducted on γ-Al$_2$O$_3$ and kaolinite at three pH levels ranging from pH 4.3 to 7 that covers the majority of well developed soils. The purposes of this study were: i) evaluate pH effects on SO$_4^{2-}$ adsorption capacities, ii) compare the simple Langmuir, two site Langmuir, Freundlich, and Temkin equations in describing SO$_4^{2-}$ equilibrium adsorption, and iii) determine the location of adsorbed SO$_4^{2-}$ ions at the mineral-water interface by a quantitative approach.

### 3-2 Materials and Methods

#### 3-2.1 Adsorbents

The Al oxide was a γ-Al$_2$O$_3$ made by the Degussa Corp., Akron, Ohio, under the name of Aluminum Oxide C®. It has a surface area of 100 m$^2$ g$^{-1}$ with impurities less than 0.4% (Ettlinger et al., 1991). The γ-Al$_2$O$_3$ was pretreated with 0.01 M KOH to minimize dissolution of a small but highly soluble portion of the solid during adsorption experiments (Girvin et al., 1993). Following a 1 hr treatment with KOH, the solid was centrifuged for 1 hr
at 15000 rpm (27500 x g) (Sorvall RC-5B Refrigerated Superspeed Centrifuge, Du Pont Instruments), rinsed four times with deionized water, and saturated with 0.01 M KCl solution. The pH of the KCl-saturated $\gamma$-Al$_2$O$_3$ suspensions was adjusted to 4.5, 5.5 or 6.5 with 0.1 M HCl or KOH. The solid/liquid ratio of $\gamma$-Al$_2$O$_3$ suspensions was 10.0 g Al$_2$O$_3$ per liter.

Poorly crystallized kaolinite (KGa-2) was purchased from the Source Clay Minerals Repository, Clay Minerals Society, Department of Geology, University of Missouri, Columbia, Missouri. This kaolinite sample, from Warren County, Georgia, has a N$_2$ gas surface area of 23.6 m$^2$ g$^{-1}$ and a cation exchange capacity of 3.3 cmol$_e$ kg$^{-1}$ (van Olphen and Fripiat, 1979). Kaolinite was pretreated with 0.1 M KOH to remove oxide and hydroxide coatings on surfaces (Phelan and Mattigod, 1984). Then, the <2 mm clay fraction was separated by centrifugation. The separated clay was washed four times with 1 M KCl adjusted to pH 3.0, once with deionized water, saturated with 0.01 M KCl, and stored as a suspension. The weight of clay per unit volume of suspension was determined by drying known volumes of suspension at 110°C for 12 hr and correcting for the occluded salt. Triplicate measurements indicated that the suspension contained 17.0 g kaolinite clay per liter. The suspension pH was adjusted to 4.3, 5.5, or 7.0 with 0.1 M HCl or KOH. The adjusted pH of both the stock suspensions changed with time, but the change was less than 0.05 pH units.

3-2.2 Adsorption Experiments

A 20-mL aliquot of $\gamma$-Al$_2$O$_3$ or kaolinite suspension was placed in a 50-mL centrifuge tube. Standard stock solutions of SO$_4^{2-}$ (made of K$_2$SO$_4$ in 0.01 M KCl) were then added to
the suspension with a 1-mL Eppendorf pipette. Concentrations of $\text{SO}_4^{2-}$ in the suspension mixture ranged from 0.05 to 2.0 mM for kaolinite and from 0.1 to 5.0 mM for $\gamma$-$\text{Al}_2\text{O}_3$. Volumes of the added $\text{SO}_4^{2-}$ stock solution were between 0.20 and 1.00 mL. After $\text{SO}_4^{2-}$ addition, the suspensions were adjusted to the original pH values with 1 M HCl with a pH-stat autotitrator (Radiometer Copenhagen, Denmark). The pH adjustment was performed twice, 2 hr and 6 hr after addition of $\text{SO}_4^{2-}$. The additions of HCl changed the total volume by $<2\%$. The treated suspensions were shaken for 12 hr in a water bath shaker at 100 oscillations/min. The final pH of the suspension was determined with a pH meter and a KG2401 combined electrode (Radiometer). The difference in pH after adjustment was less than 0.1 pH units for each pH level. The samples were centrifuged for 30 min at 27,500 x g for $\gamma$-$\text{Al}_2\text{O}_3$ and 30 min at 1950 x g for kaolinite. The supernatants were then filtered through 0.2 mm Nuclepore membranes (Nuclepore Co., Pleasanton, CA).

The filtrates were analyzed for S with an inductively coupled argon plasma atomic emission spectrophotometer (ICAP 61 system, Thermo Jarrell Ash Corporation, Franklin, MA). Sulfate adsorption was calculated by the difference between the original and the equilibrium concentrations of $\text{SO}_4^{2-}$. The exact volume of solution in each tube was calculated from the volume of suspension, volume of $\text{SO}_4^{2-}$ stock solution added, volume of acid or base added, and particle density of 2.9 g cm$^{-3}$ for $\gamma$-$\text{Al}_2\text{O}_3$ (Ettlinger et al., 1991) or 2.63 g cm$^{-3}$ for kaolinite (Dixon, 1989).
3-2.3 Adsorption Isotherm Equations

Sulfate adsorption data were fitted to four equations as described below. The simple Langmuir equation may be written:

$$\Gamma = \frac{K \Gamma_m C_{eq}}{1 + KC_{eq}}$$  \hspace{1cm} (3-1)

where $\Gamma$ is the amount of $\text{SO}_4^{2-}$ adsorbed (\(\mu\text{mol m}^{-2}\)); $\Gamma_m$ is the adsorption maximum (\(\mu\text{mol m}^{-2}\)); $C_{eq}$ is the equilibrium concentration of $\text{SO}_4^{2-}$; and $K$ is a coefficient related to the adsorption energy. With the simple Langmuir equation, the standard free energy ($\Delta G^\circ$) of adsorption may be calculated by (Parfitt, 1978)

$$\Delta G^\circ = -RT \ln K$$  \hspace{1cm} (3-2)

where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is absolute temperature (K).

The two-site Langmuir equation can be expressed by:

$$\Gamma = \frac{K_1 \Gamma_{m1} C_{eq}}{1 + K_1 C_{eq}} + \frac{K_2 \Gamma_{m2} C_{eq}}{1 + K_2 C_{eq}}$$  \hspace{1cm} (3-3)

There are two adsorption maxima, $\Gamma_{m1}$ and $\Gamma_{m2}$, and two coefficients, $K_1$ and $K_2$.

The Freundlich equation has the form of

$$\Gamma = \alpha C_{eq}^{1/A}$$  \hspace{1cm} (3-4)

where $\alpha$ and $A$ are coefficients.

The Temkin equation is

$$\Gamma = \beta \ln C_{eq} + B$$  \hspace{1cm} (3-5)

where $\beta$ and $B$ are coefficients. A plot of $\Gamma$ vs. $\ln C_{eq}$ should give a straight line if the adsorption energy decreases linearly with increasing surface coverage.
3-3 Results and Discussion

3-3.1 Adsorption Isotherms

The overall shape of the isotherms for three pH levels was similar despite the large difference in amounts of SO$_4^{2-}$ adsorbed (Fig. 3-1). Each isotherm was characterized by a large change in the amount of SO$_4^{2-}$ adsorbed at low SO$_4^{2-}$ concentrations. This was followed by a small change in the amount of SO$_4^{2-}$ adsorbed with increasing SO$_4^{2-}$ concentrations. Sulfate adsorption was highly pH-dependent, increasing with a decrease in solution pH (Fig. 3-1). The free energy of adsorption was similar for γ-Al$_2$O$_3$ and kaolinite and decreased as pH increased for both (Table 3-1).

Table 3-1. Sulfate adsorption maximum and free energy on γ-Al$_2$O$_3$ and kaolinite at three pH levels

<table>
<thead>
<tr>
<th>pH</th>
<th>γ-Al$_2$O$_3$</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.5</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>7.0</td>
</tr>
<tr>
<td>$\Gamma_m$ (μmol m$^{-2}$)</td>
<td>1.48</td>
<td>1.13</td>
</tr>
<tr>
<td>$K$</td>
<td>514</td>
<td>346</td>
</tr>
<tr>
<td>$-\Delta G'$ (KJ mol$^{-1}$)</td>
<td>15.14</td>
<td>14.18</td>
</tr>
</tbody>
</table>
Fig. 3-1. Sulfate equilibrium adsorption on (a) $\gamma$-Al$_2$O$_3$ and (b) kaolinite in 0.01 M KCl.
Four adsorption isotherms, fitted by the four adsorption equations - the simple Langmuir, two-site Langmuir, Freundlich, and Temkin, are shown in Fig. 3-2 for γ-Al₂O₃ and Fig. 3-3 for kaolinite. Sulfate adsorption was described well by all the four equations. Based on $r^2$ values, the two-site Langmuir equation provides a excellent fit between the observed and predicted adsorption at both low and high SO₄²⁻ concentrations for both γ-Al₂O₃ (Fig. 3-2) and kaolinite (Fig. 3-3). The simple Langmuir and Temkin equations were found to be superior to the Freundlich equation for γ-Al₂O₃, while generally the simple Langmuir equation was inferior to the Temkin and Freundlich equations for kaolinite.

The sulfate adsorption maxima at three pH levels were obtained from the simple Langmuir equation (Figs. 3-2 and 3-3). The adsorption capacity increased with a decrease in pH. The adsorption maxima for γ-Al₂O₃ were about five times as much as those for kaolinite (Table 3-1) based on a surface area unit for both adsorbents. This discrepancy in adsorption capacity indicates a difference in surface site density between γ-Al₂O₃ and kaolinite. The adsorption maximum of SO₄²⁻ on γ-Al₂O₃ was 1.5 mmol m⁻² at pH 4.5 (Table 3-1), which is about one half of the site density (3.2 mmol m⁻²) of γ-Al₂O₃ (Bowers and Huang, 1986). This relationship suggests that one SO₄²⁻ ion may complex with two surface sites on γ-Al₂O₃. The adsorption maximum of SO₄²⁻ by kaolinite at pH 4.3 was 0.33 mmol m⁻². If we assume that one SO₄²⁻ ion occupies two edge sites, the edge site density in kaolinite would be 0.66 mmol m⁻², which is of similar magnitude to the edge site density of 0.7-1.0 mmol m⁻² for kaolinite reported by Wieland and Stumm (1992).
Fig. 3-2. Comparison of isotherms for $\text{SO}_4^{2-}$ adsorption on $\gamma$-$\text{Al}_2\text{O}_3$ in 0.01 M KCl.
Fig. 3-3. Comparison of isotherms for $\text{SO}_4^{2-}$ adsorption on kaolinite in 0.01 M KCl.
3.3.2 Quantitative Analysis for \( \text{SO}_4^{2-} \) Adsorption Mechanisms

According to the triple layer model of surface complexation (He et al., 1995b), \( \text{SO}_4^{2-} \) ions could be adsorbed on the o-plane (inner-sphere complexes), the \( \beta \)-plane (outer-sphere complexes), or the d-plane (diffuse layer). Mechanisms for \( \text{SO}_4^{2-} \) adsorption at mineral-water interface may be estimated by quantitatively analyzing the adsorption isotherms. The analysis includes testing the three possibilities of adsorption with separate equations derived from the diffuse double layer or thermodynamic theory.

**Sulfate Adsorption on the d-plane.** Based on the Poisson-Boltzman equation and the law of Gauss, the diffuse charge density that accumulates in the d-plane can be calculated with the equation (Sposito, 1984):

\[
\sigma_d = -\text{sgn}(\Psi)(2\varepsilon_0 DRT \sum_i C_{eq}[\exp(-Z_i \psi_d / RT) - 1])^{1/2} \tag{3-6}
\]

where \( \text{sgn}(\Psi) \) is equal to +1 when \( \Psi > 0 \) and to -1 when \( \Psi < 0 \); \( \varepsilon_0 \) is the permitivity of vacuum; \( D \) is the dielectric constant of water; \( R \) is the molar gas constant; \( T \) is the absolute temperature; \( C_i \) is the concentration of ion \( i \) (mol m\(^{-3} \)); \( Z_i \) is the valence of ion \( i \); \( F \) is the Faraday constant; and \( \Psi_d \) is the electric potential at the d-plane.

For the \( \text{K}_2\text{SO}_4-\gamma-\text{Al}_2\text{O}_3 \) or kaolinite system in this study, Eq. 3-6 becomes:

\[
\sigma_d = -(2\varepsilon_0 DRT)^{1/2}[2\exp(-F\psi_d / RT) + \exp(2F\psi_d / RT) - 3]^{1/2} C_{eq}^{1/2} \tag{3-7}
\]

Since the diffuse charge density is due to the surface concentration of \( \text{SO}_4^{2-} \) ions adsorbed, the following equation may be used (Vordonis et al., 1992):

\[
\sigma_d = ZF\Gamma = -2F\Gamma. \tag{3-8}
\]
Combination of Eqs. 3-7 and 3-8 yields:

\[ \Gamma = (\varepsilon_0 DRT / 2F)^{3/2} \left[ 2 \exp(-F \psi_d / RT) + \exp(2F \psi_d / RT) - 3 \right]^{1/2} C_{eq}^{1/2}. \]  

Equation 3-9 predicts a linear increase of \( \Gamma \) with \( C_{eq}^{1/2} \) if \( \text{SO}_4^{2-} \) was adsorbed on the d-plane. This is not in agreement with the adsorption data for \( \gamma\)-\( \text{Al}_2\text{O}_3 \) and kaolinite (Figs. 3-4 and 3-5). By comparison of \( r^2 \) at different pH values, the better linear relationship between \( \Gamma \) and \( C_{eq}^{1/2} \) was found as pH increased, indicating that more \( \text{SO}_4^{2-} \) ions might be adsorbed in the diffuse layer at higher pH values.

**Sulfate Adsorption on the \( \beta \)-plane** (Spanos et al., 1990). Assuming that one adsorbed ion, \( i \), replaces one water molecule, \( w \), from the \( \beta \)-plane, the following equilibrium exists:

\[ i^i + w^0 \leftrightarrow i^0 + w^i \]  

where \( L \) represents the liquid phase and \( \beta \) is for the \( \beta \)-plane. Electrochemical potential for each species in the equilibrium above may be expressed as

\[ \tilde{\mu}^i = \mu^{0,L}_i + RT \ln x_i + Z_i F \phi_L \]
\[ \tilde{\mu}^0 = \mu^{0,\beta}_i + RT \ln \theta_i + Z_i F \phi_\beta \]
\[ \tilde{\mu}^L = \mu^{0,L}_w + RT \ln(1 - \sum x_i) \]
\[ \tilde{\mu}^\beta = \mu^{0,\beta}_w + RT \ln(1 - \sum \theta_i) \]  

where \( \tilde{\mu}_i \) and \( \tilde{\mu}_w \) are the electrochemical potentials for ion \( i \) and water, respectively; \( \mu^{0}_i \) and \( \mu^{0}_w \) are the standard state chemical potential for ion \( i \) and water, respectively; \( x_i \) is the molar ratio of ion \( i \); \( Z_i \) is the charge of ion \( i \); \( \theta_i \) is the fraction of the site covered by ion \( i \); \( \phi_L \) and \( \phi_\beta \) are the Galvani potentials in the liquid phase and the adsorption site,
Fig. 3-4. Plots for \( \text{SO}_4^{2-} \) adsorption on the d-plane for \( \gamma-\text{Al}_2\text{O}_3 \) in 0.01 M KCl.
Fig. 3-5. Plots for $\text{SO}_4^{2-}$ adsorption on the d-plane for kaolinite in 0.01 M KCl.
respectively. If the electrochemical potential of a species in the adsorbed state equals that in the bulk solution (Lyklema, 1983), we have:

\[ \bar{\mu}_i^L + \bar{\mu}_w^\beta = \bar{\mu}_i^\beta + \bar{\mu}_w^L. \] (3-12)

Combination of Eqs. 3-11 and 3-12 yields:

\[ \frac{\theta_i}{1 - \theta_i} = \frac{x_i}{1 - \sum x_i} \exp \left( -\frac{-\Delta G_{chem}^\circ + (-\Delta G_{electr}^\circ)}{RT} \right) \] (3-13)

where

\[ -\Delta G_{chem}^\circ = (\mu_i^{0,L} + \mu_w^{0,\beta}) - (\mu_i^{0,\beta} + \mu_w^{0,L}) \]

\[ -\Delta G_{electr}^\circ = ZF(\phi_L - \phi_\beta) \]

represent the contribution to the standard free energy of adsorption \(\Delta G_{ads}^\circ\) of the chemical and electrostatic potentials.

Equation 3-13 may be developed to (Spanos et al., 1990):

\[ \frac{\theta}{1 - \theta} = \frac{C_{eq}}{55.5} \exp \left( -\frac{\Delta G_{ads}^\circ}{RT} \right) \] (3-14)

\[ = C_{eq} K \]

where

\[ \Delta G_{ads}^\circ = \Delta G_{chem}^\circ + \Delta G_{electr}^\circ \]

\[ K = \frac{1}{55.5} \exp \left( -\frac{\Delta G_{ads}^\circ}{RT} \right). \]

Substituting \( \theta \) with \( \Gamma/\Gamma_m \), Eq. 3-14 becomes:

\[ \frac{1}{\Gamma} = \frac{1}{\Gamma_m} + \frac{1}{\Gamma_m KC_{eq}}. \] (3-15)
Fig. 3-6. Plots for $\text{SO}_4^{2-}$ adsorption on the $\beta$-plane for $\gamma-$Al$_2$O$_3$ in 0.01 M KCl.
Fig. 3-7. Plots for $\text{SO}_4^{2-}$ adsorption on the $\beta$-plane for kaolinite in 0.01 M KCl.
Equation 3-15 predicts a straight line for the plot of $1/\Gamma$ vs. $1/C_{eq}$. The prediction is in good agreement with the $\text{SO}_4^{2-}$ adsorption data for $\gamma$-$\text{Al}_2\text{O}_3$ and kaolinite (Figs. 3-6 and 3-7).

**Sulfate Adsorption on the o-plane.** Similarly to Eq. 3-12, it is assumed that

$$\tilde{\mu}^s = \tilde{\mu}^l$$

(3-16)

where $\tilde{\mu}^s$ and $\tilde{\mu}^l$ are the electrochemical potentials of a species in the adsorbed state and in the bulk solution, respectively. The electrochemical potentials above can be written as:

$$\tilde{\mu}^s = \mu^{0,s} + RT \ln \theta + Z \phi^s$$, and

$$\tilde{\mu}^l = \mu^{0,l} + RT \ln C_{eq} + Z \phi^l.$$  

(3-17)

(3-18)

Combination of Eqs. 3-16 to 3-18 yields:

$$\ln \theta = -\frac{\Delta G_{chem}^0}{RT} - \frac{Z F \Psi_0}{RT} + \ln C_{eq}$$

(3-19)

where

$$-\Delta G_{chem}^0 = \mu^{0,l} - \mu^{0,s},$$ and

$$\Psi_0 = \text{the surface potential} = \phi^s - \phi^l.$$  

The surface charge density, $\sigma_0$, is given by the equation:

$$\sigma_0 = C \Psi_0$$

(3-20)

where $C$ is the capacitance of the mineral-water interface. The $\sigma_0$ can also be written as:

$$\sigma_0 = Z F \Gamma.$$  

(3-21)

Substituting Eqs. 3-20 and 3-21 into Eq. 3-19, we have:

$$\ln \Gamma + \frac{Z^2 F^2 \Gamma}{RTC} = \ln \Gamma_m - \frac{\Delta G_{chem}^0}{RT} + \ln C_{eq}$$

(3-22)

where $\theta$ was replaced by $\Gamma/\Gamma_m$. 

Equation 3-22 predicts a linear relationship between \( \ln \Gamma + \frac{Z^2 F^2 \Gamma}{RTC} \) and \( \ln C_{eq} \). A linear dependence was obtained for any values of \( C \) between 0.01 and 100 F m\(^{-2}\). The prediction was plotted in Figs. 3-8 and 3-9 using a value of 1 F m\(^{-2}\) for the capacitance.

Of the three possible locations for SO\(_4^{2-}\) adsorption, the outer- and inner-sphere complexation mechanisms predicted SO\(_4^{2-}\) adsorption very well (Table 3-2). This technique failed to distinguish between outer- and inner-sphere complexation. This might imply that both the mechanisms exist for SO\(_4^{2-}\) adsorption on \( \gamma-\text{Al}_2\text{O}_3 \) and kaolinite.

<table>
<thead>
<tr>
<th>Location</th>
<th>( \gamma-\text{Al}_2\text{O}_3 )</th>
<th>Kaolinite</th>
</tr>
</thead>
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<tr>
<td></td>
<td>4.5</td>
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</tr>
<tr>
<td>d-plane</td>
<td>0.6115</td>
<td>0.7299</td>
</tr>
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<td>( \beta )-plane</td>
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<td>0.9909</td>
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<tr>
<td>o-plane</td>
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<td>0.9615</td>
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</table>
Fig. 3-8. Plots for $\text{SO}_4^{2-}$ adsorption on the $\sigma$-plane for $\gamma$-$\text{Al}_2\text{O}_3$ in 0.01 M KCl. A capacitance value of 1 F m$^{-2}$ was used in calculation.
Fig. 3-9. Plots for SO₄²⁻ adsorption on the o-plane for kaolinite in 0.01 M KCl. A capacitance value of 1 F m⁻² was used in the calculation.
3-4 References


3-5 Appendix

3-5.1 Sulfate adsorption on γ-Al₂O₃ and kaolinite in 0.01 M KCl at three pH levels.

<table>
<thead>
<tr>
<th>C&lt;sub&gt;eq&lt;/sub&gt; (mM)</th>
<th>Γ (µmol m&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>C&lt;sub&gt;eq&lt;/sub&gt; (mM)</th>
<th>Γ (µmol m&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>C&lt;sub&gt;eq&lt;/sub&gt; (mM)</th>
<th>Γ (µmol m&lt;sup&gt;-2&lt;/sup&gt;)</th>
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</thead>
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Chapter III  Sulfate adsorption isotherms  71
Chapter IV

HYDROXYL-SULFATE EXCHANGE STOICHIOMETRY

ON \( \gamma \)-Al\(_2\)O\(_3\) AND KAOLINITE

Abstract

There is a release of OH from soil colloids with the addition of SO\(_4^{2-}\). The ratio of moles of OH released per mole of SO\(_4^{2-}\) adsorbed is referred to as the OH/SO\(_4\) exchange stoichiometry. The OH/SO\(_4\) stoichiometry not only provides an important constraint on surface complexation models, but also is a critical area of research to explain the effects on soil pH from the application of SO\(_4^{2-}\) amendments such as gypsum. The OH/SO\(_4\) stoichiometry on \( \gamma \)-Al\(_2\)O\(_3\) and kaolinite was determined by a back-titration method with a pH-stat autotitrator as well as calculated from SO\(_4^{2-}\) adsorption edges at various SO\(_4^{2-}\) concentrations by the thermodynamic approach. The stoichiometry depended upon suspension pH, SO\(_4^{2-}\) equilibrium concentration, and source of adsorbents. It increased with increasing solution pH and SO\(_4^{2-}\) adsorption density. At a low pH the stoichiometry was low and was similar for \( \gamma \)-Al\(_2\)O\(_3\) and kaolinite. At higher pH levels it was higher for \( \gamma \)-Al\(_2\)O\(_3\) than for kaolinite. The average values of the stoichiometry calculated by the thermodynamic approach were in agreement with those measured by back titration for both \( \gamma \)-Al\(_2\)O\(_3\) and kaolinite. The thermodynamic approach provides an easier experimental method to evaluate the OH/anion stoichiometry as a function of pH and adsorption density. It also indicated that at low pH levels (< 5) the stoichiometry might be overestimated due to dissolution of adsorbents; whereas at higher pH levels (5-8) it might be underestimated because of precipitation of Al hydroxy sulfates and gibbsite.
4-1 Introduction

Soil acidity is a major limiting factor in crop productivity in many parts of the world (Baligar et al., 1992; Sumner, 1993). The effect of soil acidity in topsoils can be overcome by liming. This approach is much more difficult in subsoils because lime does not readily move down the profile and mechanical mixing is not usually feasible (Shainberg et al., 1989; Sumner, 1990; Sumner et al., 1986). One of the possible approaches that can be used to decrease subsoil acidity is incorporation of gypsum into surface soil (Sumner, 1993); due to its relatively high solubility gypsum readily leaches below the surface soil layer.

A commonly reported effect of gypsum application on soils is the change in soil pH. Many indicate that soil pH increased with time after gypsum addition under field and laboratory conditions (Curtin and Syers, 1990; Farina and Channon, 1988; Hue et al., 1985; Marcano-Martinez and McBride, 1989; Pavan et al., 1982; Ritchey et al., 1980; Shainberg et al., 1989; Sumner, 1993). In column leaching studies, however, gypsum application had little effect on soil solution pH, and even slightly decreased soil pH (Oates and Caldwell, 1985; Pavan et al., 1984). Increases in soil pH due to gypsum addition depend upon soil properties and range from 0.1 to 0.9 pH units (Curtin and Syers, 1990; Shainberg et al., 1989). The range of pH change is apparently controlled by soil clay mineralogy, the initial pH of soils treated, the amount of SO$_4^{2-}$ addition, and the source of added SO$_4^{2-}$. Since the amount of SO$_4^{2-}$ adsorption is proportional to the amount of Fe or Al oxides in soils (Chao et al., 1964), a greater increase in soil pH is expected from soils that have a larger quantity of sesquioxides. The largest increase in pH usually coincided with the zone of maximum SO$_4^{2-}$ adsorption.
down soil profiles (Shainberg et al., 1989). Curtin and Syers (1990) measured an increase of
0.9 pH units for a soil with an initial pH of 5.7, and only 0.4 pH units for another soil with an
initial pH of 3.8. They also found that soil pH increased with an increase in SO$_4^{2-}$ addition.
Marcano-Martinez and McBride (1989) observed a greater increase in soil pH following
K$_2$SO$_4$ than CaSO$_4$ additions.

An increase in suspension pH due to SO$_4^{2-}$ adsorption is essentially accompanied by
release of OH$^-$ from solid surfaces or consumption of H$^+$ in solution. It is possible to determine
the ratio of moles of OH$^-$ released per mole of SO$_4^{2-}$ adsorbed, which is referred to as the
OH/SO$_4$ exchange stoichiometry and designated by $\chi$. Two methods are commonly used to
determine the OH/SO$_4$ stoichiometry. One is a direct experimental method in which the
suspension is back-titrated to its original pH with simultaneous determination of the amount of
SO$_4^{2-}$ adsorption. The average number of OH$^-$ ions released for each SO$_4^{2-}$ adsorbed can be
calculated from these data. The other is an indirect method that includes the thermodynamic
approach (Perona and Leckie, 1985; Honeyman and Leckie, 1986) and the Kurbatov method
(Kurbatov et al., 1951; Harvey et al., 1983). Since $\chi$ depends on pH and adsorption density
($\Gamma$), use of the Kurbatov method is restricted because it considers neither pH nor $\Gamma$
(Honeyman and Leckie, 1986).

The OH/SO$_4$ exchange stoichiometry provides an important constraint on surface
complexation models, and also is a critical area of research aimed at explaining SO$_4^{2-}$-induced
effects on soil pH following the application of soil amendments containing SO$_4^{2-}$. The $\chi$ values
increased, with an increase in SO$_4^{2-}$ adsorption density, from 0.3 to 0.7 for hydrous alumina
(Rajan, 1978) and from 0.2 to 0.7 for kaolinite (Rao and Sridharan, 1984). In contrast,
Inskeep (1989) obtained an opposite finding for kaolinite, that is, the \( \chi \) values decreased from 0.7 to 0.1 with increasing adsorption density of \( \text{SO}_4^{2-} \). Zhang et al. (1987) found that variable charge soils in China had \( \chi \) values of 0.12 to 0.18, which are much lower than those for pure minerals. However, Curtin and Syers (1990) and Guadalix and Pardo (1991) reported \( \chi \) values between 0.5 and 0.6 for variable charge soils. More recently, Ajwa and Tabatabai (1995) calculated \( \chi \) values using the Kurbatov method. They showed that the \( \chi \) values varied with soil types and suspension pH levels, ranging from 0.5 to 0.8 for \( \text{K}_2\text{SO}_4 \) addition and 0.1 to 0.5 for \( \text{CaSO}_4 \) addition.

The conflicting reports on the \( \text{OH}/\text{SO}_4 \) exchange stoichiometry in the literature may be attributed to differences in experimental conditions and sample characteristics, such as initial pH of suspensions, amount of \( \text{SO}_4^{2-} \) added, and soil mineralogy. The objective of this study was to determine the \( \text{OH}/\text{SO}_4 \) exchange stoichiometry by the back titration method, using two model minerals, \( \gamma-\text{Al}_2\text{O}_3 \) and kaolinite, three levels of suspension pH, and various \( \text{SO}_4^{2-} \)-adsorption densities, in order to obtain a better understanding of the \( \text{OH}/\text{SO}_4 \) exchange stoichiometry. The experimental results were compared with those calculated from the adsorption edges at various \( \text{SO}_4^{2-} \) concentrations by the thermodynamic approach. Kaolinite was selected for study because it is a major soil constituent. Although \( \gamma-\text{Al}_2\text{O}_3 \) does not occur in soils, it was chosen for use in this study because it has been well characterized and widely used in cation and anion adsorption studies (Girvin et al., 1993).
4-2 Theory of Thermodynamic Approach

The mathematical derivation given here is based on the report of Perona and Leckie (1985). They developed this approach to determine the \( H^+ \) stoichiometry for cation adsorption. This method is applied here to calculate the anion exchange stoichiometry.

Suppose that there is a system consisting of a solid phase in equilibrium with a liquid phase. The two phases are separated by an interfacial region, whose composition at constant temperature is governed by the Gibbs equation, which for a system containing \( c \) components is

\[
-d\gamma = \sum_{i=1}^{c} \Gamma_i d\mu_i
\]

where \( \gamma \) is the surface tension at the solid/liquid interface and \( \Gamma_i \) and \( \mu_i \) are the surface excess concentration and chemical potential of component \( i \). The surface excess concentration is given by

\[
\Gamma_i = n_i / S_A
\]

where \( n_i \) is the surface excess moles of component \( i \), and \( S_A \) is the surface area of the solid.

Consider a typical experiment designed to measure the adsorption of an anion \( A^{2-} \) by a solid adsorbent in equilibrium with an aqueous solution containing the strong electrolytes \( M_2A \) and \( MX \), the strong base \( MOH \), and \( H_2O \). The salt \( MX \) is a supporting electrolyte, present in large excess to maintain a constant ionic strength. The components are \( M_2A \), \( MX \), \( MOH \), \( H_2O \) and adsorbent. If the solid adsorbent is insoluble in the solution, its chemical potential is
constant, and a term involving the adsorbent does not appear in the Gibbs equation. From Eq. (4-1) the Gibbs equation for this system is

\[-d\gamma = \Gamma_{_{MA}} d\mu_{_{MA}} + \Gamma_{_{MX}} d\mu_{_{MX}} + \Gamma_{_{MOH}} d\mu_{_{MOH}}.\] (4-3)

where the surface excess concentration of water has been set equal to zero.

The chemical potentials can be written in terms of ionic activities:

\[\mu_{_{MA}} = \mu_{_{MA}}^0 + 2RT\ln a_M + RT\ln a_A,\] (4-4a)

\[\mu_{_{MX}} = \mu_{_{MX}}^0 + RT\ln a_M + RT\ln a_X,\] (4-4b)

\[\mu_{_{MOH}} = \mu_{_{MOH}}^0 + RT\ln a_M + RT\ln a_{OH}.\] (4-4c)

In these and subsequent equations, the subscripts M, A, X, and OH will refer to the ions M⁺, A²⁻, X⁻, and OH⁻.

The ions M⁺ and X⁻ are present in large excess relative to the concentration of surface sites, and changes in their concentrations due to adsorption are negligible. Thus, assuming ionic activity coefficients of unity, the activities of M⁺ and X⁻ are constants and we have

\[d\mu_{_{MA}} = RT d\ln a_A.\] (4-5a)

\[d\mu_{_{MX}} = 0\] (4-5b)

\[d\mu_{_{MOH}} = RT d\ln a_{OH}.\] (4-5c)

In addition we have the stoichiometric relations

\[\Gamma_{_{MA}} = \Gamma_A\] (4-6a)

\[\Gamma_{_{MOH}} = \Gamma_{_{OH}}.\] (4-6b)
Substitution of Eqs. (4-5) and (4-6) into (4-3) yields

$$-d\gamma = RT \left( \Gamma_A d\ln a_A + \Gamma_{OH} d\ln a_{OH} \right)$$  \hspace{1cm} (4-7)

The surface tension is a state function since, at constant temperature, it depends only on the ionic activities which are themselves state functions. Thus, \(d\gamma\) is an exact differential and we have

$$\left( \frac{\partial \Gamma_A}{\partial \ln a_{OH}} \right)_{a_A} = \left( \frac{\partial \Gamma_{OH}}{\partial \ln a_A} \right)_{a_{OH}}$$  \hspace{1cm} (4-8)

Furthermore, from Eq. (4-7) we have

$$\Gamma_A = \frac{1}{RT} \left( \frac{\partial \gamma(a_A, a_{OH})}{\partial \ln a_A} \right)_{a_{OH}}$$ \hspace{1cm} (4-9a)

$$\Gamma_{OH} = \frac{1}{RT} \left( \frac{\partial \gamma(a_A, a_{OH})}{\partial \ln a_{OH}} \right)_{a_A}$$ \hspace{1cm} (4-9b)

and evidently \(\Gamma_A\) and \(\Gamma_{OH}\) each depend only on \(a_A\) and \(a_{OH}\) at constant temperature. We can write for the total differential of \(\Gamma_A\)

$$d\Gamma_A = \left( \frac{\partial \Gamma_A}{\partial \ln a_A} \right)_{a_{OH}} d\ln a_A + \left( \frac{\partial \Gamma_A}{\partial \ln a_{OH}} \right) d\ln a_{OH}$$ \hspace{1cm} (4-10)
Keeping $\Gamma_A = \text{constant}$, Eq. (4-10) yields

$$
\left( \frac{\partial \Gamma_A}{\partial \ln a_A} \right)_{a_{OH}} \, d \ln a_A = -\left( \frac{\partial \Gamma_A}{\partial \ln a_{OH}} \right)_{a_A} \, d \ln a_{OH} \tag{4-11}
$$

$$
\left( \frac{\partial \ln a_A}{\partial \ln a_{OH}} \right)_{\Gamma_A} = -\left( \frac{\partial \Gamma_A}{\partial \ln \alpha_{OH}} \right)_{a} \frac{\partial \alpha_{OH}}{\partial \ln \alpha_A} \frac{\partial \alpha_A}{\partial \ln \alpha_{OH}} \tag{4-12}
$$

which when combined with Eq. (4-8), yields

$$
\left( \frac{\partial \ln a_A}{\partial \ln a_{OH}} \right)_{\Gamma_A} = -\left( \frac{\partial \ln \alpha_A}{\partial \ln \alpha_{OH}} \right)_{a_{OH}} = \left( \frac{\partial \Gamma_{OH}}{\partial \Gamma_A} \right)_{a_{OH}} \tag{4-13}
$$

Thus, the surface excess concentrations of OH and A are not independent of one another.

Using the relations

$$
p_{OH} = -\log a_{OH}$$

$$a_A = \gamma_A [A]$$

we have

$$
\left( \frac{\partial \Gamma_{OH}}{\partial \Gamma_A} \right)_{a_{OH}} = -\left( \frac{\partial \ln a_A}{\partial \ln a_{OH}} \right)_{\Gamma_A} \tag{4-14}
$$

$$
= \left( \frac{\partial \log [A]}{\partial p_{OH}} \right)_{\Gamma_A} + \left( \frac{\partial \log \gamma_A}{\partial p_{OH}} \right)_{\Gamma_A}
$$

If the pH-dependence of the activity coefficient can be neglected, Eq. (4-14) becomes
\[
\left( \frac{\partial \Gamma_{OH}}{\partial \Gamma_A} \right)_{a_{OH}} = \left( \frac{\partial \log[A]}{\partial \rho OH} \right)_{\Gamma_A}
\]

where the left-hand side is the change in the amount of adsorbed hydroxyls divided by the change in the number of adsorbed anions. That is, the left-hand side is the hydroxyl stoichiometry, which will be symbolized by \( \chi \). The right-hand side is experimentally measurable. It is the change in the equilibrium concentration of anions with \( \rho OH \), measured at constant surface excess concentration of the anion.

Rewriting Eq. (4-15) yields

\[
\left( \frac{\partial \Gamma_{OH}}{\partial \Gamma_A} \right)_{a_{OH}} = \chi = \left( \frac{\Delta \log[A]}{\Delta \rho OH} \right)_{\Gamma_A}
\]

Since \( \Delta \rho OH = -\Delta \rho H \), Eq. (4-16) becomes

\[
\chi = -\left( \frac{\Delta \log[A]}{\Delta \rho H} \right)_{\Gamma_A}
\]

The right-hand side of Eq. (4-17) was evaluated by plotting \( \log \Gamma \), in units of moles \( A \) per \( m^2 \) of adsorbent, versus \( \log[A] \), in units of moles \( A \) per liter at constant \( \rho H \), and then by calculating \( \Delta \log[A]/\Delta \rho H \) at constant \( \Gamma_A \). In general such a plot constitutes an adsorption isotherm.
4-3 Materials and Methods

All reagents used in this study were analytical grade or better. All experimental vessels and storage containers were polyethylene or polycarbonate. All experiments were conducted at 25 ± 0.5°C. Back titration was duplicated for γ-Al₂O₃ and every fifth sample was duplicated for kaolinite. Solutions were made with deionized water from a Sybron Barnstead nanopure water system.

4-3.1 Pretreatment on γ-Al₂O₃

The Al oxide was a γ-Al₂O₃ made by the Degussa Corp., Akron, Ohio, under the name of Aluminum Oxide C®️. It has a surface area of 100 m² g⁻¹ with impurities less than 0.4% (Ettlinger et al., 1991). The γ-Al₂O₃ was pretreated with 0.01 M KOH to minimize dissolution of a small but highly soluble portion of the solid during adsorption experiments (Girvin et al., 1993). Following a 1 hr treatment with KOH, the solid was centrifuged for 1 hr at 15000 rpm (27500 x g) (Sorvall RC-5B Refrigerated Superspeed Centrifuge, Du Pont Instruments), rinsed four times with deionized water, and saturated with 0.01 M KCl solution. The pH of the KCl-saturated γ-Al₂O₃ suspensions was adjusted to 4.5, 5.5 or 6.5 with 0.1 M HCl or KOH. The solid/liquid ratio of γ-Al₂O₃ suspensions was 10.0 g Al₂O₃ per liter.

4-3.2 Preparation of <2 mm Kaolinite Clay Suspension

Poorly crystallized kaolinite (KGa-2) was purchased from the Source Clay Minerals Repository, Clay Minerals Society, Department of Geology, University of Missouri, Columbia, Missouri. This kaolinite sample, from Warren County, Georgia, has a N₂ gas
surface area of 23.6 m² g⁻¹ and a cation exchange capacity of 3.3 cmolₑ kg⁻¹ (van Olphen and Frigiat, 1979). Kaolinite was pretreated with 0.1 M KOH to remove oxide and hydroxide coatings on surfaces (Phelan and Mattigod, 1984). Then, the <2 mm clay fraction was separated by centrifugation¹. The separated clay was washed four times with 1 M KCl adjusted to pH 3.0, once with deionized water, saturated with 0.01 M KCl, and stored as a suspension. The weight of clay per unit volume of suspension was determined by drying known volumes of suspension at 110°C for 12 hr and correcting for the occluded salt. Triplicate measurements indicated that the suspension contained 17.0 g kaolinite clay per liter. The suspension pH was adjusted to 4.3, 5.5, or 7.0 with 0.1 M HCl or KOH. The adjusted pH levels of the stock suspensions of kaolinite and γ-Al₂O₃ changed with time, but it was less than 0.05 pH units.

4-3.3 Experimental Procedure and Analysis

*Back-titration method of determining χ.* The OH⁻ released as a result of SO₄²⁻ adsorption was measured with a recording pH-stat autotitrator capable of maintaining a given pH to within a nominal ± 0.001 pH (Radiometer REC80 recording titrimer system with a PHM84 digital pH meter, an ABU80 digital autoburette reading to 0.0001 mL, and a Rea270 pH Stat Unit). A 20-mL aliquot of γ-Al₂O₃ or kaolinite suspension was placed in a 50-mL titration vessel, the suspension stirred rapidly with a three bladed polyethylene propeller, and

purged with a continuous stream of moist N\textsubscript{2}. The pH end point was set to the required value. Standard stock solution of SO\textsubscript{4}\textsuperscript{2-} (made of K\textsubscript{2}SO\textsubscript{4} in 0.01 M KCl) was then injected into the suspension with a 1-mL Eppendorf pipette. Concentrations of SO\textsubscript{4}\textsuperscript{2-} in the suspension mixture ranged from 0.05 to 2.0 mM for kaolinite and 0.1 to 5.0 mM for γ-Al\textsubscript{2}O\textsubscript{3}. Volumes of the added SO\textsubscript{4}\textsuperscript{2-} stock solution were between 0.20 and 1.00 mL. The standardized HCl solution, 0.05 M for kaolinite and 0.1 M for γ-Al\textsubscript{2}O\textsubscript{3}, was automatically added to maintain the pre-set pH, and the volume of HCl consumed was recorded as a function of time. After 30 min of reaction of SO\textsubscript{4}\textsuperscript{2-} with adsorbent, the suspension was filtered through a 0.2 mm polycarbonate membrane (Nuclepore Co., Pleasanton, CA) with a 25 mm holder. Preliminary experiments indicated that >95% of the adsorption was completed within 5 min, in agreement with previous reports that the rate of SO\textsubscript{4}\textsuperscript{2-} adsorption was rapid (Rajan, 1978; Inskeep, 1989). Nuclepore filters were chosen because they minimally affect concentrations of ions in solutions (Jardine et al., 1986). The filtrates were analyzed for S and Al, and SO\textsubscript{4}\textsuperscript{2-} adsorption calculated by difference. It was necessary to account for changes in volume resulting from (i) additions of standardized HCl to keep constant pH, and (ii) additions of SO\textsubscript{4}\textsuperscript{2-} stock solution.

**Adsorption edges for SO\textsubscript{4}\textsuperscript{2-}**. Sulfate adsorption experiments were carried out in batch systems to determine adsorption edges (percent of SO\textsubscript{4}\textsuperscript{2-} adsorbed as a function of solution pH per fixed total SO\textsubscript{4}\textsuperscript{2-} concentration). Eight to fourteen 20-mL aliquots of γ-Al\textsubscript{2}O\textsubscript{3} or kaolinite suspension were placed in 50-mL centrifuge tubes, and stock solutions of K\textsubscript{2}SO\textsubscript{4} in 0.01 M KCl added. There were four batches of γ-Al\textsubscript{2}O\textsubscript{3} with initial concentrations of 0.1, 1.0, 2.5, and 5.0 mM, and five batches of kaolinite with SO\textsubscript{4}\textsuperscript{2-} concentrations of 0.01, 0.02, 0.05, 0.10, and 1.00 mM. After addition of SO\textsubscript{4}\textsuperscript{2-}, the suspensions were adjusted to the desired pH values.
with 1 M HCl or 1 M KOH additions that changed the total volume by <2%. The treated suspensions were shaken for 12 hr in a water bath shaker at 100 oscillations/min. Then, the pH of the suspension was determined with a pH meter and a KG2401 combined electrode (Radiometer). The samples were centrifuged for 30 min at 15,000 rpm (27,500 x g) for γ-Al₂O₃ and 30 min at 5,000 rpm (1950 x g) for kaolinite. The supernatants were then filtered through 0.2 mm Nuclepore membranes. The filtrates were analyzed for S and Al. The exact volume of solution in each tube was calculated from the volume of suspension, volume of SO₄²⁻ stock solution added, volume of acid or base added, and particle density of 2.9 g cm⁻³ for γ-Al₂O₃ (Ettlingier et al., 1991) or 2.63 g cm⁻³ for kaolinite (Dixon, 1989).

Analysis of the filtrates for S and Al was performed with an inductively coupled argon plasma atomic emission spectroscopy (ICAP-AES) with simultaneous analysis on an ICAP 61 system (Thermo Jarrell Ash Corporation, Franklin, MA).

4-4 Results and Discussion

4-4.1 Aluminum Dissolving from γ-Al₂O₃ and Kaolinite

Interpretation of OH/SO₄ exchange stoichiometry requires the measurement of dissolved Al since (i) dissolution reactions of γ-Al₂O₃ and kaolinite may influence the stoichiometry (Carroll and Walther, 1990; Carroll-Webb and Walther, 1988; Furrer and Stumm, 1983; Wieland and Stumm, 1992; Xie and Walther, 1992) and (ii) dissolved Al might complex with SO₄²⁻ and precipitate as Al hydroxy sulfates (Adams and Rawajfih, 1977;
Adams and Hajek, 1978; Evans, 1991; Evans and Zelazny, 1990; Nordstrom, 1982). The dissolved Al concentrations from γ-Al₂O₃ and kaolinite (Fig. 4-1) decreased dramatically with increasing pH from 4 to 5, were negligible in the pH range of 5-9, and slightly increased at high pH (9-11). The L or U-shaped pattern of dissolved Al is in agreement with the results of a-Al₂O₃ and kaolinite (Carroll-Webb and Walther, 1988) and γ-Al₂O₃ (Girvin et al., 1993). The high Al concentrations at low pH (<5) were attributed to proton-promoted dissolution of γ-Al₂O₃ (Furrer and Stumm, 1983, 1986) and kaolinite (Wieland and Stumm, 1992), while the relatively high Al concentrations at high pH (>9) were regarded as caused by hydroxyl-promoted dissolution (Carroll-Webb and Walther, 1988). For γ-Al₂O₃ (Fig. 4-1), the concentration of dissolved Al was much greater at 2.5 or 5.0 mM SO₄²⁻ as compared to that at the lower SO₄²⁻ concentrations. In the case of kaolinite, however, Al dissolution was independent of SO₄²⁻ concentration. This might be explained by the mechanism of ligand-promoted dissolution for γ-Al₂O₃ (Furrer and Stumm 1986). They found that the dissolution rate of γ-Al₂O₃ depended on the concentration of surface complexes formed in the presence of organic acids. We thus postulate that γ-Al₂O₃ dissolution increased with increasing SO₄²⁻ concentration, but only when SO₄²⁻ concentration exceeded 1 mM, was dissolution significant.

In the process of dissolution, the number of protons required to attach to the reaction site for each detachment of an Al species into solution, i.e., the H:Al stoichiometry of dissolution, is 3 for γ-Al₂O₃ (Furrer and Stumm, 1986) and 2 for kaolinite, which is the mean of 3 at the tetrahedral basal surface and 1 at the edge surface (Wieland and Stumm, 1992). The dissolution process releases OH⁻ and may result in an overestimation of the OH/SO₄ stoichiometry. According to the H:Al ratio, we may estimate the error in χ resulting from
Fig. 4-1  Dissolution of $\gamma$-$\text{Al}_2\text{O}_3$ and kaolinite as a function of pH at various concentrations of $\text{SO}_4^{2-}$.
dissolution. Considering pH 4.5 and 4.3 at which γ-Al₂O₃ and kaolinite, respectively, are most soluble in these back-titration experiments, the mean Al concentration (data not presented) of 16 samples for γ-Al₂O₃ was 11 mM which is equal to 0.22 mmol Al, and for kaolinite was 9.0 mM which equals 0.18 mmol Al in the 20-mL solution. Then, the H⁺ consumed by dissolution for γ-Al₂O₃ is 0.66 mmol, accounting for 6.6% of the total amount of H⁺ consumed in the back-titration, and for kaolinite is 0.36 mmol, accounting for only 4.8%.

The activities of Al³⁺ species in solutions for γ-Al₂O₃ and kaolinite were calculated from the total Al concentrations with the MINTEQA2 computer program (Allison et al., 1991). The Al³⁺ activities were plotted on solubility diagrams (Fig. 4-2), with the solubility constants (values of logK) reported by Nordstrom (1982), -17.8 for jurbanite [Al(SO₄)(OH)·5H₂O], -85.4 for alunite [KAl₃(SO₄)₂(OH)₆], -117.7 for basaluminite [Al₄(SO₄)(OH)₁₀·5H₂O], and -33.9 for gibbsite [Al(OH)₃]. Potassium activity was set at 10⁻² M and SO₄²⁻ activities were selected at 10⁻³ M for γ-Al₂O₃ and 10⁻⁴ M for kaolinite. It is evident that the suspensions of both γ-Al₂O₃ and kaolinite were undersaturated in the whole range of pH examined with respect to jurbanite (Fig. 4-2). With respect to basaluminite, γ-Al₂O₃ suspension was at equilibrium from pH 5 to 7 and kaolinite suspension was undersaturated. With respect to alunite, γ-Al₂O₃ solution was oversaturated in the pH range of 4 to 7, whereas kaolinite was likely oversaturated in the pH range of 5 to 6.5. These results suggest that alunite could have precipitated out of solution. But alunite may not be important in controlling solution SO₄²⁻ in these short term experiments because of its slow nucleation and precipitation (Nordstrom, 1982). Furthermore, if precipitation had taken place in solutions, Al concentrations in zero SO₄²⁻ treatments should have been higher than those in any other SO₄²⁻
Fig. 4-2  Solubility diagrams for jurbanite, alunite, basaluminite, and gibbsite with sulfate activities of $10^{-3}$ M for $\gamma$-Al$_2$O$_3$ and $10^{-4}$ M for kaolinite. Symbols represent the data points in this study.
treatments. But this is inconsistent with the data presented in Fig. 4-1. The Al concentrations with zero SO$_4^{2-}$ addition were similar to or even lower than those with SO$_4^{2-}$ additions. Fig. 4-2 also indicates that gibbsite may have precipitated from pH 5 to 8 for both γ-Al$_2$O$_3$ and kaolinite. The solubility lines in Fig. 4-2 indicate that all three Al hydroxyl sulfates were unstable compared with gibbsite at pH values greater than 5.5, and they would transform to gibbsite.

The resultant effect of possible precipitation as either Al sulfates, gibbsite, or both is a net depletion of OH$^-$, causing an underestimation of the OH/SO$_4$ stoichiometry. Therefore, it may be postulated that the overestimation of $\chi$ due to dissolution could cancel to some extent the underestimation resulting from precipitation. This seems more likely for γ-Al$_2$O$_3$ because the solutions were more oversaturated (Fig. 4-2). On the other hand, this may also explain why for kaolinite the $\chi$ values from the back titration differ from those calculated from the thermodynamic approach (see below for details).

4.4.2 Back-titration and Measured $\chi$

There was an instantaneous increase in suspension pH after the addition of SO$_4^{2-}$. This pH increase invoked an immediate addition of HCl to regain the initial pH. The period of continuous HCl addition lasted for about 1 min with the exact time depending on the rate of titrant delivery speed. Subsequently, there was relatively little release of OH$^-$. This relationship is similar to divalent cation adsorption in which metal adsorption on Fe oxides was also divided into two steps, fast and slow (Benjamin and Leckie, 1981; Bruemmer et al., 1988; Kinniburgh, 1983).
The variation of HCl addition and the exchange stoichiometry ($\chi$) with the total SO$_4^{2-}$ concentration is shown in Fig. 4-3 for $\gamma$-Al$_2$O$_3$ and kaolinite at three pH levels. The volume (mL) of HCl consumed to maintain the preset pH is assumed to indicate the amount of OH$^-$ that has been released after SO$_4^{2-}$ addition. That is, the greater the volume of HCl required to regain the pH to the preset level, the higher the OH$^-$ release. For $\gamma$-Al$_2$O$_3$ the effect of a preset pH on OH$^-$ release was pH 5.5 $\approx$ 6.5 $> 4.5$ (Fig. 4-3a), indicating that $\gamma$-Al$_2$O$_3$ released more OH$^-$ at a higher pH. This is consistent with the reports of Rajan et al. (1974) and Shang et al. (1992), in which phosphate was adsorbed by Al hydroxide. But for kaolinite the effect of a preset pH on OH$^-$ release was pH 4.3 $> 5.5 > 7.0$ (Fig. 4-3b), suggesting that kaolinite released more OH$^-$ at a lower pH. Zhang et al. (1987) observed similar results in SO$_4^{2-}$ adsorption by variable charge soils. This may imply that, for soils consisting mainly of kaolinite, the more acid the soil, the greater the release of OH$^-$ with addition of SO$_4^{2-}$. On the other hand, for both $\gamma$-Al$_2$O$_3$ and kaolinite there are higher values of the OH/SO$_4$ stoichiometry at higher pH levels (Fig. 4-3c,d). Similar results were obtained by Shang et al. (1992), and Zhang et al. (1987). It is unclear why, the higher OH$^-$ release results in a greater $\chi$ value for $\gamma$-Al$_2$O$_3$, whereas the higher OH$^-$ release has a lower $\chi$ value for kaolinite. This trend for kaolinite might suggest that the change in the total amount of OH$^-$ released is not necessarily proportional to the change in the amount of SO$_4^{2-}$ adsorbed. This might indicate that some fraction of SO$_4^{2-}$ that disappeared from the equilibrium solution may not be attributable to adsorption, if SO$_4^{2-}$ adsorption is considered strictly as a ligand exchange reaction. Or it might mean that another mechanism other than ligand exchange is involved in SO$_4^{2-}$ adsorption. It is evident, however, that pH has a greater effect on $\chi$ than does SO$_4^{2-}$.
Fig. 4-3  
Consumption of HCl ($V_{HCl}$) (a, b) and the OH'/SO$_4^{2-}$ exchange stoichiometry ($\chi$) (c, d) as a function of the total SO$_4^{2-}$ concentration for $\gamma$-Al$_2$O$_3$ and kaolinite at three pH levels.
concentration. For instance, the values of $\chi$ for $\gamma$-$\text{Al}_2\text{O}_3$ at pH 5.5 increased from 0.8 to 1.0 as the total $\text{SO}_4^{2-}$ concentration increased from 0.5 to 5.0 mM, while at the concentration of 2 mM $\text{SO}_4^{2-}$ $\chi$ increased from 0.4 at pH 4.5, to 1.0 at pH 5.5, and to 1.3 at pH 6.5.

4-4.3 Adsorption Edges and Calculated $\chi$

The percent $\text{SO}_4^{2-}$ adsorption is greater at lower pH and decreases as pH increases for both $\gamma$- concentration. For instance, the $\text{Al}_2\text{O}_3$ and kaolinite (Fig. 4-4). The $\text{SO}_4^{2-}$ adsorption falls to zero around pH 10 for $\gamma$-$\text{Al}_2\text{O}_3$ and pH 11 for kaolinite. The curves shift to lower pH and to lower adsorption plateaus with increasing $\text{SO}_4^{2-}$ concentrations. Thus, as the total $\text{SO}_4^{2-}$ concentration increases, the percent adsorption at a given pH decreases (Sigg and Stumm, 1981). At 1.0 mM $\text{SO}_4^{2-}$, the adsorption edge becomes relatively flat below pH 4.5, implying site saturation for kaolinite. However, in this experiment, site saturation for $\gamma$-$\text{Al}_2\text{O}_3$ is not evident at the highest $\text{SO}_4^{2-}$ concentration (5.0 mM).

The amount of adsorbed $\text{SO}_4^{2-}$ ($I$) and $\text{SO}_4^{2-}$ equilibrium concentration ($C_{eq}$) at selected pH values can be obtained from Fig. 4-4. The pH values were chosen to bracket those in the back-titration experiments. For example, since one of the pH levels in the back titration for $\gamma$-$\text{Al}_2\text{O}_3$ was 4.5, two pH values were selected, i.e., 4.4 and 4.6, which average 4.5. With a smaller pH interval, the calculated $\chi$ is more representative of the target pH. A similar narrow pair of adsorption isotherms at two pH levels, which bracket the pH value examined in the back titration, were obtained from Fig. 4-4 and plotted in Fig. 4-5 for $\gamma$-$\text{Al}_2\text{O}_3$ and kaolinite. The data points shown by closed symbols in Fig. 4-5 are for the amounts of $\text{SO}_4^{2-}$ adsorption at lower pH, and open symbols are for higher pH values. The isotherms of
Fig. 4-4  Adsorption edges for $\text{SO}_4^{2-}$ on $\gamma$-$\text{Al}_2\text{O}_3$ and kaolinite.
Fig. 4-5  
Adsorption isotherms of $SO_4^{2-}$ on $\gamma$-$Al_2O_3$ and kaolinite at various pH levels.
logΓ vs logC_{eq} (Fig. 4-5) are nonlinear with slopes less than 1. This relationship differs from adsorption isotherms of phosphate in which the slope of approximately 1 (Hingston et al., 1967; Huang, 1975; Ryden et al., 1977) indicates one dominant type of phosphate binding (ligand exchange) site. If the slope of an isotherm in a log-log plot is about 1, adsorption is proportional to equilibrium concentration. Thus, the adsorption isotherm is linear (1.0 slope) at low concentrations and becomes flat (zero slope) at high concentrations. Such an isotherm implies that adsorption affinity remains constant until site saturation is approached. For SO_{4}^{2-} adsorption (Fig. 4-5) the slopes are less than 1, indicating that SO_{4}^{2-} adsorption is not proportional to equilibrium concentration. This relationship suggests that the affinity of SO_{4}^{2-} for γ-Al_{2}O_{3} and kaolinite is lower than that of phosphate.

The calculated OH/SO_{4} stoichiometries are compared with experimentally measured values in Fig. 4-6. To calculate χ from a narrow pair of adsorption isotherms in Fig. 4-5, a value of logΓ must first be chosen. At that selected logΓ value, logC_{1} and logC_{2}, which correspond to pH_{1} and pH_{2}, respectively, were obtained from the adsorption curves in Fig. 4-5. Since logC_{2} - logC_{1} = ΔlogC and pH_{2} - pH_{1} = ΔpH, the χ value at this logΓ can be calculated using ΔlogC/ΔpH, i.e., Eq. 17. The calculated χ occurs at the average pH between the narrow pair of adsorption isotherms (Fig. 4-6). The mean χ values across all measured Γ at each pH level examined are also presented in Table 1. The negative sign of χ results from the fact that adsorption of an anion is accompanied by the desorption of OH⁻, i.e., dΓ_{A} is positive, whereas dΓ_{OH} is negative. At a low pH (e.g., 4.5), the OH/SO_{4} stoichiometry was similar between γ-Al_{2}O_{3} and kaolinite (Table 4-1). At higher pH χ values for γ-Al_{2}O_{3} were
greater than those for kaolinite, indicating that the effect of pH on $\chi$ is more significant for $\gamma$-Al$_2$O$_3$ than for kaolinite. Honeyman and Leckie (1986) observed that titania shows little change in H/Cd stoichiometry with either pH or surface coverage, while amorphous Fe oxyhydroxide and Al oxide exhibit large ranges in the stoichiometry. The calculated values of $\chi$ are in good agreement with experimental results for $\gamma$-Al$_2$O$_3$ (Table 4-1 and Fig. 4-6). Although for kaolinite the average $\chi$ values determined from the back titration were rather close to those calculated from the thermodynamic approach (Table 4-1), there was a discrepancy between the two methods, particularly at pH 4.3 and 5.5 (Fig. 4-6). Several factors may be involved for this discrepancy. Greater dissolution of kaolinite might have taken place in the adsorption edge than in the back-titration experiment since the former had a much longer equilibrium time. Dissolution of kaolinite by detaching Si as well as Al depletes H$^+$ in solution as indicated earlier. Furthermore, the detached Si may compete with SO$_4^{2-}$ in adsorption. So, the calculated $\chi$ from the adsorption edge experiments may be overestimated.
Fig. 4-6  Variation of the sulfate exchange stoichiometry ($\chi$) with pH and adsorption density ($\Gamma$) for $\gamma$-Al$_2$O$_3$ and kaolinite.
and greater than those from the back titration experiments. This is more evident at low pH levels (Fig. 4-6) where dissolution of kaolinite is more prominent.

The non-integer $\chi$ values are reasonable considering the complexity of these heterogeneous systems. This complexity includes the reactions of surface protolysis, adsorbent dissolution, adsorbate precipitation, and electrolyte ion adsorption as well as the $\text{SO}_4^{2-}$ adsorption reaction. Thus, $\chi$ may be better referred to as the macroscopic $\text{OH}/\text{SO}_4$ stoichiometry because it represents the net release of $\text{OH}^-$ or consumption of $\text{H}^+$ by all reactions which results in the release of $\text{OH}^-$ and the removal of $\text{SO}_4^{2-}$ from solution. When using surface complexation models, many researchers assume that the $\text{OH}/\text{SO}_4$ stoichiometry is 1 for Fe hydroxides (Balistrieri and Murray, 1981; Davis and Leckie, 1980; Zhang and Sparks, 1990). From this research it appears that the assumption above is acceptable since the average of $\chi$ values from pH 4.5, 5.5, and 6.5 for $\gamma$-$\text{Al}_2\text{O}_3$ is 0.88. However, for kaolinite the average stoichiometry is 0.64, far less than 1.

4-4.4 Mechanism of $\text{SO}_4^{2-}$ Adsorption

This study observed that (i) at constant pH, the $\text{OH}/\text{SO}_4$ stoichiometry ($\chi$) increases with increasing surface coverage ($\Gamma$) (Fig. 4-6); (ii) at constant adsorption density ($\Gamma$), $\chi$ increases with increasing pH; and (iii) at a low pH (i.e., 4.5), $\chi$ values for $\gamma$-$\text{Al}_2\text{O}_3$ are very close to those for kaolinite, while at a higher pH $\chi$ values for $\gamma$-$\text{Al}_2\text{O}_3$ are greater than those for kaolinite. These experimental results may be explained by two completely opposite mechanisms for $\text{SO}_4^{2-}$ adsorption onto $\gamma$-$\text{Al}_2\text{O}_3$ and kaolinite.
Anion adsorption reactions take place by at least two mechanisms: (1) ligand exchange (i.e., inner-sphere complexation) on the surface (i.e., 0-plane) and (2) specific adsorption (i.e., outer-sphere complexation) on the β-plane that is away from the surface plane by some distance. The type of adsorption reaction can vary with differences in surface properties between γ-Al₂O₃ and kaolinite. The reactive surface sites on γ-Al₂O₃ are all Al-OH groups. The distance between two adjoining Al atoms in Al oxide is 0.29 nm (Rajan, 1978), which is close to the distance of 0.24 nm between two oxygen atoms in SO₄²⁻ ions (Parfitt and Smart, 1977). It is possible that one SO₄²⁻ ion may complex with two adjoining Al-OH groups to form a binuclear ring structure, i.e., bidentate bonding (Harrison and Berkheiser, 1982; Parfitt and Smart, 1978; Rajan, 1978). These surface complexes are formed by sharing the edge of a SO₄²⁻ tetrahedron with two corners from two adjacent Al octahedra in γ-Al₂O₃, and therefore is referred to as a corner-sharing structure (O'Day et al., 1994). Kaolinite surface sites are divided into three types, octahedral Al-OH (aluminol), tetrahedral Si-OH (silanol), and transitional tetrahedral-octahedral Al-OH-Si (White and Zeliazy, 1988). Of the three types, Al-OH and Si-OH groups are considered as reactive surface sites (Sposiro, 1984), although they differ in protolysis of surface groups. Since the Al-Al distance in the octahedral sheet of kaolinite is very similar to that in γ-Al₂O₃, it is probable that each SO₄²⁻ ion forms a bidentate bonding structure with two corners of two adjacent Al octahedra. However, the Si-Si distance is about 0.32 nm, from which the O-O distance between adjacent tetrahedra was calculated at about 0.5 nm based on the findings of Bish and Dreele (1989). Therefore, the formation of bidentate bonding between SO₄²⁻ tetrahedra and Si tetrahedra is unlikely because
of the large difference in O-O distance, and thus monodentate bonding must be assumed, i.e., one corner of a $\text{SO}_4^{2-}$ tetrahedron is bound to the corner of a Si tetrahedron in kaolinite.

Considering the inner-sphere complexation (ligand exchange) mechanism for $\text{SO}_4^{2-}$ adsorption, possible reactions at varying pH levels may be expressed as follows. For $\gamma-\text{Al}_2\text{O}_3$,

1. At low pH where surface reactive groups are more protonated, each $\text{SO}_4^{2-}$ displaces two $\text{OH}_2$ groups in $\gamma-\text{Al}_2\text{O}_3$ (Eq. 4-18), resulting in a low OH/$\text{SO}_4$ stoichiometry. (2) At intermediate pH where the surface is less protonated, each $\text{SO}_4^{2-}$ may replace one OH and one $\text{OH}_2$, causing a stoichiometry of 1 (Eq. 4-19). (3) At high pH each $\text{SO}_4^{2-}$ displaces two OH groups (Eq. 4-20), causing a OH/$\text{SO}_4$ value of 2. This implies that the OH/$\text{SO}_4$ stoichiometry increases with increasing suspension pH and would theoretically range from 0 to 2 for $\gamma-\text{Al}_2\text{O}_3$. (4) At low concentrations, $\text{SO}_4^{2-}$ would possibly only displaces OH$_2$ groups. As $\text{SO}_4^{2-}$ concentration increases, more $\text{SO}_4^{2-}$ ions would displace OH groups. Consequently, the stoichiometry increases with increasing $\text{SO}_4^{2-}$ concentration (i.e., adsorption density).
For kaolinite, we need to consider the tetrahedral Si-OH groups as well as the octahedral Al-OH groups. The Al-OH groups on kaolinite would function similar to those on γ-Al₂O₃, while the Si-OH groups could only adsorb SO₄²⁻ by forming a monodentate structure as follows:

\[
\text{Si-OH}^0 + \text{SO}_4^{2-} \rightarrow \text{Si-SO}_4 + \text{OH}^-.
\]  

(4-21)

Thus, the OH/SO₄ stoichiometry for kaolinite would be the average of tetrahedra and octahedra adsorption and would theoretically range from 0 to 1.5, which is lower than that in γ-Al₂O₃, if the assumption is made that there are two aluminol and one silanol group available for SO₄²⁻ per unit area (Sposito, 1984).

The reactions of SO₄²⁻ adsorption at varying pH levels for the second case, i.e., outer-sphere complexation, may be described below. For γ-Al₂O₃,

\[\text{at low pH,} \quad (4-22)\]

\[\text{at intermediate pH,} \quad (4-23)\]

\[\text{at high pH.} \quad (4-24)\]

(1) at low pH, the surface reactive groups are all protonated, thus each SO₄²⁻ is attracted by two positively charged OH₂ sites (Eq. 4-22), forming an ion pair electrostatically. (2) At high pH some surface groups are deprotonated into the form of OH, which must be protonated.
before $\text{SO}_4^{2-}$ is adsorbed by $\gamma$-$\text{Al}_2\text{O}_3$ (Eqs. 4-23 and 4-24). Protonation of surface sites consumes $\text{H}^+$ in solution in an amount equal to the release of $\text{OH}^-$ in solution. Thus, the stoichiometry of $\text{SO}_4^{2-}$ adsorption would range from 0 to 2 for $\gamma$-$\text{Al}_2\text{O}_3$ and increase with increasing solution pH. (3) At low $\text{SO}_4^{2-}$ concentrations, $\text{SO}_4^{2-}$ ions are paired with $\text{OH}_2^-$ groups, resulting in a low $\text{OH}/\text{SO}_4$ stoichiometry. As $\text{SO}_4^{2-}$ concentration increases, protonation of more surface $\text{OH}$ groups followed by the interaction with $\text{SO}_4^{2-}$ ions causes an increase in the stoichiometry.

In the case of kaolinite, the Si-$\text{OH}$ groups again need to be considered as well as Al-$\text{OH}$ groups. The Al-$\text{OH}$ groups would again behave like those on $\gamma$-$\text{Al}_2\text{O}_3$, whereas the Si-$\text{OH}$ groups would behave as follows:

$$\text{Si-OH}^0 + \text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{Si-OH}_2^+ \ldots \text{SO}_4^{2-}. \quad (4-25)$$

On the analogy of inner-sphere complexation in kaolinite, the stoichiometry for outer-sphere complexation would change from 0 to 1.5. These $\text{OH}/\text{SO}_4$ stoichiometry values are similar comparing ligand exchange to specific adsorption mechanisms.

Both of the mechanisms described above have been proposed to account for the adsorption of $\text{SO}_4^{2-}$ by soils and soil constituents. Many studies have concluded that, like phosphate, $\text{SO}_4^{2-}$ is adsorbed by a ligand exchange mechanism (Bolan et al., 1993; Guadalix and Pardo, 1991; Marcano-Martinez and McBride, 1989; Parfitt, 1978; Rajan, 1978, 1979; Zhang et al. 1987). An increase in suspension pH during $\text{SO}_4^{2-}$ adsorption has been regarded as evidence for this conclusion. But from the viewpoint of the surface complexation reactions described above, $\text{OH}^-$ release is not necessarily responsible for the exchange reaction of surface $\text{OH}$ with anions in solution.
Sposito (1989) considered that $\text{SO}_4^{2-}$ is possibly adsorbed on soil colloids by an outer-sphere complexation mechanism because of the readily exchangeable character of adsorbed $\text{SO}_4^{2-}$. Ryden et al. (1987) have shown that $\text{SO}_4^{2-}$ adsorption by a ferric oxide gel was completely eliminated when this anion was added together with equimolar amounts of phosphate, suggesting that $\text{SO}_4^{2-}$ does not compete effectively with phosphate for adsorption sites. Bolan and Borrow (1984) and Borrow (1985) considered the importance of the location of the plane of adsorption, and suggested that the mean plane of $\text{SO}_4^{2-}$ adsorption was more distant from the adsorbent surface than that of phosphate. Marsh et al. (1987) have explained $\text{SO}_4^{2-}$ adsorption by soils in electrostatic terms, with the process taking place in a plane distinct from the surface but closer than the plane of adsorption of monovalent anions such as $\text{Cl}^-$ and $\text{NO}_3^-$. Curtin and Syers (1990) observed that adsorbed $\text{SO}_4^{2-}$ was completely recovered by washing with 1 M KCl and concluded that $\text{SO}_4^{2-}$ may not be chemisorbed as commonly supposed. The findings of Zhang and Sparks (1990) confirmed the outer-sphere complexation mechanism for $\text{SO}_4^{2-}$ adsorption on goethite, that is, $\text{SO}_4^{2-}$ is adsorbed on a positive site by electrostatic attraction.

Therefore, OH$^-$ release is not unambiguous evidence that a ligand exchange reaction occurs in anion adsorption, even though it has long been used as such. The ionic strength effect on ion adsorption may be a better technique to ascertain the mechanism of cation or anion adsorption (Hayes et al., 1988; Goldberg, 1993). For an inner-sphere complex, there is little effect of ionic strength on the behavior of ion adsorption. In contrast, if an ion forms an outer-sphere complex with a surface, an increase in ionic strength markedly inhibits the adsorption of the ion. However, obtaining direct molecular-level information may only be
possible with invasive techniques such as x-ray adsorption fine structure spectroscopy (Fendorf et al., 1994).

4-5 Summary and Conclusions

The precise determination of the OH/\text{SO}_4 stoichiometry is not easily made by either the direct method (i.e., back titration) or the indirect (i.e., thermodynamic) approach, however the macroscopic stoichiometries have been measured by both methods and are in agreement with each other for $\gamma$-\text{Al}_2\text{O}_3 and kaolinite. Although a short reaction time (30 min) was used in the back titration method, it is still time consuming since each value represents a sample titration. The experiments for the indirect method are relatively more easily conducted and the method is applicable at relatively low adsorbate concentrations. This method permits the evaluation of \text{OH}/anion stoichiometry as a function of pH and adsorption density. But it is important to note that, at a low pH, the stoichiometry might be overestimated due to dissolution; while underestimated at a high pH because of possible precipitation of basic Al sulfates and gibbsite.

Both the amount of released OH$^-$ due to the adsorption of \text{SO}_4^{2-} by $\gamma$-\text{Al}_2\text{O}_3 or kaolinite, and the \text{OH}/\text{SO}_4 stoichiometry, depend upon suspension pH, \text{SO}_4^{2-} equilibrium concentration, and source of adsorbents. At a low pH, the \text{OH}/\text{SO}_4 stoichiometry was low with similar values for $\gamma$-\text{Al}_2\text{O}_3 and kaolinite. At higher pH levels the stoichiometry for $\gamma$-\text{Al}_2\text{O}_3 was greater than that for kaolinite. The results from the direct determination and the indirect calculation have substantiated that there was a significant difference in the \text{OH}/\text{SO}_4
stoichiometry for the two minerals, γ-Al₂O₃ and kaolinite. The adsorption of SO₄²⁻ resulted in the net release of about 0.9 mol OH⁻ per mol SO₄²⁻ adsorbed for γ-Al₂O₃, versus 0.6 mol OH⁻ per mol SO₄²⁻ adsorbed for kaolinite. Variation in the stoichiometry with pH, adsorption density, and surface type may be explained by two contrasting mechanisms for SO₄²⁻ adsorption on γ-Al₂O₃ and kaolinite, i.e., by either ligand exchange (inner-sphere complexation) or specific adsorption (outer-sphere complexation). It suggests that OH⁻ release during anion adsorption is not necessarily responsible for the exchange reaction of surface OH with anions in solution. It is plausible that similar OH⁻ release could occur through surface site protonation and outer-sphere complexation reactions.

From the results in this work it may be concluded that the amount of OH⁻ released from soils after the addition of SO₄²⁻ depends on the amount of SO₄²⁻ added, initial pH, and mineralogy of soils. The soils high in Fe and Al oxides would have a high release of OH⁻. These soils also would produce more OH⁻ at a pH of about 6 than at a pH of 4.5. Considering that soil is a buffering system, it is uncertain if SO₄²⁻ addition would increase soil pH. The released OH⁻ may be depleted by weak acids present in soils and the pH increase thus not detectable. Nevertheless, the application of SO₄²⁻ as K₂SO₄ to soils would not decrease soil pH provided that the precipitation of SO₄²⁻ as a basic Al sulfate is negligible and K⁻ ions cannot effectively exchange with the adsorbed Al³⁺ and H⁺. On the other hand, for the addition of gypsum (CaSO₄·2H₂O) to soils, while soil pH would increase in most cases, a decrease in pH may occur. For instance, in soils high in exchangeable Al, Ca²⁺ from CaSO₄ could replace Al³⁺ that hydrolyzes to give H⁺ (Berry et al., 1990). If the released H⁺ exceeds the released OH⁻ due to SO₄²⁻ adsorption, soil pH would decrease.
4-6 References


Some stability relations in the system $\text{Al}_2\text{O}_3\cdot\text{SO}_3\cdot\text{H}_2\text{O}$ at 298 K. Geochim. Cosmochim. Acta 46:681-692.


### 4-7 Appendices

#### 4-7.1 Aluminum dissolving from γ-Al₂O₃ as a function of pH at various SO₄²⁻ concentrations.

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### Consumption of HCl ($V_{HCl}$) and the OH/SO$_4^{2-}$ stoichiometry ($\chi$) as a function of the total SO$_4^{2-}$ concentrations for $\gamma$-Al$_2$O$_3$ and kaolinite at three pH levels ($l = 0.01$ M KCl).

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The OH/SO$_4^{2-}$ exchange stoichiometry ($\chi$) for $\gamma$-Al$_2$O$_3$ and kaolinite as a function of SO$_4^{2-}$ adsorption densities ($\Gamma$) by the back-titration method.

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$\gamma$-Al$_2$O$_3$

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Kaolinite
Chapter V

IONIC STRENGTH EFFECTS ON SULFATE AND PHOSPHATE

ADSORPTION ON $\gamma$-Al$_2$O$_3$ AND KAOLINITE: TRIPLE LAYER MODEL

Abstract

It is known that PO$_4$ is retained by soils through ligand exchange, i.e., inner-sphere complexation, but the mechanism for SO$_4$ adsorption at the mineral-water interface has been in debate. By studying the effects of ionic strength on ion adsorption, it is possible to distinguish between inner- and outer-sphere ion surface complexes. This study was conducted to evaluate ionic strength effects on SO$_4$ and PO$_4$ adsorption on $\gamma$-Al$_2$O$_3$ and kaolinite at varying solution pH (3-11), and to infer SO$_4$ and PO$_4$ adsorption mechanisms at the mineral-water interface. The adsorption of SO$_4$ on $\gamma$-Al$_2$O$_3$ and kaolinite decreased monotonically with increasing solution pH and was markedly reduced by increasing the concentration of background electrolyte. On the contrary, PO$_4$ adsorption on $\gamma$-Al$_2$O$_3$ and kaolinite increased from pH 3-4 and decreased from pH 6 to 11, with an adsorption plateau between pH 4 and 6. Phosphate adsorption was little affected by changes in ionic strength. At low pH, PO$_4$ adsorption showed a slight decrease with increasing ionic strength; whereas, at high pH, PO$_4$ adsorption increased slightly with increasing ionic strength, resulting in a crossover point where there was no ionic strength effect. The triple layer model (TLM) was applied to model the adsorption of SO$_4$ and PO$_4$ with both inner- and outer-sphere complexes using the FITEQL 3.1 computer program. The SO$_4$ adsorption was better modeled by assuming outer-sphere complex formation, while PO$_4$ adsorption was better modeled by assuming inner-sphere complex formation.
5-1 Introduction

Phosphate\(^1\) adsorption on soil colloids is generally considered as inner-sphere complexation, i.e., ligand exchange reaction (McBride, 1994; Sposito, 1989). Several different kinds of experimental evidence support this conclusion: (i) adsorbed PO\(_4^–\) is only slightly leached with anions like Cl\(^–\); (ii) PO\(_4^–\) is adsorbed at pH values > PZNC; and (iii) infrared (IR) spectroscopy reveals this mechanism (Sposito, 1984, 1989).

In contrast to PO\(_4^–\) adsorption, two mechanisms have been proposed to account for SO\(_4^{2–}\) adsorption by soils and soil constituents. It was concluded in many studies that, like PO\(_4^–\), SO\(_4^{2–}\) is adsorbed by a ligand exchange mechanism (Bolan et al., 1993; Gebhardt and Coleman, 1974; Guadalix and Pardo, 1991; Kooner et al., 1995; Marcano-Martinez and McBride, 1989; Rajan, 1978, 1979; Zhang et al., 1987). An increase in both suspension pH and surface negative charge during SO\(_4^{2–}\) adsorption has been regarded as evidence for this conclusion. It was also reported that IR spectroscopic analysis confirmed the formation of a bidentate bridging complex for SO\(_4^{2–}\) adsorbed on Fe oxides (Harrison and Berkheiser, 1982; Parfitt and Russell, 1977; Parfitt and Smart, 1978) and Al oxides (Gessa et al., 1984). However, the reliability of the experimental procedure used by these researchers was questioned since these IR studies were conducted by drying the samples after SO\(_4^{2–}\) adsorption (Manceau and Charlet, 1994; Zhang and Sparks, 1990). Drying samples could induce a structural rearrangement of surface complexes and particularly the interconversion of bidentate and monodentate

\(^1\) For convenience, PO\(_4^–\) and SO\(_4^{2–}\) are used to represent all aqueous species of phosphate and sulfate in solution, respectively.
phosphate complexes (Goldberg and Sposito, 1985). The NO$_3^-$ and Cl$^-$ ions have also been observed to undergo an outer-sphere complex to inner-sphere complex transition upon air drying (Parfitt and Russell, 1977).

Sposito (1989) considered that SO$_4^{2-}$ is possibly adsorbed on soil colloids by an outer-sphere complexation mechanism because of the observed readily exchangeable character of adsorbed SO$_4$. The SO$_4$ adsorption on Fe oxides was completely eliminated when this anion was added together with equimolar amounts of PO$_4$ and suggested that SO$_4$ does not compete effectively with PO$_4$ for the adsorption sites (Parfitt, 1982; Ryden et al., 1987). Bolan and Barrow (1984) and Barrow (1985) noted the importance of the location of the plane of adsorption, and suggested that the mean plane of SO$_4$ adsorption was further away from the adsorbent surface than that of PO$_4$. The SO$_4$ adsorption by soils has been explained using electrostatic terms, with the process taking place in a plane distinct from the surface but closer than the plane of adsorption of monovalent anions such as Cl$^-$ and NO$_3^-$(Marsh et al., 1987). Curtin and Syers (1990) indicated that SO$_4$ may not be chemisorbed as commonly supposed; they used the term "low affinity specific adsorption", in which the sorbed anion does not become chemically coordinated with the surface metal atoms. Recently, based on the hydroxyl exchange stoichiometry of SO$_4$ adsorption onto γ-Al$_2$O$_3$ and kaolinite, He et al. (1995) proposed a two-step mechanism, i.e., firstly surface protonation and then SO$_4$ outer-sphere complexation. However, the exact mechanism for SO$_4$ adsorption has not yet been identified (Goldberg, 1991).
By studying the effects of ionic strength on ion adsorption, it is plausible to distinguish between inner-sphere and outer-sphere anion surface complexes. For example, SeO$_4^{2-}$ adsorption onto Fe oxides was markedly decreased by increasing ionic strength, whereas SeO$_3^{2-}$ showed little ionic strength dependence (Hayes et al., 1988). By modeling the adsorption behavior of SeO$_4^{2-}$ and SeO$_3^{2-}$ with a triple layer surface complexation model, Hayes et al. (1988) proposed that SeO$_4^{2-}$ formed an outer-sphere surface complex, and SeO$_3^{2-}$ formed an inner-sphere surface complex. Goldberg et al. (1993) observed that B adsorption by goethite, gibbsite, and kaolinite was little affected by ionic strength and could be modeled by a constant capacitance surface complexation model, indicating that B formed inner-sphere surface complexes. But B adsorption by montmorillonite was significantly influenced by ionic strength, implying the formation of outer-sphere complexes.

The objectives of this study were to: (i) investigate the ionic strength effects on SO$_4$ and PO$_4$ adsorption by γ-Al$_2$O$_3$ and kaolinite, (ii) model the adsorption behavior of SO$_4$ and PO$_4$ at different ionic strengths using the triple layer surface complexation model, and (iii) evaluate the nature of SO$_4$ and PO$_4$ surface complexation at the mineral-water interface.

5-2 Triple Layer Model

The triple layer model (TLM) with specific counterion binding was proposed for the oxide-water interface by Yates et al. (1974). Quantitative application of the TLM to adsorption data for hydrous oxides was subsequently developed by Davis et al. (1978). The
TLM, based on the model modified by Hayes (1987), has three planes: $\alpha$-plane (surface), $\beta$-plane, and $d$-plane (diffuse layer) (Fig. 5-1a). Adsorbing ions are allowed to form surface complexes on either the $\alpha$- or $\beta$-plane instead of on the $\beta$-plane only as described in the original surface complexation version (Davis et al., 1978). Inner-sphere surface complexes are formed by placing the adsorbing ion on the $\alpha$-plane; outer-sphere surface complexes are formed by placing the adsorbing ion on the $\beta$-plane. The $d$-plane represents the distance of closest approach of completely hydrated counterions that balance out the charge resulting from the formation of surface complexes.

The TLM has been extensively used for a number of applications, which include modeling the adsorption of inorganic cations and anions and organic chemicals onto oxides, hydroxides, oxyhydroxides, and phyllosilicates (Hayes and Leckie, 1987; Hayes et al., 1988, 1991; Katz and Hayes, 1995a, 1995b; Singh and Mattigod, 1992; Toner and Sparks, 1995; Zachara and Smith, 1994; Zachara et al., 1988; 1990; Zhang and Sparks, 1990). Unlike the other simpler surface complexation models, such as the diffuse layer model (DLM) and the constant capacitance model (CCM), the TLM accommodates both inner- and outer-sphere complexation of cations and anions at the solid-liquid interface. Furthermore, the TLM is applicable to systems with various ionic strengths from low to high, whereas the DLM is often limited to a low ionic strength and the CCM is limited to a high ionic strength (Hayes et al., 1991). The major disadvantage in using the TLM is that it has at least seven adjustable parameters, compared with two parameters for the DLM and three parameters for the CCM.
Fig. 5-1. Triple layer model. (a) Assume that (i) PO₄ is adsorbed on the o-plane with inner-sphere complexes, and PO₄ ions are directly linked to the metal ions in the solid, forming covalent bonds; (ii) SO₄ ions are attracted by the positive charges from the surface groups. (b) Illustration for the distribution of potentials, charges, and capacitances with distances.
5-2.1 Chemical Reaction Equations and Mass Action Expressions

_Aqueous phase reactions_ The solution equilibria involving components $\text{H}^+$, $\text{H}_2\text{O}$, $\text{K}^+$, and $\text{SO}_4^{2-}$ or $\text{PO}_4^{3-}$ can be formulated:

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \\
K_w = \{\text{H}^+\}\{\text{OH}^-\} \\
\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^- \\
K_s = \{\text{HSO}_4^-\}/\{\text{H}^+\}\{\text{SO}_4^{2-}\} \\
\text{K}^+ + \text{SO}_4^{2-} \rightarrow \text{KSO}_4^- \\
K_{KS} = \{\text{KSO}_4^-\}/\{\text{K}^+\}\{\text{SO}_4^{2-}\} \\
\text{H}^+ + \text{PO}_4^{3-} \rightarrow \text{HPO}_4^{2-} \\
K_m = \{\text{HPO}_4^{2-}\}/\{\text{H}^+\}\{\text{PO}_4^{3-}\} \\
\text{H}^+ + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{PO}_4^- \\
K_{P2} = \{\text{H}_2\text{PO}_4^-\}/\{\text{H}^+\}\{\text{HPO}_4^{2-}\} \\
\text{H}^+ + \text{H}_3\text{PO}_4^- \rightarrow \text{H}_2\text{PO}_4^0 \\
K_{P3} = \{\text{H}_3\text{PO}_4^0\}/\{\text{H}^+\}\{\text{H}_2\text{PO}_4^-\} \\
\text{K}^+ + \text{HPO}_4^{2-} \rightarrow \text{KHPO}_4^- \\
K_{PK} = \{\text{KHPO}_4^-\}/\{\text{K}^+\}\{\text{HPO}_4^{2-}\}
\]

where \{i\} represents the activity of species i.

_Protolyis of surface groups_ Surface protolysis reactions and mass action expressions for $\gamma-\text{Al}_2\text{O}_3$ and kaolinite may be written as:

\[
\text{XOH} + \text{H}^+ \rightarrow \text{XOH}_2^+ \\
(5-8a)
\]
\[ K_X^+ = \frac{[XOH^+]}{[XOH][H^+]} \exp \left( \frac{F \psi_o}{RT} \right) \] (5-8b)

\[ XOH \rightarrow XO^- + H^+ \] (5-9a)

\[ K_X^- = \frac{[XO^-][H^+]}{[XOH]} \exp \left( -\frac{F \psi_o}{RT} \right) \] (5-9b)

where XOH denotes surface groups, with X being Al for γ-Al₂O₃ and Al or Si for kaolinite, [i] represents the concentration of species i, F is Faraday constant (96487 C mol⁻¹), \( \Psi_o \) electrical potential (V) on the o-plane, R gas constant (8.314 J mol⁻¹ K⁻¹), T absolute temperature (°K), and \( K_X^+ \) and \( K_X^- \) are intrinsic equilibrium constants, or referred to as surface acidity constants. In the literature, \( K_X^+ \) and \( K_X^- \) are often written as \( K_X^+(\text{intr}) \) and \( K_X^-(\text{intr}) \), respectively. In this paper, the "intr" in all intrinsic equilibrium constants will be omitted.

It is worth noting the difference in the equilibrium constant expressions between the aqueous phase reactions and the surface protolysis reactions. Activity is used for each species in the aqueous phase reactions, and activity coefficients are needed in these equations. However, concentration is used for the species in the surface protolysis reactions where there is an exponential term, \( \exp(\pm F \Psi_o/RT) \). Based on the defined standard and reference states, Hayes and Leckie (1987) showed that this exponential term represents the ratio of activity coefficients for species involved in the reactions. For instance, \( \exp(F \Psi_o/RT) \) in Eq. 5-8b is equal to \( \gamma_{XOH^+}/\gamma_{XOH}\gamma_{H^+} \), where \( \gamma_i \) is the activity coefficient of species \( i \).
Surface complexation of electrolyte ions

In the TLM, electrolyte ions are considered to form outer-sphere complexes, i.e., ion-pairs (Hayes, 1987; Davis and Kent, 1990). If counterions are allowed to bind in the β-plane, electrolyte surface reactions and equilibrium constants can be expressed as:

\[ \text{XOH} + \text{K}^+ \rightarrow \text{XO}^-\text{K}^+ + \text{H}^+ \]  \hspace{1cm} (5-10a)

\[ K_k = \frac{[\text{XO}^- - \text{K}^+][\text{H}^+]}{[\text{XOH}][\text{K}^+]} \exp\left(\frac{F(\psi_\beta - \psi_o)}{RT}\right) \]  \hspace{1cm} (5-10b)

\[ \text{XOH} + \text{H}^+ + \text{Cl}^- \rightarrow \text{XO}^-\text{H}_2\text{O}^-\text{Cl}^- \]  \hspace{1cm} (5-11a)

\[ K_{ei} = \frac{[\text{XO}^-\text{H}_2\text{O}^- - \text{Cl}^-]}{[\text{XOH}][\text{H}^+][\text{Cl}^-]} \exp\left(\frac{F(\psi_o - \psi_\beta)}{RT}\right) \]  \hspace{1cm} (5-11b)

where \( \psi_\beta \) is the electrical potential on the β-plane.

Surface complexation of adsorbing ions

We need to consider all possible surface complexation reactions of SO₄ and PO₄ species with γ-Al₂O₃ and kaolinite surface groups. These reactions may be divided into two categories, inner- and outer-sphere complexation. The inner-sphere complexation reactions can be described by the following generalized equation:

\[ \text{XOH} + pA^{m-} + q\text{H}^+ + r\text{C}^+ \rightarrow \text{XH}_{q+1}A_p^{(q-m)p} - \text{C}_r^+ + \text{H}_2\text{O} \]  \hspace{1cm} (5-12a)

\[ K_{A,p,q}^{\text{r,t}} = \frac{[\text{XH}_{q+1}A_p^{(q-m)p} - \text{C}_r^+]}{[\text{XOH}][A^{m-}][\text{H}^+][\text{C}^+]} \exp\left(\frac{F(r\psi_\beta + (q - mp)\psi_o)}{RT}\right) \]  \hspace{1cm} (5-12b)
where $A^m$ represents an anion component with a valence of $m$ (i.e., $SO_4^{2-}$ and $PO_4^{3-}$ herein); $C^+$ represents the electrolyte cation with a valence of $+1$; $p$, $q$, and $r$ are stoichiometrical numbers for ions $A^m$, $H^+$, and $C^+$, respectively; and the superscript IS is for inner-sphere complexes. For example, the reaction

$$XOH + SO_4^{2-} + H^+ \rightarrow XSO_4^- + H_2O$$ \hspace{1cm} (5-13a)

gives

$$K^{IS}_{5,11} = \frac{[XSO_4^-]}{[XOH][SO_4^{2-}][H^+]} \exp \left( -\frac{F\psi_\rho}{RT} \right)$$ \hspace{1cm} (5-13b)

The outer-sphere complexation reactions and mass action expressions are given as follows:

$$XOH + pA^m - qH^+ \rightarrow XOH_2^+ - H_{q-1}A_p^{(q-mp-1)}$$ \hspace{1cm} (5-14a)

$$K^{OS}_{A,p,q} = \frac{[XOH_2^+ - H_{q-1}A_p^{(q-mp-1)}]}{[XOH][A^m]^p[H^+]^q} \exp \left( \frac{F(\Psi_0 + (q - mp - l)\Psi_\rho)}{RT} \right)$$ \hspace{1cm} (5-14b)

where the superscript OS represents an outer-sphere complex. For example, the reaction

$$XOH + SO_4^{2-} + H^+ \rightarrow XO_2^+\cdot SO_4^{2-}$$ \hspace{1cm} (5-15a)

gives

$$K^{OS}_{5,11} = \frac{[XO_2^+\cdot SO_4^{2-}]}{[XOH][SO_4^{2-}][H^+]} \exp \left( \frac{F(\psi_\rho - 2\psi_\rho)}{RT} \right)$$ \hspace{1cm} (5-15b)
5-2.2 Surface Mass Balance Equations

Surface mass balance equations can be formulated as follows. For SO$_4$ and PO$_4$ inner-sphere complexation,

\[
\begin{align*}
\left[XO \cdot H\right]_{TOT}^{IS} &= \left[XO \cdot H\right] + \left[XO \cdot H^2\right] + \left[XO^{-}\right] + \left[XO \cdot H^{-}\right] - CT \\
&\quad + \left[XO^{-} - K^+\right] + \Sigma \left[XH_{q=1} \cdot A_p^{q-mp} - C^+_p\right].
\end{align*}
\] (5-16)

For outer-sphere complexation,

\[
\begin{align*}
\left[XO \cdot H\right]_{TOT}^{OS} &= \left[XO \cdot H\right] + \left[XO \cdot H^2\right] + \left[XO^{-}\right] + \left[XO \cdot H^{-}\right] - CT \\
&\quad + \left[XO^{-} - K^+\right] + \Sigma \left[XOH^+_2 - H_{q=1} \cdot A_p^{q-mp-1}\right].
\end{align*}
\] (5-17)

5-2.3 Surface Charge Balance Equations

The following are the equations for $\sigma_{\beta}$, the surface charge density (C m$^{-2}$), and $\sigma_{\beta}$, the net $\beta$-plane charge density (C m$^{-2}$). For SO$_4$ and PO$_4$ inner-sphere complexation,

\[
\sigma_{\beta}^{IS} = B \left[\left[XO^{-} - K^+\right] - \left[XOH^+_2 - CT\right] + \Sigma r \left[XH_{q=1} \cdot A_p^{q-mp} - C^+_p\right]\right].
\] (5-19)

where $B = F/C_s A_s$, $C_s$ is the solid concentration in g L$^{-1}$, and $S_A$ is the specific surface area of the solid in m$^2$ g$^{-1}$.

For outer-sphere complexation.
\[
\sigma^0_{\beta} = B \left( \left\{ \text{XOH}^2_+ \right\} + \left\{ \text{XOH}^2_+ - \text{Cl}^- \right\} - \left\{ \text{XO}^- \right\} \right)
\]
\[
- \left\{ \text{XO}^- - \text{K}^+ \right\} + \Sigma \left\{ \text{XOH}^2_+ - H_{q-1} A_{p}^{(q-mp-1)} \right\} \right), \tag{5-20}
\]
\[
\sigma^0_{\alpha} = B \left( \left\{ \text{XO}^- - \text{K}^+ \right\} - \left\{ \text{XOH}^2_+ - \text{Cl}^- \right\} + \Sigma (q - mp - 1) \left\{ \text{XOH}^2_+ - H_{q-1} A_{p}^{(q-mp-1)} \right\} \right). \tag{5-21}
\]

Electroneutrality requires that
\[
\sigma_{\alpha} + \sigma_{\beta} + \sigma_{d} = 0 \tag{5-22}
\]

where \(\sigma_{d}\) is the net charge density (C m\(^{-2}\)) in the diffuse layer. According to the Gouy-Chapman diffuse layer theory (for a symmetrical electrolyte with valence \(Z\)), \(\sigma_{d}\) is related to the mean potential at the start of diffuse layer (\(\Psi_{d}\), in volts) by
\[
\sigma_{d} = -(8RT\varepsilon_{0}I \times 10^{5})^{1/2} \sinh(ZF\Psi_{d}/2RT) \tag{5-23}
\]

where \(\varepsilon\) is the dielectric constant (dimensionless), \(\varepsilon_{0}\) the permittivity of free space (8.854 x 10\(^{-12}\) C V\(^{-1}\) m\(^{-1}\)), and \(I\) the molar electrolyte concentration (Dzombak and Morel, 1990).

At 25°C (\(T = 298\) K), the dielectric constant of water is 78.5, and Eq. 5-23 becomes
\[
\sigma_{d} = -0.1174I^{1/2} \sinh(19.46Z\Psi_{d}) \tag{5-24}
\]

In addition to Eqs.5-18 to 23, the following charge potential relationships are needed in the TLM:
\[
\sigma_{\alpha} = C_{1}(\Psi_{\alpha} - \Psi_{\beta}) \tag{5-25}
\]
\[
-\sigma_{d} = C_{2}(\Psi_{\beta} - \Psi_{d}) \tag{5-26}
\]

where \(C_{1}\) and \(C_{2}\) are the integral capacitances (F m\(^{-2}\)) of the respective regions. The TLM potentials, charges, and capacitances on different planes are illustrated in Fig. 5-1b.
5-3 Modeling Protocol

5-3.1 Selection of Parameters

When the TLM is used to model the adsorption behavior of ions at the solid-liquid interface, the values of adjustable parameters must be evaluated. These parameters include the surface site density, \( N_s \) (sites m\(^{-2}\)), the inner- and outer-sphere capacitance densities, \( C_1 \) and \( C_2 \) (F m\(^{-2}\)), respectively, equilibrium constants for surface group ionization reactions, \( K_X^+ \) and \( K_X^- \), and equilibrium constants for the surface complexation of electrolyte ions, \( K_C^- \) and \( K_A^- \).

*Site density* The value of surface site density for oxides has been either measured by tritium exchange (James and Parks, 1982), acid-base titration (Hohl and Stumm, 1976; Sigg and Stumm, 1981), F adsorption (Sigg and Stumm, 1981), and maximum solute adsorption (i.e., PO\(_4^2-\)) (Goldberg, 1985, 1986; Goldberg and Sposito, 1984), estimated from crystallographic parameters (Sposito, 1984), or optimized to fit experimental adsorption data (Hayes et al., 1991). These techniques often yield different estimates of site density, with the values being the lowest for acid-base titration, intermediate for solute adsorption, and highest for tritium exchange. The site density for \( \gamma-\text{Al}_2\text{O}_3 \) of 2 sites nm\(^{-2}\) from acid-base titration (Bowers and Huang, 1986; Wieland et al., 1988) was used herein.

For kaolinite, direct measurements for site density are difficult because of the multiple-site surface. There are four types of surface sites: edge-AlOH, edge-SiOH, basal-AlOH, and permanent charge SO (Wieland and Stumm, 1992). It is generally considered that the basal-AlOH groups are not reactive to ion adsorption (Sposito, 1984) and that the permanent
charge SO on kaolinite is negligible (Dixon, 1989). The edge groups, which account for reactive sites, have a density of 7.6 (Sposito, 1984) and 8.2 (White and Zelazny, 1988) sites per nm$^2$-edge surface area when estimated by crystallographic methods, and 12.5 sites per nm$^2$-edge surface area (Wieland and Stumm, 1992) when optimized to fit acid-base titration data. We used the B-chain edge site density of White and Zelazny (1988), i.e., 8.2 sites per nm$^2$-edge surface area, with one SiOH and two AlOH sites per unit cell. This value results in 5.5 and 2.7 sites per nm$^2$-edge surface area for AlOH and SiOH, respectively. A site density on the basis of total surface area needs to be estimated since the total surface area, not the edge surface area, is usually measured by various techniques. This conversion is possible when the percentage of edge surface area to total surface area is known. The percentage was estimated to be 7.9% (Sposito, 1984) and 20% (Wieland and Stumm, 1992), depending on the size of kaolinite particles. A value of 10% was assumed in this work. Consequently, the edge site densities on the basis of total surface area became 0.55 and 0.27 sites nm$^2$ for AlOH and SiOH, respectively.

The site concentration, $N_t$ (mol L$^{-1}$), which was actually used in the TLM, can be calculated as follows:

\[ N_t = S_A N_S C_S 1.66 \times 10^6 \]  \hspace{1cm} (5-27)

where $S_A$ is surface area (m$^2$ g$^{-1}$) and $C_S$ is solid concentration (g L$^{-1}$). All the information about the solid and suspension properties of $\gamma$-Al$_2$O$_3$ and kaolinite is summarized in Table 5-1.
Table 5-1. Solid and suspension properties used in TLM modeling for SO$_4$ and PO$_4$

<table>
<thead>
<tr>
<th>Property</th>
<th>$\gamma$-Al$_2$O$_3$</th>
<th>kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_A$, surface area (m$^2$ g$^{-1}$)</td>
<td>100</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>ALOH</td>
<td>SiOH</td>
</tr>
<tr>
<td>$N_S$, site density (sites nm$^{-2}$)</td>
<td>2.0</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO$_4$</td>
<td>PO$_4$</td>
</tr>
<tr>
<td>$C_S$, solid concentration (g L$^{-1}$)</td>
<td>10.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>$N_o$, site concentration (mol L$^{-1}$)</td>
<td>$3.32 \times 10^3$</td>
<td>$3.32 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

*Capacitance density* Although there is no method for independently determining the two TLM capacitance densities, $C_1$ and $C_2$, their values have been calculated using the electric double layer theory and the data of electrolyte ion adsorption on TiO$_2$ and $\gamma$-Al$_2$O$_3$ (Sprycha, 1984, 1989). These calculations indicate that both $C_1$ and $C_2$ vary with changing pH and ionic strength. However, a value of $0.2$ F m$^{-2}$ for $C_2$ is generally assumed (Davis et al., 1978; Katz and Hayes, 1995a; Hayes et al., 1991; Yates et al., 1974), based on direct measurements of the capacitance of the AgI-electrolyte interface (Pieper and de Voogt, 1974). While this value is arbitrarily selected for the mineral-water interface, justifications for its use were given by Bousse and Bergveld (1983). According to the definition of integral capacitance, a theoretical value for $C_1$ was calculated between 0.1 to 2.0 F m$^{-2}$ (Hayes et al., 1991). In practical application, the value of $C_1$ was usually optimized to fit the titration data. Using the titration data of Yates et al. (1974), Davis et al. (1978) found that $C_1$ was 1.4 and
1.0 F m\(^2\) for the TiO\(_2\)-LiNO\(_3\) and TiO\(_2\)-KNO\(_3\) systems, respectively. Hayes et al. (1991) reported that values between 0.8 and 1.2 F m\(^2\) provided satisfactory fits to their data. We selected 1.0 and 0.2 F m\(^2\) as the values of \(C_1\) and \(C_2\), respectively.

Surface ionization constants For a simple system such as (hydr)oxide suspensions, the surface ionization constants, \(K^+\) and \(K^-\), can be estimated from acid-base titration data using a graphic extrapolation technique (Goldberg, 1992; James and Parks, 1982) or an optimization procedure (Hayes et al., 1991). Goldberg (1992) presented a comprehensive compilation of the surface ionization constants for different (hydr)oxides, aluminosilicates, and a few soils. For Al oxides the surface ionization constants are in the following ranges: \(\log K^+ = 5.2 \sim 7.9\) and \(\log K^- = -8.1 \sim -10.0\) (Schindler and Stumm, 1987). We selected the values of \(\log K_{Al}^+ = 7.89\) and \(\log K_{Al}^- = -9.05\) as reported by Huang and Stumm (1973). Selection of these values for kaolinite is even more complicated since it has two types of edge sites, i.e., AIOH and SiOH groups. Although few data are available directly measured for these edge groups, it is assumed that the edge AIOH and SiOH groups on kaolinite behave similarly to the surface groups on Al and Si oxides, respectively. Thus, we selected \(\log K_{Al}^- = 7.89\) and \(\log K_{Al}^- = -9.05\) for edge AIOH groups, and \(\log K_{Si}^- = 2.0\) and \(\log K_{Si}^- = -6.8\) for edge SiOH groups (Xie and Walther, 1992).

Electrolyte ion complexation constants Like surface ionization constants, surface complexation constants for electrolyte ions, \(K_{C^-}\) and \(K_{A^-}\), can be independently determined by a graphic technique (Strycha, 1984, 1989) or numeric method (Hayes et al., 1991) using the adsorption data of the electrolyte ions. These values can also be estimated...
simultaneously with the surface ionization constants from titration data (James and Parks, 1982; Herbelin and Westall, 1994). For $\gamma$-$Al_2O_3$, we selected $\log K^+_\text{Al} = -9.2$ and $\log K_{\text{A}^-} = 7.9$ (James and Parks, 1982). In the case of kaolinite, the same assumption must be made as that for the surface ionization constants. The selected values of TLM parameters for $\gamma$-$Al_2O_3$ and kaolinite, as well as solution equilibrium constants, are listed in Table 5-2.

5-3.2 Selection of $SO_4$ and $PO_4$ Surface Complexation Reactions and Extraction of the Complexation Constants

Both inner- and outer-sphere complexes were used to model the ionic strength dependence of $SO_4$ and $PO_4$ adsorption onto $g$-$Al_2O_3$ and kaolinite. The computer program FITEQ (Herbelin and Westall, 1994) was utilized to optimize the surface complexation constants by fitting the adsorption data of $SO_4$ (Tables 5-3) and $PO_4$ (Table 5-5) using the parameters and equilibrium constants listed in Tables 5-1 and 5-2. The surface complexation constants (Tables 5-3 and 5-4) were extracted from a single experimental data set varying in ionic strength. The Davies equation was applied for activity corrections to all ionic strengths (Herbelin and Westall, 1994). All surface species for $SO_4$ or $PO_4$ adsorption, including monodentate (e.g., $AlSO_4$) and binuclear (e.g., $Al_2SO_4$) complexes, were considered in TLM modeling, starting with simple species and then adding more complicated species. The goal was to fit a data set with the lowest value of goodness of fit for inner- or outer-sphere complexes. There usually was no model convergence when more than two constants were adjustable, and the problem of overflow often occurred.
Table 5-2. Reactions and equilibrium constants used in TLM modeling for SO$_4$ and PO$_4$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>logK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aqueous phase equilibria</strong> †</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$</td>
<td>14.00</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^-$</td>
<td>1.99</td>
</tr>
<tr>
<td>$\text{K}^+ + \text{SO}_4^{2-} \rightarrow \text{KSO}_4$</td>
<td>0.85</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{PO}_4^{3-} \rightarrow \text{HPO}_4^{2-}$</td>
<td>12.35</td>
</tr>
<tr>
<td>$2\text{H}^+ + \text{PO}_4^{3-} \rightarrow \text{H}_2\text{PO}_4^-$</td>
<td>19.55</td>
</tr>
<tr>
<td>$3\text{H}^+ + \text{PO}_4^{3-} \rightarrow \text{H}_3\text{PO}_4^{0}$</td>
<td>21.71</td>
</tr>
<tr>
<td>$\text{K}^+ + \text{H}^+ + \text{PO}_4^{3-} \rightarrow \text{KHPO}_4$</td>
<td>12.64</td>
</tr>
<tr>
<td><strong>Surface protolysis</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{AlOH} + \text{H}^+ \rightarrow \text{AlOH}_2^+$</td>
<td>7.89 ‡</td>
</tr>
<tr>
<td>$\text{AlOH} \rightarrow \text{AlO}^- + \text{H}^+$</td>
<td>-9.05 ‡</td>
</tr>
<tr>
<td>$\text{SiOH} + \text{H}^+ \rightarrow \text{SiOH}_2^+$</td>
<td>2.00 §</td>
</tr>
<tr>
<td>$\text{SiOH} \rightarrow \text{SiO}^- + \text{H}^+$</td>
<td>-6.80 §</td>
</tr>
<tr>
<td><strong>Electrolyte ion complexation</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{AlOH} + \text{K}^+ \rightarrow \text{AlO}^-\text{K}^+ + \text{H}^+$</td>
<td>-9.20 ¶</td>
</tr>
<tr>
<td>$\text{AlOH} + \text{H}^+ + \text{Cl}^- \rightarrow \text{AlOH}_2^+\text{Cl}^-$</td>
<td>7.90 ¶</td>
</tr>
<tr>
<td>$\text{SiOH} + \text{K}^+ \rightarrow \text{SiO}^-\text{K}^+ + \text{H}^+$</td>
<td>-3.50 #</td>
</tr>
</tbody>
</table>

† Schecher and McAvoy, 1994  
‡ Huang and Stumm, 1973  
§ Xie and Walther, 1992  
¶ James and Parks, 1982  
# Zachara et al., 1988
Table 5-3. Sulfate surface complexation reactions and complexation constants optimized with FITEQL

<table>
<thead>
<tr>
<th>Reactions</th>
<th>logK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma$-Al$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>0.01 0.1 1.0</td>
</tr>
</tbody>
</table>

| Inner-sphere complexes                     |
|------------------------------------------|------------|
| $\text{XOH} + \text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{XSO}_4^- + \text{H}_2\text{O}$ | 8.56 8.23 5.75 | 9.62 7.58 6.22 |

| Outer-sphere complexes                    |
|------------------------------------------|------------|
| $\text{XOH} + \text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{XOH}_2^-\text{SO}_4^{2-}$ | 12.46 11.79 10.88 | 9.69 8.60 8.28 |
| $\text{XOH} + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow \text{XOH}_2^+\text{HSO}_4^-$ | 19.07 15.01 15.28 | - - 13.96 |

Table 5-4. Phosphate surface complexation reactions and complexation constants optimized with FITEQL

<table>
<thead>
<tr>
<th>Reactions</th>
<th>logK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma$-Al$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>0.01 0.1 1.0</td>
</tr>
</tbody>
</table>

| Inner-sphere complexes                     |
|------------------------------------------|------------|
| $\text{AlOH} + \text{PO}_4^{3-} + \text{H}^+ \rightarrow \text{AlPO}_4^{2-} + \text{H}_2\text{O}$ | 18.49 19.25 19.85 | 17.44 17.14 19.22 |
| $\text{AlOH} + 2\text{PO}_4^{3-} + 2\text{H}^+ \rightarrow \text{AlHPO}_4^- + \text{H}_2\text{O}$ | 24.04 24.76 24.91 | - 22.37 24.53 |

| Outer-sphere complexes                    |
|------------------------------------------|------------|
| $\text{AlOH} + \text{PO}_4^{3-} + 2\text{H}^+ \rightarrow \text{AlOH}_2^+\text{HPO}_4^{2-}$ | 28.92 28.28 28.48 | - - - |
| $\text{SiOH} + \text{PO}_4^{3-} + \text{H}^+ \rightarrow \text{SiOH}_2^-\text{PO}_4^-$ | - - - | 18.60 19.12 20.85 |
For each convergent optimization, FITEQ4L provides the goodness of fit for a set of surface constants. The best sets of surface complexation reactions and their constants for each set of adsorption data were selected and are given in Table 5-5. The goodness of fit, \( V_Y \), which is the weighted sum of squares of residuals (SOS) divided by the degree of freedom (DF), may be calculated by the equation (Dzombak and Morel, 1990; Herbelin and Westall, 1994):

\[
V_Y = \frac{SOS}{DF} = \frac{\sum [Y_j / S_j]^2}{N_p \times N_c - N_a}
\]  

(5-28)

where \( Y_j \) is the mass balance residual calculated from the deviation between the calculated and the experimental mass balance for component j, \( S_j \) is the error calculated for \( Y_j \) from the experimental error estimates, \( N_p \) is the number of data points, \( N_c \) is the number of components for which both the total and the free concentration are known, and \( N_a \) is the number of adjustable parameters. Obviously, the value of \( V_Y \) depends upon the experimental error estimates, and higher error estimates produce lower values of \( V_Y \). In this study, the absolute error estimate for \( pH \) was set to 0.02 and the relative error estimate for \( H^+ \) concentration was 0.05. For \( SO_4 \) or \( PO_4 \) adsorption data, a relative error estimate of 5% was used for both aqueous and adsorbed phases. In general, for a given set of error estimates, lower values of \( V_Y \) indicate better agreement between the experimental data and the model fit. A comparison was made between inner- and outer-sphere complexes for \( SO_4 \) or \( PO_4 \) adsorption by using their respective values of \( V_Y \) (Table 5-5).
Table 5-5. Values of the goodness of fit for modeling SO₄ and PO₄ adsorption on γ-Al₂O₃ and kaolinite

<table>
<thead>
<tr>
<th>Ionic strength (M)</th>
<th>γ-Al₂O₃</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inner-sphere</td>
<td>Outer-sphere</td>
</tr>
<tr>
<td>0.01</td>
<td>116.3</td>
<td>10.6</td>
</tr>
<tr>
<td>0.1</td>
<td>208.2</td>
<td>30.2</td>
</tr>
<tr>
<td>1.0</td>
<td>330.8</td>
<td>20.1</td>
</tr>
</tbody>
</table>

SO₄ adsorption

<table>
<thead>
<tr>
<th>Ionic strength (M)</th>
<th>γ-Al₂O₃</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inner-sphere</td>
<td>Outer-sphere</td>
</tr>
<tr>
<td>0.01</td>
<td>6.1</td>
<td>28.7</td>
</tr>
<tr>
<td>0.1</td>
<td>17.6</td>
<td>32.3</td>
</tr>
<tr>
<td>1.0</td>
<td>31.8</td>
<td>51.1</td>
</tr>
</tbody>
</table>

PO₄ adsorption

To obtain the surface complexation constants, it is convenient to set up the equilibrium problem in a tabular format by matrix algebra. An example is given for SO₄ adsorption on γ-Al₂O₃ (Tables 5-6 and 5-7). The application of matrix algebra to the solution of surface chemical equilibrium problems has been discussed in detail by Westall (1987) and Dzombak and Morel (1990). The key to the procedure is the definition of species (every chemical entity in the system), components (a minimal set of reactants out
Table 5-6. Species, components, and stoichiometry for SO₄ adsorption on γ-Al₂O₃ (A matrix)

<table>
<thead>
<tr>
<th>Species</th>
<th>Components</th>
<th>logK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pₚ Pₚ₁ Pₚ₂ SO₄²⁻ AlOH I/S SO₄₄⁺ Cl⁻ K⁺ H⁺</td>
<td></td>
</tr>
<tr>
<td>1 H⁺</td>
<td>0 0 0 0 0 0 0 0 0 0 1 0</td>
<td></td>
</tr>
<tr>
<td>2 OH⁻</td>
<td>0 0 0 0 0 0 -2 0 0 0 -1 -14.0</td>
<td></td>
</tr>
<tr>
<td>3 SO₄²⁻</td>
<td>0 0 0 1 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>4 HSO₄⁻</td>
<td>0 0 0 1 0 4 0 0 0 1 1.99</td>
<td></td>
</tr>
<tr>
<td>5 KSO₄⁻</td>
<td>0 0 0 1 0 4 0 0 1 0 0.85</td>
<td></td>
</tr>
<tr>
<td>6 AlOH₂⁺</td>
<td>1 0 0 0 1 1 0 0 0 1 7.89</td>
<td></td>
</tr>
<tr>
<td>7 AlOH</td>
<td>0 0 0 0 1 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>8 AlO⁻</td>
<td>-1 0 0 0 1 -1 0 0 0 -1 -9.05</td>
<td></td>
</tr>
<tr>
<td>9 AlO⁻⁻K⁺</td>
<td>-1 1 0 0 1 0 0 0 1 -1 -9.20</td>
<td></td>
</tr>
<tr>
<td>10 AlOH₂⁺⁻Cl⁻</td>
<td>1 -1 0 0 1 2 0 1 0 1 7.90</td>
<td></td>
</tr>
</tbody>
</table>

SO₄ outer-sphere complexes

11 AlOH₂⁺⁻SO₄²⁻ | 1 -2 0 1 1 5 1 0 0 1 Fit
12 AlOH₂⁺⁻HSO₄⁻ | 1 -1 0 1 1 6 1 0 0 2 Fit

SO₄ inner-sphere complexes

13 AlSO₄⁻ | -1 0 0 1 1 3 1 0 0 1 Fit
14 AlSO₄⁻⁻K⁺ | -1 1 0 1 1 4 1 0 1 1 Fit
15 AlHSO₄ | 0 0 0 1 1 4 1 0 0 2 Fit

† Adsorbed SO₄.
Table 5-7. Species, components, and stoichiometry for SO₄ adsorption on γ-Al₂O₃ (B matrix)

<table>
<thead>
<tr>
<th>Species</th>
<th>Components</th>
<th>logK</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₀ 160</td>
<td>P₁ 161</td>
<td>P₂ 162</td>
</tr>
<tr>
<td>1 H⁺</td>
<td>0 0 0 0 0 0 0.5 0 0 0 0.5 0 0 0 0 0 0 1 0.5 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>2 OH⁻</td>
<td>0 0 0 0 0 0 0.5 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>3 SO₄²⁻</td>
<td>0 0 0 1 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>4 HSO₄⁻</td>
<td>0 0 0 1 0 0 0.5 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>5 KSO₄⁻</td>
<td>0 0 0 1 0 0 0.5 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>6 AlOH₂⁺</td>
<td>1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>7 AlOH</td>
<td>0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>8 AlO⁻</td>
<td>-1 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>9 AlO⁻⁺K⁺</td>
<td>-1 1 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>10 AlOH₂⁺⁻Cl⁻</td>
<td>1 -1 0 0 1 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
</tbody>
</table>

**SO₄ outer-sphere complexes**

|    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|
| 11 AlOH₂⁺⁻SO₄²⁻ | 1 -2 0 1 1 0 0 1 0 0 1 0 0 1 Fit |
| 12 AlOH₂⁺⁻HSO₄⁻ | 1 -1 0 1 1 0 1 0 0 0 2 0 0 2 Fit |

**SO₄ inner-sphere complexes**

|    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|
| 13 AlSO₄⁻  | -1 0 0 1 1 0 0 1 0 0 1 0 0 1 Fit |
| 14 AlSO₄⁻⁺K⁺ | -1 1 0 1 1 0 1 0 1 1 1 0 1 1 Fit |
| 15 AlHSO₄  | 0 0 0 1 1 0 0 1 0 0 2 0 0 2 Fit |

† Adsorbed SO₄.
of which all the species can be formed), a mass action stoichiometry matrix (denoted the A matrix) (Table 5-6), and a mass balance stoichiometry matrix (denoted the B matrix) (Table 5-7). All chemical species to be considered in the equilibrium problem are listed in the first column, and the components are listed on the top row. The rows of the A matrix are the coefficients in the mass action equations, and the columns of the B matrix are the coefficients in the mass balance equations.

The colomic term, \( P_i (= \exp(-ZF\Psi_i/RT)) \), where \( i \) denotes o, \( \beta \), or d, appears in the same form as a chemical component in the A and B matrixes (Table 5-6 and 5-7). This construct makes it possible to easily incorporate the total surface charge constraint in equilibrium calculations. The total concentration of the dummy component \( P_i \) corresponds to the surface charge, and it is calculated at each iteration in the solution procedure, using the theoretical charge-potential relationships (Eqs. 5-22 to 26) (Dzombak and Morel, 1990).

The ionic strength component \( I/S \) can be incorporated in the new version of the FITEQL program when ionic strength needs to be calculated. The \( I/S \) values in the A matrix (Table 5-6) are calculated by the general equation (Herbelin and Westali, 1994):

\[
I/S_{(A)} = \sum_{j=1}^{n} a_j Z_j^2 - Z_s^2
\]

(5-29)

where \( a_j \) is the stoichiometrical number of the \( j \)th component, \( Z_j \) is the valence of the \( j \)th component, and \( Z_s \) is the valence of species that is formed with the \( n \) components. But charges on surface species are not considered since they are incorporated in the colomic terms. For example, the species \( \text{AlOH}_2^+-(\text{SO}_4)^{2-} \) is formed by

\[
\text{AlOH} + H^+ + \text{SO}_4^{2-} \rightarrow \text{AlOH}_2^+-(\text{SO}_4)^{2-},
\]
and therefore

\[ I/S_{(A)} = [0^2 + 1^2 + (-2)^2] - 0^2 = 5. \]

The I/S in the B matrix (Table 5-7) is simply calculated by the equation (Herbelin and Westall, 1994):

\[ I/S_{(B)} = Z^2_s / 2. \]  

(5-30)

As in the A matrix, the surface species are excluded in calculating the I/S_{(B)}.

5-4 Adsorption Experiments

5-4.1 Materials

The Al oxide was a \( \gamma - \text{Al}_2\text{O}_3 \) made by the Degussa Corp., Akron, Ohio, under the name of Aluminum Oxide C\(^*\). It has a surface area of 100 m\(^2\) g\(^{-1}\) with impurities less than 0.4\% (Ettlinger et al., 1991). Poorly crystallized kaolinite (KGa-2) was purchased from the Source Clay Minerals Repository, Clay Minerals Society, Department of Geology, University of Missouri, Columbia, Missouri. This kaolinite sample, from Warren County, Georgia, has a N\(_2\) gas surface area of 23.6 m\(^2\) g\(^{-1}\) and a cation exchange capacity of 3.3 cmolc kg\(^{-1}\) (van Olphen and Fripiat, 1979). The samples were pretreated and the suspensions of \( \gamma - \text{Al}_2\text{O}_3 \) and kaolinite were prepared with the methods described elsewhere (He et al., 1995).
5-4.2 Adsorption Edges

The SO₄ and PO₄ adsorption experiments were carried out in batch systems to determine adsorption edges (SO₄ or PO₄ adsorption percent as a function of solution pH). Sixteen 20-ml aliquots of γ-Al₂O₃ or kaolinite suspension were placed in 50-ml centrifuge tubes, and an equal amount of stock solutions of SO₄ or PO₄ added in each batch. Three levels of ionic strength (KCl) were used with a difference in three orders of magnitude (Table 5-8).

<table>
<thead>
<tr>
<th>Solid</th>
<th>SO₄</th>
<th>PO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total conc. (mM)</td>
<td>Ionic strength (M)</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>1.0</td>
<td>0.01, 0.1, and 1.0</td>
</tr>
<tr>
<td>kaolinite</td>
<td>0.05</td>
<td>0.001, 0.01, and 0.1</td>
</tr>
</tbody>
</table>

After adding SO₄ or PO₄ these suspensions were then adjusted to the desired pH values using 1 M HCl or 1 M KOH additions that changed the total volume by <2%. The change in ionic strength due to acid or base addition was less than 0.003 M, although the ionic strength of 0.001 M would be increased to 0.002 M for the samples with highest pH values. The treated suspensions were shaken for 12 hr for SO₄ (He et al., 1994) and 24 hr for PO₄ (Colombo et al., 1994) in a water bath shaker (25°C) at 100 oscillations min⁻¹. The samples were centrifuged for 30 min at 15,000 rpm (27500 x g) (Sorvall RC-5B Refrigerated Superspeed
Centrifuge, Du Pont Instruments), and the pH of the supernatant was determined with a pH meter and a KG2401 combined electrode (Radiometer Copenhagen, Denmark). The supernatants were then filtered through 0.2 μm polycarbonate membranes (Nuclepore Co., Pleasanton, CA) with a 25 mm holder. The filtrates were analyzed for S or P. The exact volume of solution in each tube was calculated from the volume of suspension, volume of SO₄ or PO₄ stock solution added, volume of acid or base added, and particle density of γ-Al₂O₃ (2.9 g cm⁻³) (Ettlinger et al., 1991) or kaolinite (2.63 g cm⁻³) (Dixon, 1989).

Analyses of the filtrates for S were performed with an inductively coupled plasma atomic emission spectrophotometer (Model JY 46P). Phosphate was measured by the colorimetric method of Murphy and Riley (1962) at the wave length of 882 nm using a Hitachi spectrophotometer (model 100-20).

5-5 Results And Discussion

5-5.1 pH Effect

Sulfate adsorption on γ-Al₂O₃ (Fig. 5-2) and kaolinite (Fig. 5-3) decreased monotonically with increasing pH. This phenomenon can be simply explained by the electrical double layer theory. Negative surface charge increased as the suspension pH increased. The higher the negative charge on the surface, the greater the repulsive force between the surface and the negatively charged anions. Consequently, SO₄ adsorption decreases as pH increases. This is consistent with the results of SO₄ adsorption on one of the soils studied by Bolan et al.
(1986) and on goethite (Hoins et al., 1993). Courchesne (1991) and Bolan et al. (1986) observed a slight increase in SO$_4$ adsorption with increasing pH while pH was below 4.

On the other hand, PO$_4$ adsorption on $\gamma$–Al$_2$O$_3$ (Fig. 5-4) and kaolinite (Fig. 5-5) initially increased as the suspension pH increased. An adsorption plateau was obtained in an intermediate pH region and PO$_4$ adsorption subsequently declined as the pH continued to increase. The adsorption plateaus were found between pH 5 and 7 for $\gamma$–Al$_2$O$_3$ and between pH 4 and 6 for kaolinite. A similar behavior of PO$_4$ adsorption was reported on $\gamma$–Al$_2$O$_3$ (Chen et al., 1973; Huang, 1975), kaolinite (Chen et al., 1973), and soils (Bolan et al., 1986). Bolan et al. (1986) related the decreasing in PO$_4$ adsorption at low pH values to the dissolution of adsorbents. In this study, dissolution of $\gamma$–Al$_2$O$_3$ or kaolinite would produce Al$^{3+}$ ions, which would precipitate PO$_4$. This process would result in a decrease in PO$_4$ equilibrium concentration, i.e., an increase in PO$_4$ adsorption, which was not observed herein. Thus, the change in species of PO$_4$ with pH might be critical. As pH decreased, H$_2$PO$_4^-$ and even H$_3$PO$_4^0$ were predominant species in solution. Obviously, the affinity of H$_3$PO$_4^0$ or H$_2$PO$_4^-$ for the surface was lower than that of HPO$_4^{2-}$ or PO$_4^{3-}$ for the surface. As a result, PO$_4$ adsorption decreased as the pH decreased at low pH levels.

5-5.2 Ionic Strength Effect

Sulfate adsorption on $\gamma$–Al$_2$O$_3$ (Fig. 5-2) and kaolinite (Fig. 5-3) was markedly influenced by ionic strength and decreased with increasing ionic strength throughout the pH range examined. This coincides with the results of SO$_4$ adsorption on soils (Bolan et al., 1986;
Fig. 5-2. Sulfate adsorption edge on γ-Al₂O₃ as a function of pH and ionic strength.
Fig. 5-3. Sulfate adsorption edge on kaolinite as a function of pH and ionic strength.
Fig. 5-4. Phosphate adsorption edge on γ-Al₂O₃ as a function of pH and ionic strength.
Fig. 5-5. Phosphate adsorption edge on kaolinite as a function of pH and ionic strength.
Courchesne, 1991) and of SeO₄ adsorption on hydrous Fe oxide (Hayes et al., 1988) and on soils (Barrow and Whelan, 1989). On the contrary, PO₄ adsorption on γ-Al₂O₃ (Fig. 5-4) and kaolinite (Fig. 5-5) showed little ionic strength dependence. In the low pH range, PO₄ adsorption, like SO₄, decreased with increasing ionic strength. At high pH values, however, the effect of ionic strength was reversed, that is, PO₄ adsorption increased with an increase in ionic strength. Therefore, a cross-over point was observed where there was no effect of ionic strength on adsorption. This point was referred to as the point of zero salt effect of the phosphated surface (PZSE_p) (Barrow and Whelan, 1989). The PZSE_p was found to occur at about pH 8 for γ-Al₂O₃ (Fig. 5-4) which was lower than the PZSE of pure γ-Al₂O₃; and pH 5 for kaolinite (Fig. 5-4) which was close to the PZSE of pure kaolinite (Sposito, 1984). Similar results were observed for PO₄ adsorption on Fe oxides (Barrow et al., 1980) and soils (Bolan et al., 1986), and SeO₃ (selenite) adsorption on soils (Barrow and Whelan, 1989).

From the results of ionic strength effects, the mechanism for SO₄ adsorption is apparently different from that for PO₄ adsorption. It may be reasonably assumed that SO₄ is adsorbed by forming an outer-sphere complex while PO₄ is adsorbed by forming an inner-sphere complex. Thus, SO₄ is adsorbed on the β-plane (Fig. 5-1a) by electrostatic force between the positive charge from the surface groups and the negatively charged SO₄ ions. Electrolyte ions may reach the β-plane and compete with SO₄ for adsorptive sites (Davis and Kent, 1990). Sulfate adsorption is associated with a surface that consists of surface functional groups. This type of surface is usually termed the variable charge (or constant potential) surface since surface charge varies with pH and ionic strength (van Olphen, 1977). Phosphate
is adsorbed on the o-plane through ligand exchange and coordinate covalent bonding between the metal ions in the solid and PO$_4$ ions (Fig. 5-1a). Phosphate adsorption is directly related to the surface metal ions, not to functional groups. This surface charge does not change with either solution pH or ionic strength. This type of surface may be referred to as the permanent charge surface. In this case, OH$^-$ ions and other inner-sphere complex-forming ions in solution will compete with PO$_4$ for surface sites, although electrolyte ions will not do so.

Changing background electrolyte concentration influences the adsorption of ions at the interface by affecting: (i) the double layer thickness and then the competition between electrolyte ions and adsorbing ions for available surface sites (Bar-Yosef et al., 1988; Hayes et al., 1988); (ii) electrical charge (Courchesne, 1991; Hingston, 1981); (iii) electrical potential (Barrow and Whelan, 1989; Bolan et al., 1986; Bowden et al., 1980; Hayes et al., 1988); or (iv) speciation of adsorbing ions (Courchesne, 1991). For SO$_4$, since the surface of γ-Al$_2$O$_3$ and kaolinite responds as variable charge, the absolute value of the surface charge density increased as ionic strength increased. The surface became more negative at high pH values (pH > PZC) and therefore adsorption decreased with increasing ionic strength. In the low pH range (pH < PZC), it appears that more SO$_4$ would be adsorbed as ionic strength increased since the surface turned out to be more positively charged. However, as electrolyte concentration increased, the double layer thickness was compressed, thus making it easier for electrolyte ions to reach the β-plane. That is, electrolyte ions competed with SO$_4$ for adsorptive sites, resulting in a decrease in SO$_4$ adsorption. Hence, SO$_4$ adsorption decreased monotonically with increasing ionic strength.
For PO₄, the surface responds as constant charge (or variable potential). The absolute value of potential, not the charge density, decreased with increasing ionic strength. In the low pH range (pH < PZC), the potential on the o-plane was positive. Increasing ionic strength decreased this potential and thus decreased PO₄ adsorption. At high pH levels (pH > PZC), the potential on the o-plane was negative. Increasing ionic strength increased this potential, i.e., made it less negative and thus increased PO₄ adsorption (Barrow et al., 1980; Barrow and Whelan, 1989).

5.5.3 TLM Modeling

Both inner- and outer-sphere complexes were used to model the adsorption of SO₄ and PO₄ onto γ-Al₂O₃ and kaolinite at three levels of ionic strengths. For SO₄ adsorption on γ-Al₂O₃, the outer-sphere modeling described the experimental data better than the inner-sphere modeling for all three ionic strengths (Figs. 5-6 to 8). A statistical analysis indicated that the values of the goodness of fit were much lower for the outer-sphere modeling than for the inner-sphere modeling (Table 5-5). Surface complexation constants for SO₄ adsorption decreased with increasing ionic strength for both inner- and outer-sphere complexes (Table 5-3). The values of the surface complexation constants were greater for outer-sphere complexes than for inner-sphere complexes. These values for outer-sphere complexes are comparable to those obtained by other researchers (Goldberg, 1992), except for the AlOH₂⁺-(HSO₄)⁻ species in the 0.01 M electrolyte, which had a logK value of 19.07 (Table 5-3). Both SO₄²⁻ and HSO₄⁻ species must be incorporated into the outer-sphere modeling to obtain the best fit to the data.
Fig. 5-6. TLM outer- and inner-sphere modeling of sulfate adsorption on γ-Al₂O₃ in 0.01 M KCl. The outer-sphere modeling curve is the sum of the two surface species of AlOH₂⁺-(HSO₄)⁻ and AlOH₂⁺-(SO₄)²⁻. The inner-sphere modeling curve represents the AlSO₄ surface species.
Fig. 5-7. TLM outer- and inner-sphere modeling of sulfate adsorption on γ-Al₂O₃ in 0.1 M KCl. The outer-sphere modeling curve is the sum of the two surface species of AlOH₂⁺-(HSO₄)⁻ and AlOH₂⁺-(SO₄)²⁻. The inner-sphere modeling curve represents the AIOSO₄ surface species.
Fig. 5-8. TLM outer- and inner-sphere modeling of sulfate adsorption on γ-Al₂O₃ in 1.0 M KCl. The outer-sphere modeling curve is the sum of the two surface species of $\text{Al(OH)}_2^+-(\text{HSO}_4)^-$ and $\text{Al(OH)}_2^+-\text{(SO}_4)^{2-}$. The inner-sphere modeling curve represents the $	ext{AlSO}_4^+$ surface species.
In the case of inner-sphere modeling, only one species, i.e., \( \text{SO}_4^{2-} \), could be used to fit the experimental data; otherwise there was no convergence in FITEQL. Suffice it to say that, from the point of view of solution equilibrium chemistry, the outer-sphere complexes for \( \text{SO}_4 \) adsorption on \( \gamma-\text{Al}_2\text{O}_3 \) are more reasonable than the inner-sphere complexes, since both \( \text{HSO}_4^- \) and \( \text{SO}_4^{2-} \) species do exist in solution. Monodentate complex modeling was better than binuclear complex modeling, and in many cases there was no convergence for binuclear complex modeling. For the low ionic strength of 0.01 M, the \( \text{AlOH}_2^+-(\text{HSO}_4^-) \) species predominated at low pH (pH < 6), while the \( \text{AlOH}_2^+-(\text{SO}_4)^2- \) species became more important as the pH increased (Fig. 5-6). However, for the higher ionic strengths of both 0.1 and 1.0 M, the \( \text{AlOH}_2^+-(\text{HSO}_4^-) \) species was always dominant throughout the pH range. As electrolyte concentration increased, there was more competition between \( \text{Cl}^- \) and \( \text{SO}_4 \) ions for surface sites. The bisulfate surface species was more stable on the surface (Davis and Leckie, 1980).

In contrast to \( \text{SO}_4 \) adsorption, \( \text{PO}_4 \) adsorption on \( \gamma-\text{Al}_2\text{O}_3 \) was better modeled by inner-sphere complexation than outer-sphere complexation (Figs. 5-9 to 11), with the inner-sphere complexes having lower values of goodness of fit than the outer-sphere complexes (Table 5-5). For the inner-sphere complexes, a combination of \( \text{AlPO}_4^{2-} \) and \( \text{AlHPO}_4^- \) surface species provided the best fit to the experimental data. Similarly, the \( \text{PO}_4 \) adsorption on Fe oxides was described very well by the CCM (Sigg and Stumm, 1981) and TLM inner-sphere complexes (Hawke et al., 1989). At low pH, the concentration of species \( \text{AlPO}_4^{2-} \) increased with increasing pH. A maximum was obtained around pH 7 and the \( \text{AlPO}_4^{2-} \) concentration decreased as the pH continued to increase (Figs. 5-9 to 11). However, the
Fig. 5-9. TLM outer- and inner-sphere modeling of phosphate adsorption on γ-Al₂O₃ in 0.01 M KCl. The inner-sphere modeling curve is the sum of the AlPO₄²⁻ and AlHPO₄⁻ surface species. The outer-sphere modeling curve represents the AlOH⁺-(HPO₄)²⁻ surface species.
Fig. 5-10. TLM outer- and inner-sphere modeling of phosphate adsorption on γ-Al₂O₃ in 0.1 M KCl. The inner-sphere modeling curve is the sum of the AlPO₄²⁻ and AlHPO₄⁻ surface species. The outer-sphere modeling curve represents the AlOH₂⁺-(HPO₄)²⁻ surface species.
Fig. 5-11. TLM outer- and inner-sphere modeling of phosphate adsorption on γ-Al₂O₃ in 1 M KCl. The inner-sphere modeling curve is the sum of the AlPO₄²⁻ and AlHPO₄⁻ surface species. The outer-sphere modeling curve represents the AlOH₃⁻-(HPO₄)²⁻ surface species.
concentration of the AlHPO$_4^-$ surface species always decreased with increasing pH and was lower than that of AlPO$_4^{2-}$ except at pH < 3.5 for 0.1 M electrolyte (Fig. 5-10). As for the outer-sphere complexes, only one species could be assigned to FITEQL and the best fit was obtained using the AlOH$_2^+$-(HPO$_4$)$_2^-$ species without exception for all three ionic strengths. The PO$_4$ complexation constants for inner-sphere complexes increased with increasing ionic strength, whereas this trend failed for outer-sphere complexes (Table 5-5). Binuclear or bidentate complex modeling failed to fit the experimental data, although these complexes have been observed on goethite in high surface coverage using FTIR (Tejedor-Tejedor and Anderson, 1990).

The modeling results of SO$_4$ adsorption on kaolinite (Figs. 5-12 to 14) are similar to those presented above for γ-Al$_2$O$_3$ (Figs. 5-6 to 8). The outer-sphere modeling gave better agreement with the experimental data than did inner-sphere modeling, and the former had lower values for the goodness of fit (Table 5-5). The SO$_4$ adsorption on kaolinite was also well modeled by Zachara et al. (1988) using the TLM outer-sphere complexes. All surface species for both outer- and inner-sphere complexes were divalent sulfate associated with the surface except for the outer-sphere modeling of 1.0 M KCl, where both mono- and di-valent sulfate could be assigned to FITEQL (Table 5-3). A chemical justification for this phenomenon is not evident.

The inner-sphere modeling for PO$_4$ adsorption on kaolinite (Figs. 5-15 to 17) predicted the data better than the outer-sphere modeling (Table 5-5). For inner-sphere modeling, although only one PO$_4$ species was allowed for input in order for the convergence of the
Fig. 5-12. TLM outer- and inner-sphere modeling of sulfate adsorption on kaolinite in 0.001 M KCl, with the outer-sphere surface species $\text{Al(OH}_2^+-(\text{SO}_4)^2^-$ and the inner-sphere surface species $\text{AlSO}_4^2^-$. 
Fig. 5-13. TLM outer- and inner-sphere modeling of sulfate adsorption on kaolinite in 0.01 M KCl, with the outer-sphere surface species $\text{AlOH}_2^+-(\text{SO}_4)^2-$ and the inner-sphere surface species $\text{AlSO}_4^-$.
Fig. 5-14. TLM outer- and inner-sphere modeling of sulfate adsorption on kaolinite in 0.1 M KCl, with two outer-sphere surface species $\text{AlOH}_2^+-(\text{HSO}_4)^-$ and $\text{AlOH}_2^+-(\text{SO}_4)^2^-$, and the inner-sphere surface species $\text{AlSO}_4$. 
Fig. 5-15. TLM outer- and inner-sphere modeling of phosphate adsorption on kaolinite in 0.01 M KCl, with the inner-sphere surface species $\text{AlPO}_4^{2-}$ and the outer-sphere surface species $\text{SiOH}_2^+-(\text{PO}_4)^3^-$. 
Fig. 5-16. TLM outer- and inner-sphere modeling of phosphate adsorption on kaolinite in 0.1 M KCl, with two inner-sphere surface species AlHPO$_4^-$ and AlPO$_4^{2-}$, and one outer-sphere surface species SiOH$_2^-$-(PO$_4^{3-}$).
Fig. 5-17. TLM outer- and inner-sphere modeling of phosphate adsorption on kaolinite in 1 M KCl, with two inner-sphere surface species AlHPO$_4^-$ and AlPO$_4^{2-}$, and one outer-sphere surface species SiOH$_5^+$-(PO$_4^{3-}$).
FITEQL program for 0.01 M electrolyte (Fig. 5-15; Table 5-5), two species were needed to obtain the best fit to the data for 0.1 and 1.0 M electrolyte (Figs. 5-16 and 17; Table 5-5). It is important to note that, for outer-sphere modeling, PO₄ adsorption data on kaolinite could not be modeled without using the SiOH₂⁺-(PO₄)²⁻ surface species. This surface species makes less sense than do the inner-sphere complexes since there is such a low value of logK for SiOH₂⁺ (Xie and Walther, 1992).

5-6 Conclusions

Ionic strength has different effects on SO₄ and PO₄ adsorption on γ-Al₂O₃ and kaolinite. The SO₄ adsorption was greatly reduced with increasing ionic strength, whereas PO₄ adsorption was little influenced with an increase in ionic strength. Based on the TLM modeling, SO₄ adsorption conformed to outer-sphere complexation, while PO₄ adsorption occurred as inner-sphere complexation.

There is no doubt that PO₄ forms an inner-sphere complex during adsorption at the solid-water interface, but the mechanism for SO₄ adsorption has been in debate. Surface complexation modeling alone cannot be used to support mechanistic conclusions regarding surface speciation or interfacial structure (Zachara and Westall, 1995). The technique of extended X-ray absorption fine structure (EXAFS) provides in situ structural information for ions adsorbed at the solid-water interface (Fendorf et al., 1994). The EXAFS measurements showed that SeO₄ (selenate) formed an outer-sphere complex at the goethite-water interface (Hayes et al., 1987). This finding supported the observation of the effects of ionic strength on
SeO$_4$ adsorption (Hayes et al., 1988). It was then postulated that the mechanism for SO$_4$ adsorption would be the same as that for SeO$_4$ adsorption, i.e., outer-sphere complexation. This expectation has been challenged by the recent report of Manceau and Charlet (1994). Using EXAFS spectroscopy, they found that SeO$_4$ always formed inner-sphere complexes on both dry and wet goethite and hydrous ferric oxide regardless of hydration state, yet they postulated that SO$_4$ adsorption had the identical mechanism to SeO$_4$ adsorption, i.e., inner-sphere complexation.

5-7 References


5-8 Appendices

5-8.1 Sulfate adsorption on γ-Al₂O₃ as a function of pH and ionic strength
(γ-Al₂O₃ = 10 g L⁻¹, SO₄ = 1 mM)

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5.8.3 Phosphate adsorption on γ-Al₂O₃ as a function of pH and ionic strength
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5-8.4 Phosphate adsorption on kaolinite as a function of pH and ionic strength
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Chapter VI

SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

Sulfate is a major anion in acid deposits and acid mine drainage that has received great consideration in the past decades. In recent years coal combustion by-products with a high content of CaSO₄ have been used to ameliorate acid soils in the southeastern US. Interactions of PO₄ with soils have long been recognized as the main cause of low availability of phosphorus for plants. In this dissertation, SO₄ and PO₄ adsorption on γ-Al₂O₃ and kaolinite was investigated, with an emphasis on quantitatively describing surface complexation behavior at the mineral-water interfaces. The laboratory experiments included (1) SO₄ equilibrium adsorption at three pH levels (pH 4.3 to 7.0), (2) OH⁻ ions release with SO₄ addition at three pH levels, and (3) effects of ionic strength on SO₄ and PO₄ adsorption. Based on these studies, the following conclusions can be made:

1. The adsorption of both SO₄ and PO₄ was highly pH-dependent, increasing with a decrease in pH.
2. Sulfate adsorption was markedly decreased by increasing ionic strength, whereas PO₄ adsorption was little affected by changes in ionic strength.
3. The adsorption capacity of SO₄ for γ-Al₂O₃ was five times as much as that for kaolinite.
4. The SO₄/OH exchange stoichiometry increased with increasing solution pH and SO₄ adsorption density.
5. At a low pH the stoichiometry was low and was similar for $\gamma$-Al$_2$O$_3$ and kaolinite. At higher pH levels it was higher for $\gamma$-Al$_2$O$_3$ than for kaolinite.

6. The average values of the stoichiometry calculated by the thermodynamic approach were in agreement with those measured by back titration.

7. Mathematical analyses for the SO$_4$ adsorption isotherms demonstrated that SO$_4$ may not be adsorbed on the d-plane, i.e., in the diffuse layer. However, this approach failed to distinguish between outer- and inner-sphere complexation for SO$_4$ adsorption.

8. Based on the triple layer surface complexation model, SO$_4$ adsorption was better modeled by assuming outer-sphere complex formation, while PO$_4$ adsorption conformed to the inner-sphere complexation mechanism.

Future work may include the following:

1. The triple layer model should be applied to model ion adsorption on soils or sediments. In this case, difficulties need to be considered in characterizing the reactive site density, surface reactions, surface species, and the distribution of surface sites among sorbing phases.

2. Surface site density and surface ionization constants are important parameters in surface complexation models. The values of these parameters vary with methods used. Further research is needed to determine the most appropriate experimental measurement of these parameters for surface complexation modeling.
3. Model sensitivity to surface site density should be analyzed for SO$_4$ and PO$_4$
adsorption, i.e., would varying site density change the modeling results of SO$_4$
and PO$_4$ adsorption?

4. Other systems (e.g., PO$_4$-$\gamma$-Al$_2$O$_3$) should be studied to test if the
thermodynamic approach is applicable to measure the exchange stoichiometry.

5. In situ X-ray absorption spectroscopy should be used to investigate the
structure and composition of ions adsorbed at mineral-water interface,
providing quantitative information with respect to coordinate number and
bonding distances of adsorbed species.
VITA

The author was born on August 1, 1959 and grew up in a rural setting in Xinchang County, Zhejiang Province, People's Republic of China. After graduating from Dashiu High School in 1977, he enrolled in Zhejiang Forestry University in Hangzhou, China in April 1978. With a special training in Forest Soils at Northeast Forestry University in Harbin, China in 1981, he was awarded the Bachelor of Science degree with a major in Forestry in February 1982.

After graduation, he worked as an instructor of forest soils at Zhejiang Forestry University. During the period of working, he studied geology at Zhejiang University in Hangzhou in 1983. In August 1984 he enrolled for graduate study in the Department of Soil Science at Zhejiang Agricultural University in Hangzhou, China. He received the Master of Science degree in Soil Science in July 1987.

From 1987 to 1991 he worked as a soils instructor at Zhejiang Forestry University and as a visiting scientist at Nanjing Institute of Soil Science, Chinese Academy of Sciences. In the Fall of 1991 he was admitted to the graduate school for study leading to the degree of Ph.D. in Soil Chemistry in the Department of Agronomy and Soils at Clemson University, Clemson, South Carolina. In the Fall of 1992 he transferred to Virginia Polytechnic Institute and State University in Blacksburg, Virginia in pursuit of a Ph.D. degree in Soil Environmental Science under the direction of Drs. Lucian W. Zelazny and David C. Martens. Upon completion of doctoral studies, he accepted an offer of employment at Scripps Institution of Oceanography, University of California, San Diego.

He married Min Lu in 1984. They have two daughters, Lulu and Virginia. He was elected to the Honor Society of Phi Kappa Phi in 1993. He is a recipient of the Charles I. Rich Graduate Fellowship from the Department of Crop and Soil Environmental Sciences in 1994. He is a member of the Soil Science Society of America, the Society of Environmental Toxicology and Chemistry, and the American Geophysical Union.