Adsorption of Radium and Thorium onto Quartz and Kaolinite: A Comparison of Solution/Surface Equilibria Models

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ADSORPTION OF RADIUM AND THORIUM ONTO QUARTZ AND KAOLINITE: A COMPARISON OF SOLUTION/SURFACE EQUILIBRIA MODELS

by

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Date: Sept 3, 1982

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ABSTRACT

A variety of empirical and theoretical models have been used in the past to explain or fit laboratory trace metal adsorption data (cf. Truesdell and Christ, 1968; James and Healy, 1972; Schindler, et al., 1976; Harmsen, 1977; Davis, et al., 1978; Langmuir, 1981). However, the application of these models to complex systems has usually been seriously limited. In this study, the adsorption of thorium and radium onto α-SiO₂ and kaolinite was examined as a function of pH, ionic strength, competing ions, complexing ligands, and sorbent properties. Particular attention was given to the adsorption of thorium-hydroxy-sulfate complexes and to the competitive adsorption of calcium versus radium. The following methods were used to characterize the listed properties of the sorbents: composition by x-ray diffraction; particle size and morphology by SEM; surface area by BET-N₂ gas adsorption; and surface charge and pH_{pzc} by potentiometric titration and electrophoretic mobility. Total starting metal concentrations used were 10^{-5} to 10^{-6} m Th and 10^{-11} m Ra. Both minerals strongly adsorbed thorium from pure water at pHs above 3 to 4, with adsorption increasing with pH.

Thorium sulfate complexing strongly inhibited both the adsorption and precipitation of thorium oxyhydroxide...
solids. Adsorption of radium increased with increasing pH above about pH 3 for α-SiO₂ and pH 2 for kaolinite. Approximately 10 percent of the initial Ra remained in solution at pH 8 to 9 for both sorbents. The adsorption data were modeled using an improved version of the thermodynamic adsorption approach of James and Healy (1972); the surface complexation site-binding model of Davis et al. (1978); and the power exchange function of Langmuir (1981). The study results indicate that the adsorption of strongly complexed elements such as thorium cannot be predicted using simple distribution coefficients (Kds). The value of Kd varies as a function of pH, thorium complexing, and the character of the sorbent mineral. Application of the site-binding model shows that thorium adsorption occurs primarily as the 1:1 and 1:2 hydroxy complexes; that radium adsorption is chiefly as Ra²⁺; and that Ca²⁺ competes with Ra²⁺ for adsorption sites.

The solution-equilibria plus adsorption results indicate the following conclusions regarding Th and Ra mobility in water-rock systems: in acid sulfate waters or at metal concentrations less than the solubility of Th(OH)₄, Th mobility is limited by adsorption of mononuclear hydroxyl complexes. Adsorption limits Ra mobility in low sulfate waters above pH 3 to 4. Ra mobility is greatest in Ca-rich
waters and least in waters low in these metals. These results have applicability to prediction of the mobility of Th and Ra from uranium mill tailings disposal, and from disposal sites of low and high-level radioactive wastes.
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Finally, I thank J.L. Newman for her patience and support.
INTRODUCTION

A fundamental understanding of the geochemical processes which control the transport of radium and thorium in natural environments is needed in many contexts. These elements are of environmental concern because of: (1) the disposal of low and high-level nuclear wastes; (2) metal beneficiation, and pollution control in solution mining for uranium; and (3) the surface mining and milling of uranium ores and the disposal of mill tailings. Additionally, radium in groundwater and thorium in host rocks and stream sediments are useful as pathfinder elements in uranium exploration, and are important in understanding the origin of strata-bound uranium deposits.

As with most solutes the partitioning of radium and thorium between an aqueous phase and sediments is controlled by precipitation-dissolution, and adsorption-desorption reactions (Riese and Langmuir, 1979). Thermodynamic data are available or may be estimated for the most common radium and thorium minerals and aqueous inorganic complexes (Parker et al., 1971; Langmuir and Herman, 1980). These data permit equilibrium modeling of the simplest precipitation and dissolution reactions. However, adsorption, although generally overlooked, is probably the dominant process controlling the mobilities of minor and trace constituents
in aqueous solution (Jenne, 1968; Hem, 1970; Leckie and James, 1974). This is because adsorption reactions equilibrate in the order of seconds to days, at all concentration levels of a dissolved sorbate species, whereas groundwater-mineral solution and precipitation reactions involving metals, usually require months or years to attain equilibrium and tend to operate at only relatively high solute concentrations.

When adsorption reactions in natural environments are considered, they are typically oversimplified (cf. Benjamin, 1978), and neglect cation hydrolysis, complexation, and metal ion competition reactions. Most solute transport models for example, utilize linear adsorption isotherms or one or more simple ion exchange isotherms (Inoue, 1967; Leckie and James, 1974). As currently formulated and applied, virtually all adsorption isotherms and ion exchange models are incapable of accounting for complicated solution-phase chemistry, or changes in the solid surface. As a result, they must be parameterized by empirical measurements performed under conditions characteristic of the rock-water system of interest. Such distribution coefficients (Kds) are specific to the conditions for which the data have been derived, cannot be quantitatively adjusted to changing conditions, and are therefore of little predictive value in
dynamic systems (Reardon, 1981). Isotherms are valid for only single solids, yet most soils and rocks are polymineralic.

Adsorption is a complex process involving physical, chemical, and electrical interactions at sorbate surfaces, which can be exceedingly more complicated than reactions in the bulk solution. As a result, only in recent years have detailed, comparatively rigorous mathematical models of trace metal adsorption onto mineral oxides been developed. These include the thermodynamic model of James and Healy (1972c), the surface complexation site-binding model of Davis et al., (1978), and several others (cf. Schindler, 1976; Bowden et al., 1977; Langmuir, 1981). In spite of the importance of adsorption–desorption reactions to the behavior of trace metals in groundwaters, successful application of sophisticated adsorption models to metal adsorption by naturally occurring mineral phases has been seriously limited.

The purposes of this study were (1) to quantitatively examine the adsorption of thorium and radium on naturally occurring sorbent minerals, and (2) to develop and extend the application of existing adsorption models to the experimental data, so as to explain and predict the behavior of these metals in natural environments containing these
specific minerals. Two adsorbent minerals were chosen for study based on their surface properties and/or importance in natural systems. They are quartz (\(\alpha\)-SiO\(_2\)) and kaolinite (Al\(_2\)Si\(_2\)O\(_5\))(OH)\(_4\)). \(\alpha\)-SiO\(_2\) is a model silica mineral found in most geologic environments and is negatively charged in the pH range of most soil and groundwaters. Kaolinite was chosen because it is a common secondary mineral formed by weathering or alteration of aluminosilicates particularly feldspars. In addition, its selection allowed for adsorption experiments to be performed on a multicomponent substrate.

The laboratory experiments described in this study were designed to provide adsorption data for thorium and radium on both \(\alpha\)-SiO\(_2\) and kaolinite as a function of (1) solution pH, (2) ionic strength, (3) concentration of competing ions which compete for adsorption sites, (4) concentration of ligands which result in the formation of solution complexes, and (5) the surface properties of the sorbent minerals, e.g., surface area, surface charge, and potential. Particular attention was given to the adsorption behavior of thorium in sulfate solutions, and to the adsorption of radium in calcium-bearing solutions. The experimental work also included the examination of the adsorption behavior of calcium.
The experimental results were interpreted in terms of chemical equilibrium among dissolved species plus adsorption onto quartz or kaolinite. The adsorption data were modeled using three different adsorption models: (1) a modified version of the James-Healy thermodynamic model (James and Healy, 1972c); (2) the surface complexation site-binding model of Davis, et al., (1978); and (3) the power exchange function model of Langmuir (1981). A detailed discussion is provided of each model, the theoretical basis, and application.
GEOCHEMISTRY OF THORIUM AND RADIIUM

Thorium

Natural Distribution

Thorium is found in nature only as a quadrivalent cation. It usually occurs in rocks and soils as a trace constituent in solid solution within phosphate, oxide and silicate minerals, or adsorbed onto clays and other soil minerals (Hansen, 1970; Bondietti, 1974). Thorium occurs as a major component only in the minerals thorianite (ThO₂) and thorite (ThSiO₄) and in hydrothermal uraninite (Th, U)O₂ where it forms a complete solid solution with UO₂. The chief commercial source of thorium is monazite, (Ce, La, Y, Th)PO₄ which along with other resistate minerals most commonly occurs in stream sediments and beach sands (Rankama and Sahama, 1958). The natural distribution of thorium in rocks and soils has been examined by Pliler (1956), Adams and Weaver (1958), Murray and Adams (1958), Adams and Richardson (1960), Billings (1962), Heier and Rogers (1963), Heier and Carter (1964), and Rogers (1964). Results of these studies have been summarized by Ames and Rai (1978), and are given in Table 1.
Table 1. Thorium content of common rocks and soils. Data are from Ames and Rai (1978).

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Thorium Range, (ppm)</th>
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<tbody>
<tr>
<td><strong>Igneous Rocks</strong></td>
<td></td>
</tr>
<tr>
<td>Granite</td>
<td>10-20</td>
</tr>
<tr>
<td>Intermediate</td>
<td>2-10</td>
</tr>
<tr>
<td>Basalt and Gabbro</td>
<td>0.5-2</td>
</tr>
<tr>
<td><strong>Sedimentary Rocks</strong></td>
<td></td>
</tr>
<tr>
<td>Shale</td>
<td>10-15</td>
</tr>
<tr>
<td>Bauxite</td>
<td>49</td>
</tr>
<tr>
<td>Bentonite</td>
<td>24</td>
</tr>
<tr>
<td>Limestone</td>
<td>1.1</td>
</tr>
<tr>
<td>Sandstone</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>Metamorphic Rocks</strong></td>
<td></td>
</tr>
<tr>
<td>Marble</td>
<td>0.03</td>
</tr>
<tr>
<td>Slate</td>
<td>7.5</td>
</tr>
<tr>
<td>Phyllite</td>
<td>5.5</td>
</tr>
<tr>
<td>Schist</td>
<td>7.5</td>
</tr>
<tr>
<td>Gneiss</td>
<td>13.1</td>
</tr>
</tbody>
</table>
Chemistry

There are thirteen isotopes of thorium, but only six are found in nature. Of those six, five are quantitatively unimportant members of the U-235 or Th-232 decay series. Thorium-232 is the major isotope with a half-life \( t^{1/2} \) of \( 1.39 \times 10^{10} \) years (Ryabshikov and Golbraikh, 1969). Other thorium radionuclides of interest in waste disposal operations include Th-227 \( (t^{1/2} = 18.5 \text{ d}) \), Th-228 \( (t^{1/2} = 1.91 \text{ yr}) \), Th-229 \( (t^{1/2} = 25.5 \text{ hr}) \), and Th-234 \( (t^{1/2} = 24.1 \text{ d}) \). All are alpha emitters except Th-231 and Th-234 which are beta emitters.

Thorium forms insoluble oxide, hydroxide, fluoride, and phosphate compounds, and soluble chloride, nitrate, and sulfate compounds. In solution, thorium exists as a tetravalent cation that undergoes extensive complexation with hydroxide and other anions. Strong complexes are formed with \( H_2PO_4^- \), \( SO_4^{2-} \), and \( F^- \) (Langmuir and Herman, 1980). The strongest common inorganic complexes are formed with \( OH^- \) and \( HPO_4^{2-} \). Weak 1:1 complexes are formed with \( Cl^- \), \( NO_3^- \), and \( H_3PO_4 \). The organic species, oxalate, citrate, and EDTA, also form strong complexes with thorium.

Distribution of Aqueous Species

Stability constants for aqueous thorium complexes have been tabulated by Langmuir and Herman (1980). Application
of the equilibrium constants shows that thorium in natural waters is usually complexed with sulfate, fluoride, phosphate, hydroxide, or organic anions. According to these authors, formation of these complexes greatly increases the solubility of thorium minerals and the mobility of thorium in surface, soil, and groundwaters.

Using the thermodynamic data in Tables 2 and 3, the distribution of aqueous thorium species for different water compositions was calculated in order to establish the relative importance of the various thorium complexes. Figure 1 shows the range of predominance of dissolved thorium species in 0.01m NaNO₃ which is essentially equivalent to a pure water system. Since the degree of thorium complexation is independent of its total concentration when complexing ligands such as hydroxide are in large excess over thorium and polynuclear Th(IV) complexes do not occur, the distribution diagram applies to a wide range of thorium concentrations. The calculations were made for 10⁻⁶m total thorium. The figure shows that free Th⁴⁺ ion is dominant in solution at pHs below 3. From about pH 3 to 4.5, the 1:1 and 1:2 hydroxy complexes predominate. Above pH 4.5, Th(OH)⁰₄ is the major dissolved species. At low (< 10⁻⁴m) concentrations of dissolved thorium, the contribution of polynuclear complexes to the aqueous distribution of thorium is negligible.
Table 2. Thermochemical data for thorium minerals and aqueous species at 25°C and 1 atm total pressure. Data are from Langmuir and Herman (1980) except for the nitrate complexes which are from Wagman et al. (1977).

<table>
<thead>
<tr>
<th>Mineral or Aqueous Species</th>
<th>$\Delta H_f^\circ$ (kcal/mol)</th>
<th>$\Delta G_f^\circ$ (kcal/mol)</th>
<th>$S_f^\circ$ (cal/mol deg)</th>
</tr>
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<tbody>
<tr>
<td>Th$^{4+}$</td>
<td>-183.8</td>
<td>-168.4</td>
<td>-101</td>
</tr>
<tr>
<td>ThOH$^{3+}$</td>
<td>-246.2</td>
<td>-220.7</td>
<td>-79</td>
</tr>
<tr>
<td>Th(OH)$_2^{2+}$</td>
<td>-306.5</td>
<td>-272.3</td>
<td>-53</td>
</tr>
<tr>
<td>Th(OH)$_3^+$</td>
<td>-368.4</td>
<td>-322.5</td>
<td>-36</td>
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<tr>
<td>Th(OH)$_4^0$</td>
<td>-438.4</td>
<td>-373.5</td>
<td>-24</td>
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<tr>
<td>Th$_2$(OH)$_6^{4+}$</td>
<td>-489.4</td>
<td>-441.8</td>
<td>-147</td>
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<tr>
<td>Th$<em>4$(OH)$</em>{8+}$</td>
<td>-1224</td>
<td>-1098.3</td>
<td>-173</td>
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<tr>
<td>Th$<em>6$(OH)$</em>{15}^{9+}$</td>
<td>-2019</td>
<td>-1810.6</td>
<td>-160</td>
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<tr>
<td>Th(OH)$_4^-$</td>
<td>-449.5</td>
<td>-408.0</td>
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<td>ThO$_2$(c)</td>
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<td>-273.2</td>
<td>-</td>
</tr>
<tr>
<td>ThO$_2$(c)</td>
<td>-293.12</td>
<td>-279.35</td>
<td>15.59</td>
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Thorianite

<table>
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<tr>
<th>Mineral or Aqueous Species</th>
<th>$\Delta H_f^\circ$ (kcal/mol)</th>
<th>$\Delta G_f^\circ$ (kcal/mol)</th>
<th>$S_f^\circ$ (cal/mol deg)</th>
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<tbody>
<tr>
<td>ThNO$_3^{3+}$</td>
<td>-</td>
<td>-192.32</td>
<td>-</td>
</tr>
<tr>
<td>Th(NO$_3$)$_2^{2+}$</td>
<td>-</td>
<td>-224.37</td>
<td>-</td>
</tr>
<tr>
<td>Th(NO$_3$)$_4^0$</td>
<td>-382.04</td>
<td>-274.96</td>
<td>39.48</td>
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<tr>
<td>ThSO$_4^{2+}$</td>
<td>-397.2</td>
<td>-353.8</td>
<td>-59</td>
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<tr>
<td>Th(SO$_4$)$_2^0$</td>
<td>-611.0</td>
<td>-537.6</td>
<td>-22</td>
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<tr>
<td>Th(SO$_4$)$_3^{2-}$</td>
<td>-</td>
<td>-716.6</td>
<td>-</td>
</tr>
<tr>
<td>Th(SO$_4$)$_4^{4-}$</td>
<td>-</td>
<td>-891.6</td>
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Table 3. Thermochemical data for auxiliary minerals and aqueous species at 25°C and 1 atm total pressure.

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<thead>
<tr>
<th>Mineral or Aqueous Species</th>
<th>$\Delta H_f^0$ (kcal/mol)</th>
<th>$\Delta G_f^0$ (kcal/mol)</th>
<th>$S^0$ (cal/mol deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2(\text{g})$</td>
<td>0</td>
<td>0</td>
<td>31.207</td>
</tr>
<tr>
<td>$\text{O}_2(\text{g})$</td>
<td>0</td>
<td>0</td>
<td>49.005</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}(\text{l})$</td>
<td>-68.315</td>
<td>-56.687</td>
<td>16.71</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>-54.977</td>
<td>-37.604</td>
<td>-2.560</td>
</tr>
<tr>
<td>$\text{Cl}^-$</td>
<td>-39.933</td>
<td>-31.379</td>
<td>13.56</td>
</tr>
<tr>
<td>$\text{HClO}$</td>
<td>-</td>
<td>-23.3</td>
<td>-</td>
</tr>
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<td>$\text{Br}^-$</td>
<td>-29.039</td>
<td>-24.867</td>
<td>19.80</td>
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<tr>
<td>$\text{I}^-$</td>
<td>-13.60</td>
<td>-12.41</td>
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<td>$\text{NO}_3^-$</td>
<td>-49.56</td>
<td>-26.64</td>
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<tr>
<td>$\text{SiO}_2(\text{c})$ quartz</td>
<td>-217.66</td>
<td>-204.66</td>
<td>9.91</td>
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<tr>
<td>$\text{SiO}_2(\text{am})$</td>
<td>-215.33</td>
<td>-202.91</td>
<td>11.8</td>
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<td>-299.18</td>
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<td>$\text{SO}_4^{2-}$</td>
<td>-217.40</td>
<td>-177.95</td>
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<td>$\text{HSO}_4^-$</td>
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<td>-180.67</td>
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<td>$\text{CO}_2(\text{aq})$</td>
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<td>-92.26</td>
<td>-</td>
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<td>$\text{CO}_3^{2-}$</td>
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<td>-13.6</td>
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<td>$\text{HCO}_3^-$</td>
<td>-165.39</td>
<td>-140.26</td>
<td>21.8</td>
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<tr>
<td>$\text{H}_2\text{CO}_3^0$</td>
<td>-167.22</td>
<td>-148.94</td>
<td>44.8</td>
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</table>
Figure 1. Distribution of thorium-hydroxy complexes vs pH at 25°C with $\Sigma$Th = $10^{-6}$ m in $10^{-2}$ m NaNO$_3$ solution.
Figures 2 to 4 show the distribution of species in solutions of Na$_2$SO$_4$ having an ionic strength of 10$^{-3}$, 10$^{-2}$, and 10$^{-1}$m, respectively. In a solution with an ionic strength of 10$^{-3}$m (approximately 30 ppm total sulfate), Th(SO$_4$)$_2^{0}$ is vastly more important than other sulfate complexes or than free Th$^{4+}$ ion. At acid pHs, ThSO$_4^{2+}$ also predominates, but as pH increases, the hydroxy complexes increase in importance. Above pH 4.5, Th(OH)$_4^{0}$ predominates. As ionic strength rises from 0.01 to 0.1m, Th(SO$_4$)$_3^{2-}$ increases in importance below pH = 5, but the hydroxy complexes predominate at higher pHs. As ionic strength increases, the significance of ThOH$^{3+}$, Th(OH)$_2^{2+}$, and Th(OH)$_3^{+}$ decreases. Similarly, Th(OH)$_4^{0}$ is the major hydroxy complex above pH 5 at 10$^{-2}$m, and pH 5.5 at 10$^{-1}$m. At all three ionic strengths, Th(SO$_4$)$_2^{0}$ predominates below pH = 5. It should be noted that the thorium-hydroxy-sulfate diagrams presented here are different slightly from those presented by Langmuir and Herman (1980), below pH 4, in that the formation of HSO$_4^{-}$ is considered.

It is apparent from the thorium distribution plots and information given by Langmuir and Herman (1980) that the effect of NO$_3^{-}$ ion on thorium solubility is negligible. Even in solutions of 0.01m NaNO$_3$, Th-NO$_3^{-}$ complexes never approach
Figure 2. Distribution of thorium-hydroxy and sulfate complexes vs pH at 25°C with $\Sigma$Th = $10^{-5}$ m and $I = 10^{-3}$ m (Na$_2$SO$_4$).
Figure 3. Distribution of thorium-hydroxy and sulfate complexes vs pH at 25°C with \( \sum \text{Th} = 10^{-5}\) m and \( I = 10^{-2}\) m (Na\(_2\)SO\(_4\)).
Figure 4. Distribution of thorium-hydroxy and sulfate complexes vs pH at 25°C with $\Sigma$Th = $10^{-5}$ m and I = $10^{-1}$ m (Na$_2$SO$_4$).
3% of total Th-OH\(^-\) complexes. Sulfate, however, increases thorium solubility below pH 5 and is particularly important in acid mine waters, acid sulfate soils, and H\(_2\)SO\(_4\)-rich tailing liquors from the processing of uranium ores. Langmuir and Herman (1980) discuss in detail the effects of fluoride, phosphate, and organic complexing ligands on the solubility of thorium minerals.

Adsorption Studies

Thorium adsorption studies using a variety of sorbent materials have been performed by several investigators. Stanton and Maatman (1963), Dugger et al. (1964), Vydra and Galba (1967), and James and Healy (1972b) studied the adsorption of thorium on α-SiO\(_2\). These authors concluded that minor thorium adsorption occurs below pH 2, but that sorption increases with pH to maximum values at about pH 5.5. Stanton and Maatman (1963) and Dugger et al. (1964) describe the adsorption of thorium as the free metal ion, Th\(^{4+}\), occupying four silanol surface sites. James and Healy (1972b) indicate that because the thorium ion is largely hydrolyzed at pHs above 3.2, thorium hydroxy complexes are involved in the sorption process and that Th\(^{4+}\) is not as readily adsorbed. James and Healy (1972b) also suggested that both mononuclear and polynuclear thorium hydroxy complexes are responsible for adsorption and that
precipitation of thorium at the sorbent/solution interface is likely at high surface coverages.

Matijevic et al. (1961) and Abramson et al., (1964) examined thorium adsorption on AgI sols and concluded that simple hydrolysis products are the principal species adsorbed. Abramson et al., (1964) suggested that polynuclear complexes were adsorbed above pH 4.2; however, these studies were conducted at extremely high aqueous thorium concentrations (ITH = 10^{-3} M).

Adams et al., (1959) and Schulz (1965) concluded that thorium is strongly concentrated in clay-rich soils and sediments. Schulz (1965) found that thorium in soils is adsorbed by clay particles or is present as insoluble oxides and hydroxides. Holland and Kulp (1954) showed that red clay, globigerina ooze and green clay from deep-sea sediments readily adsorbed thorium. They concluded that ion exchange was the principal mechanism responsible for adsorption of thorium from seawater.

Nishawaki et al., (1972) added thorium to seawater, and diluted seawater solutions, and measured Th adsorption on a medium sand, fine sand, and silt-clay. The measured Kd for thorium increased as the particle size decreased (Kd is defined as the metal concentration on the solid/weight of solid, divided by the metal concentration in
solution/solution volume). Kd values for the medium sand, fine sand, and silt-clay were 40 to 130, 310 to 470, and 2,700 to 10,000 ml/g, respectively. Efforts to determine the effect of varying solution properties on the adsorption were complicated by the variable pH of the solutions.

Rancon (1973) measured Kd values for thorium on three different soils. Employing a quartz-illite soil as sorbent, he measured a Kd value of 5 ml/g at pH 2, which rose to $10^3$ ml/g at pH 4 and finally $5 \times 10^5$ ml/g at pH 6. With a quartz-illite calcite-organic matter soil, Kd decreased from $10^6$ ml/g at pH 8 to 100 ml/g at pH 10. This reduction in adsorption with increasing pH was attributed to dissolution of soil humic acids which complexed with thorium in solution. For a pure illite sorbent, the thorium Kd increased from 500 ml/g at pH 1 to $10^5$ ml/g at pH 6.5. In general, Rancon found three major soil-solution type reactions involving thorium: (1) strong adsorption of thorium on clay-containing soils at pHs above 2; (2) $\text{Th(OH)}_4$ precipitation at intermediate pHs; and (3) strong adsorption on organic-containing soils at neutral and acid pHs, but reduced adsorption on these soils at alkaline pHs.

Bondietti (1974) investigated the adsorption of hydrolyzed thorium by calcium-treated reference clays (montmorillonite and kaolinite) and humate. Adsorption
increased with increasing pH and was essentially complete at pH 6.5. Inhibition of adsorption and desorption was found when strong organic complexing ligands such as citric acid, DTPA, or EDTA were present.

Radium

Natural Distribution

The natural distribution of radium in rocks and soils has been examined by a number of authors, including Bell et al., (1940), Evans and Goodman (1941), Evans et al., (1942), Senftle and Keevil (1947), Davis (1947), and Vinogradov (1959). Recently, Ames and Rai (1978) have summarized the results of these authors. The average radium contents of various rock types as reported by Rankama and Sahama (1950) and Ames and Rai (1978) are given in Table 4.

Radium occurs chiefly as an impurity in uranium minerals. Uraninite is the principal ore mineral of radium. The largest uraninite deposits are found in the vicinity of Great Bear Lake in Canada.

During weathering, radium becomes separated from its parent elements because of the differences in their chemical behavior. As a result, radium, which resembles the alkaline-earth metals chemically, is taken up in soils or
Table 4. Average radium contents of various rock types. Data are from Ames and Rai (1978).

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Radium (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultramafic Igneous</td>
<td>$0.009 \times 10^{-6}$</td>
</tr>
<tr>
<td>Basic Igneous</td>
<td>$0.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>Intermediate Igneous</td>
<td>$0.917 \times 10^{-6}$</td>
</tr>
<tr>
<td>Granitic Igneous</td>
<td>$1.395 \times 10^{-6}$</td>
</tr>
<tr>
<td>Shales</td>
<td>$1.08 \times 10^{-6}$</td>
</tr>
<tr>
<td>Limestones</td>
<td>$0.42 \times 10^{-6}$</td>
</tr>
<tr>
<td>Soils</td>
<td>$1.1 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
transported to the ocean. In general, however, radium is strongly depleted in seawater. The explanation for this depletion compared with the considerably higher content of uranium is that the isotope Th-230, which is the immediate parent of Ra-226, is precipitated or adsorbed on ferric and manganese oxides and oxyhydroxides.

Chemistry

There are sixteen isotopes of radium between Ra-213 and Ra-230, with no Ra-218 or Ra-229. All of these isotopes are unstable, and all of the naturally occurring isotopes occur in the Th-230 (Ra-228, Ra-224), the U-238 (Ra-236), and the U-235 (Ra-223) decay series (Ames and Rai, 1978). All are alpha emitters except Ra-228, which is a beta emitter. With the present uranium fuel cycle, only Ra-226 is of particular importance because of its long half-life (1622 yr).

Radium has a (II) oxidation state only. Of the alkaline-earth metal cations, Ra$^{2+}$ shows the least tendency for complex formation, although Schubert et al., (1950) detected 1:1 complexes with citric, tartaric, succinic, aspartic, pyruvic, oxalacetic, fumaric, and sulfosalicylic acids at pH 7.2 to 7.4. In these experiments, the organic acid concentration was approximately $10^{-2}\text{m}$, while total radium was $10^{-10.7}\text{m}$. In general, the compounds formed by radium and their solubilities are similar to those of
barium. Radium forms soluble nitrate, chloride, and iodate compounds, and insoluble sulfate compounds.

Thermochemical Data

Thermodynamic data have been published for radium nitrate, chloride, iodate, sulfate, and Ra$^{2+}$ ion (Latimer, 1952; Parker et al., 1971). Weigel (1977) lists estimated enthalpy data for other radium compounds and their data sources. No thermodynamic data have been published for radium hydroxyl complexes.

The thermodynamic data for radium compounds and solute species compiled and estimated in this study are given in Table 5. Footnotes to the table explain the data sources and methods of calculation and estimation. Data in the tables marked with an asterisk are internally consistent with that of Parker et al., (1971). Table 3 lists the thermodynamic data for non-radium minerals and solute species used for estimations of the data in Table 5.

Application of the thermodynamic data given in Table 5 indicates that in most natural waters and waste--waters, Ra$^{2+}$ is the principal dissolved species over the pH range 2-10. All solid compounds of radium are extremely soluble except the sulfate, which is essentially insoluble. Under conditions of high total dissolved radium or high sulfate, it is expected that RaSO$_4$(c) will limit the concentration of Ra$^{2+}$. 
Table 5. Thermochemical data for radium minerals and other compounds, and aqueous species at 25°C and 1 atm total pressure. Parentheses enclose approximate or estimated values determined in this study. An asterisk denotes values adopted for use in this work.

<table>
<thead>
<tr>
<th>Mineral or Aqueous Species</th>
<th>$\Delta H_f^O$ (kcal/mol)</th>
<th>$\Delta G_f^O$ (kcal/mol)</th>
<th>$S^O$ (cal/mol deg)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra(c)</td>
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<td>0</td>
<td>17.*</td>
<td>Parker et al. (1971)</td>
</tr>
<tr>
<td>Ra$^{2+}$</td>
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<td>(14.2)</td>
<td>Latimer (1952)</td>
</tr>
<tr>
<td></td>
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<td>-134.2*</td>
<td>13.*</td>
<td>Parker et al. (1971)</td>
</tr>
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<td>RaOH$^+$</td>
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<td>(-172.6)*</td>
<td>-</td>
<td>See Footnotes</td>
</tr>
<tr>
<td>Ra(OH)$_2$(c)</td>
<td>-227.*</td>
<td>(-205.4)*</td>
<td>(24.7)*</td>
<td>Weigel (1977)</td>
</tr>
<tr>
<td>RaO(c)</td>
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<td>16.3</td>
<td>Latimer (1952)</td>
</tr>
<tr>
<td></td>
<td>-137.2</td>
<td>(-118.2)*</td>
<td>-</td>
<td>Weigel (1977)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(18.8)*</td>
<td></td>
<td>See Footnotes</td>
</tr>
<tr>
<td>RaF$_2$(c)</td>
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<td>(-280.1)*</td>
<td>(2.5)*</td>
<td>Weigel (1977)</td>
</tr>
<tr>
<td>RaCl$^+$</td>
<td>-</td>
<td>(-165.7)*</td>
<td>-</td>
<td>See Footnotes</td>
</tr>
<tr>
<td>RaCl$_2^O$ (m = 1)</td>
<td>-206.0*</td>
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<td>40.*</td>
<td>Parker et al. (1971)</td>
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<td>(-196.6)*</td>
<td>(31.6)*</td>
<td>Weigel (1977)</td>
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<td></td>
<td></td>
<td>32.</td>
<td></td>
<td>Parker et al. (1971)</td>
</tr>
<tr>
<td>Mineral or Aqueous Species</td>
<td>$\Delta H_f^\circ$ (kcal/mol)</td>
<td>$\Delta G_f^\circ$ (kcal/mol)</td>
<td>$S^\circ$ (cal/mol deg)</td>
<td>Source</td>
</tr>
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<td>---------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>------------------------</td>
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<tr>
<td></td>
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<td>-311.4*</td>
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<td>RaBr$_2$(c)</td>
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<td>(37.)*</td>
<td>Weigel (1977)</td>
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<td>-</td>
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<td>Weigel (1977)</td>
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<td>Ra(IO$_3$)$_2$(c)</td>
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</tr>
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<td>-</td>
<td>See Footnotes</td>
</tr>
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<td>Ra(NO$_3$)$_2$</td>
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<tr>
<td></td>
<td>237.*</td>
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<td>52.</td>
<td></td>
</tr>
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<td>RaCO$_3^O$</td>
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<td>See Footnotes</td>
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<td>-</td>
<td>Latimer (1952) Weigel (1977) See Footnotes</td>
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<td></td>
<td>-291.8</td>
<td>-277.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-291.7)*</td>
<td>(-272.2)*</td>
<td>(26.3)*</td>
<td></td>
</tr>
<tr>
<td>RaC$_2$O$_4^O$</td>
<td>-337.</td>
<td>-</td>
<td>-</td>
<td>Weigel (1977)</td>
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</table>
Table 5. (continued)

<table>
<thead>
<tr>
<th>Mineral or Aqueous Species</th>
<th>$\Delta H^0_f$ (kcal/mol)</th>
<th>$\Delta G^0_f$ (kcal/mol)</th>
<th>$S^0$ (kcal/mol deg)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
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<td>-343.4</td>
<td>-312.2</td>
<td>18.</td>
<td>Parker, et al., (1971)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-315.4*</td>
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<td>See Footnotes</td>
</tr>
<tr>
<td>RaSO$_4$ (c)</td>
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<td>-326.</td>
<td>34.</td>
<td>Latimer (1952)</td>
</tr>
<tr>
<td></td>
<td>-351.6</td>
<td>-326.4</td>
<td>33.</td>
<td>Parker, et al., (1971)</td>
</tr>
<tr>
<td></td>
<td>(354.2)*</td>
<td>(-327.7)*</td>
<td>(33.6)*</td>
<td>See Footnotes</td>
</tr>
<tr>
<td>RaS(c)</td>
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<td>-</td>
<td>-</td>
<td>Weigel (1977)</td>
</tr>
<tr>
<td>RaScO$_4$ (c)</td>
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<td>-</td>
<td>-</td>
<td>Weigel (1977)</td>
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<tr>
<td>RaMoO$_4$ (c)</td>
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<td>-</td>
<td>-</td>
<td>Weigel (1977)</td>
</tr>
<tr>
<td>RaWO$_4$ (c)</td>
<td>-380.4</td>
<td>-</td>
<td>-</td>
<td>Weigel (1977)</td>
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</tbody>
</table>

Ra(c): $S^0$ adopted from Parker et al. (1971). Ra$^{2+}$: $S^0$ estimated from data reported by Latimer (1952). $\Delta H^0_f$, $\Delta G^0_f$, and $S^0$ adopted from Parker et al. (1971). RaOH$^+$: $\Delta G^0_f$ based on extrapolation of formation constants (Kassoc values) for other Group II alkali earth metals vs ionic radius. In this and following extrapolations of Kassoc values for Ra complexes, a radius for Ra$^{2+}$ of 1.43A was assumed (Ahrens, 1952). Log Kassoc values (from Smith and Martell,
1976) and ionic radii (from Ahrens, 1952) used in the extrapolation were; Ca (1.3, 0.99A), Sr (0.8, 1.12A), and Ba (0.6, 1.34A). The extrapolation led to \( \log K_{assoc} = 0.58 \). Ra(OH)\(_2\)(c): \( S^0 \) estimated using Latimer's method for the reaction: \( \text{Ra}(c) + \text{Ba(OH)}_2(c) = \text{Ba}(c) + \text{Ra(OH)}_2(c) \), with component entropies from Latimer (1952) and Parker et al. (1971). \( \Delta G_f^0 \) based on \( \Delta S_f^0 \) from the formation of Ra(OH)\(_2\)(c) by: \( \text{Ra}(c) + O_2(g) + H_2(g) = \text{Ra(OH)}_2(c) \), and \( \Delta H_f^0 \) from Weigel (1977). RaO(c): \( S^0 \) estimated from the reaction: \( \text{Ra}(c) + \text{BaO}(c) = \text{Ba}(c) + \text{RaO}(c) \), assuming \( \Delta S_f^0 = 0 \). \( \Delta G_f^0 \) based on \( \Delta S_f^0 \) for \( \text{Ra(c)} + 1/2 O_2(g) = \text{RaO}(c) \), and \( \Delta H_f^0 \) from Latimer (1952). RaF\(_2\)(c): \( S^0 \) estimated from \( \text{Ra(c)} + \text{BaF}_2(c) = \text{Ba}(c) + \text{RaF}_2(c) \), assuming \( \Delta S_f^0 = 0 \). \( \Delta G_f^0 \) based on \( \Delta S_f^0 \) for \( \text{Ra(c)} + F_2(g) = \text{RaF}_2(c) \), and \( \Delta H_f^0 \) from Weigel (1977). RaCl\(^+\): \( \Delta G_f^0 \) based on extrapolation of association constants for Group II elements vs ionic radius. Log Kassoc values for CaCl\(^+\) (Harned and Owen, 1958) and BaCl\(^+\) (Smith and Martell, 1976) and ionic radii from Ahrens (1952) used in the extrapolation were; Ca (-1.00, 0.99A), and Ba (-0.13, 1.34A). The extrapolation led to \( \log K_{assoc} = 0.1 \). RaCl\(^0\): \( S^0 \) estimated from \( \text{Ra(c)} + \text{BaCl}_2(c) = \text{Ba}(c) + \text{RaCl}_2(c) \), assuming \( \Delta S_f^0 = 0 \) with entropies from Parker et al. (1971). \( \Delta G_f^0 \) computed from \( \Delta S_f^0 \) for \( \text{Ra(c)} + Cl_2(g) = \text{RaCl}_2(c) \), and \( \Delta H_f^0 \) from Weigel (1977). RaBr\(_2\)(c): \( S^0 \) estimated from \( \text{Ra(c)} + \)
BaBr$_2$(c) = Ba(c) + RaBr$_2$(c), assuming $\Delta S^O_r = 0$, with entropies from Parker et al. (1977). $\Delta G^O_f$ computed from $\Delta S^O_r$ for Ra(c) + Br$_2$(l) = RaBr$_2$(c), and $\Delta H^O_f$ from Weigel (1977). RaNO$_3^+$: $\Delta G^O_f$ based on extrapolation of association constants for Group II elements vs ionic radius. Log Kassoc values from Smith and Martell (1976) and ionic radii from Ahrens (1952) used in the extrapolations were; Ca (0.7, 0.99A), Sr (0.8, 1.12A), and Ba (0.9, 1.34A). The extrapolation led to log Kassoc = 0.9. RaCO$_3^O$: $\Delta G^O_f$ based on extrapolation of association constants for Group II elements vs ionic potential. Log Kassoc values from Langmuir (unpublished data) and ionic potentials used in the extrapolation were; Ca (2.88, 2.0), Sr (2.85, 1.8), and Ba (2.5, 1.5). The extrapolation led to log Kassoc = 2.35. RaCO$_3$(c): $S^O$ estimated from Ra(c) + BaCO$_3$(c) = Ba(c) + RaCO$_3$(c), assuming $\Delta S^O_r = 0$, with component entropies from Parker et al. (1971). $\Delta G^O_f$ based on $\Delta S^O_r$ from the formation of RaCO$_3$(c) by: Ra(c) + 3/2 O$_2$(g) + C (graphite) = RaCO$_3$(c), and $\Delta H^O_f$ from Weigel (1977). RaSO$_4^O$: $\Delta G^O_f$ based on extrapolation of association constants vs ionic potential for Group II elements. Log Kassoc values from Reardon and Langmuir (1975), and ionic potentials used in the extrapolation were; Ca (2.31, 2.0), and Ba (2.37, 1.50). The extrapolation led to log Kassoc = 2.38. RaSO$_4$(c): $\Delta G^O_f$ computed
from Ksp = 10^{-11.4} based on extrapolation of solubility product constants for other alkali-metal sulfates and lead sulfate vs ionic radii of the metals (See Figure 5).
Figure 5. Solubility product constants of lead and alkali-metal sulfates at 25°C plotted against metal cation radius. Radii are from Ahrens (1952).
Adsorption Studies

Adsorption of radium on a variety of minerals has been studied by several investigators, and the results have been compiled and summarized by Ames and Rai (1978).

Arnold and Crouse (1965) performed batch adsorption experiments on some natural exchange materials including the zeolites, clinoptilolite and chabazite, and onto natural barite. The results of the adsorption tests were reported as distribution coefficients. The solution phase was a "lime-neutralized waste-water" of pH 7.7, containing 4100 pCi/l Ra, 500 ppm Ca\(^{2+}\), 80 ppm Mg\(^{2+}\), 1,000 ppm Na\(^+\), 2,500 ppm SO\(_4^{2-}\), and 900 ppm Cl\(^-\). Kd values ranged from 490 for the barite, to 646 for the clinoptilolite, and 707 for the chabazite.

Serne (1974) determined radium distribution coefficients using soils from Utah and a simulated river water. The soils contained quartz and feldspar as the primary minerals with 2 to 5% calcite. Minor constituents included muscovite and some smectite clay. Results of these studies yielded Kds ranging from 214 to 467 for four different soil samples with a solution pH of 7.6 to 8.0.

Field studies of radium mobility were conducted by Granger et al. (1961) and Granger (1963). These authors showed that radium has migrated out of the uranium ores at
Ambrosia Lake, New Mexico, and has been reconstituted in the minerals barite (BaSO₄) and cryptomelane (K(Mn²⁺Mn₇.25O₁₆·H₂O)) associated with the ore deposits. The Ra-226 substitutes for Ba²⁺ in barite and Mn²⁺ position in cryptomelane.

Analyses of surface and groundwater samples in the Colorado Basin and Grants, New Mexico areas, illustrate the mobility of radium away from uranium ore deposits (Wruble et al., 1964; Kaufmann et al., 1976).

Laboratory Leaching Studies

Several investigators have studied the leaching of Ra-226 from uranium wastes and mill-tailings (Moffet and Teller, 1978; Nathwani and Phillips, 1979; Ryan and Levins, 1980). Other authors have shown that radium can be leached from soils, stream sediments and minerals (cf. Starek and Lazerev, 1960; Nathwani and Phillips, 1978). The factors that influence leachability of Ra-226 from uranium mill wastes and river sediments were investigated by Shearer and Lee (1964). These authors showed that the extent of leaching is directly proportional to the solid-water ratio, and is greatest for acid leach process tailings, less with alkaline leach process tailings, and least from river sediments. They demonstrated that the sulfate present in the waste solids was rapidly solubilized. Trace amounts of
barium present led to precipitation of BaSO₄ and coprecipitation of RaSO₄. In their study, 0.01m solutions were used to study radium leaching. MgCl₂, KCl, NaCl, and HCl solutions, and pure water all leached less than 1 μg of radium, while CaCl₂ leached 1.2 μgRa/g of solid. These authors concluded that radium is as exchangeable Ra²⁺ on the sediment surface.

Havlik, et al., (1968a) examined the leaching of Ra-226 from uranium mill-tailings and ores as a function of pH and concluded that equilibrium leaching was achieved in 15 to 30 minutes. In their study, suspensions of uranium mill-tailings and ores (3g/30ml) were shaken for various times with the solution pH adjusted from 1 to 14. At pH 1, 20% of the initial radium was liberated. At pH 9, the amount leached had decreased to 2.8%; however, at pH 13, the amount of Ra-226 removed increased to 5%.

Havlik et al., (1968b) studied the leaching of radium from the same solids as a function of leach solution composition as well as pH. Contrary to the results of Shearer and Lee (1964), they found that radium was most effectively leached by 1 M KCl and 1 M NaCl solutions, whereas 1 M BaCl₂, SrCl₂, and CaCl₂ solutions liberated much less radium.
DISCUSSION OF ADSORPTION MODELS

In recent years, much experimental and theoretical work has focused on adsorption phenomena in aqueous systems, resulting in the development of an array of adsorption models. These models can be separated into several types: (1) isotherm equations, such as the Langmuir and Freundlich isotherms (Posselt et al., 1968; Soldatini et al., 1976; Garcia-Miragaya and Page, 1976; Harmsen, 1977); (2) thermodynamic adsorption models (James and Healy, 1972a, 1972c; Bowden et al., 1973; NacNaughton and James, 1974; James et al., 1975); (3) exchange models with mass-action type equations (Krishnamoorthy and Overstreet, 1949, 1950; Garrels and Christ, 1956, 1965; Dugger et al., 1964; Truesdell and Christ, 1968; Maes et al., 1975; Langmuir, 1981); and (4) surface complexation site-binding models which combine exchange concepts with double layer theory (Huang and Stumm, 1973; Yates, 1975; Schindler et al., 1976; Hohl and Stumm, 1976; Davis et al., 1978; James and Parks, 1981). However, these model types are not totally unrelated. For instance, the thermodynamic adsorption model proposed by James and Healy (1972a, 1972c) combines considerations of double layer theory with Langmuir isotherm equations. Similarly, many of the more recent adsorption models share the same underlying assumptions and differ only
in the set of surface species considered and their
definition of the electrostatic aspects of adsorption
(Westall and Hohl, 1980; Morel et al., 1981).

Clearly, modeling of the adsorption of ions at solid-
liquid interfaces has advanced considerably from empirical
descriptions of adsorption as a function of dissolved
adsorbate concentrations to rather complicated thermodynamic
models that describe adsorption as a function of adsorbate
concentration, pH, and ionic strength. Unfortunately, the
applicability of these models to complicated natural systems
has generally been seriously limited. Only recently have
surface complexation site-binding models been applied with
reasonable success to trace metal adsorption on mineral
surfaces from moderately concentrated solutions (Balistrieri
and Murray, 1979, 1981; Davis and Leckie, 1980).

In this study, thorium (IV) and radium (II) adsorption
data were examined using (1) a modified thermodynamic
adsorption model (James and Healy, 1972a, 1972b, 1972c), (2)
the surface complexation site-binding model (Davis et al.,
1978), and (3) the power exchange function model (Ozsvath,
1979; Langmuir, 1981). These models were selected for use
in this study, since each represents the most advanced, yet
versatile model of its type. Details of each of the three
models are discussed below.
A Thermodynamic Adsorption Model

James and Healy (1972a, 1972b, 1972c) developed a thermodynamic model for the adsorption of hydrolyzeable metal ions at the oxide-water interface based on simple electrostatic ion-solid and ion-solvent interactions. In this model, the energy of adsorption of ions at the oxide-water interface is treated in terms of the competition between free energy changes both favorable to adsorption (coulombic and chemical) and unfavorable to adsorption (solvation). That is, the change in the standard free energy of adsorption ($\Delta G^{\circ}_{\text{ads},j}$) of each species $j$, is the sum of the change in the coulombic energy ($\Delta G^{\circ}_{\text{coul},j}$), the solvation energy ($\Delta G^{\circ}_{\text{solv},j}$), and the specific chemical energy ($\Delta G^{\circ}_{\text{chem},j}$):

$$\Delta G^{\circ}_{\text{ads},j} = \Delta G^{\circ}_{\text{coul},j} + \Delta G^{\circ}_{\text{solv},j} + \Delta G^{\circ}_{\text{chem},j} \quad (1)$$

Coulombic Forces

According to the classical approaches of Gouy-Chapman, Stern, and Stern-Grahame, the electrostatic work required to bring an ion from the bulk solution to the solid-water interface is given by:

$$\Delta G^{\circ}_{\text{coul},j} = Z_j F \Delta \psi_x \quad \text{J/mol} \quad (2)$$
where $Z_j$ is the charge on the adsorbing species and $F$ is the 
Faraday constant. The change in the potential across the 
distance $x$ from the surface, $\Delta \psi_x$, is given by

$$
\Delta \psi_x = \frac{2RT}{zF} \ln \frac{(e^Y + 1) + (e^Y - 1)e^{-kx}}{(e^Y + 1) - (e^Y - 1)e^{-kx}}
$$

(3)

where

$$
Y = zF\psi_o/2RT
$$

(4)

$$
k = 0.328 \times 10^{10} \ (I)^{1/2} \quad \text{l/m}
$$

(5)

$$
x = (r_{\text{ion}} + 2r_w) \quad \text{m}
$$

(6)

and

$$
z = 1 \ (\text{for } 1:1 \text{ background electrolyte})
$$

(7)

The surface potential, $\psi_o$, is calculated from the Nernst 
equation using the solution $pH$ and solid $pH_{\text{pzc}}$ according to:

$$
\psi_o = \frac{2.3RT}{zF} (pH_{\text{pzc}} - pH)
$$

(8)

where $pH_{\text{pzc}}$ is the solution $pH$ at which the surface 
potential is zero. From these equations, simple 
electrostatic adsorption is favored for cations so long as 
the surface is negatively charged.
Secondary Solvation Energy

Ion-solvent interactions oppose adsorption and must be overcome by the electrostatic and chemical energy terms in order to accomplish adsorption of the metal species at the solid surface. In order to move an ion from the bulk solution to the solid-liquid interface, work must be done to remove the secondary solvation sheath so that the change in free energy, $\Delta G^0_{\text{solv},j}$, is always positive. By employing the equations of Anderson and Bockris (1964) which describe the free energy required to establish a field in a spherically continuous dielectric medium about an ion, and evaluating the dielectric constant for interfacial water, James and Healy (1972c) solved for the change in secondary solvation free energy of an ion moving from the bulk solution to the Inner Helmholtz Plane. The resulting expression is:

$$\Delta G_{\text{solv},j} = \left( \frac{Z^2 e^2}{16 \pi \varepsilon_o} \right) \left( \frac{1}{r_{\text{ion}}} + \frac{1}{2r_w} - \frac{r_{\text{ion}}}{2(r_{\text{ion}} + 2r_w)^2} \right)$$

$$\left( \frac{1}{\varepsilon_{\text{int}}} - \frac{1}{\varepsilon_{\text{bulk}}} \right) + \left( \frac{Z^2 e^2}{32 \pi \varepsilon_o} \right) \left( \frac{1}{r_{\text{ion}}} + \frac{1}{2r_w} \right)$$

$$\left( \frac{1}{\varepsilon_{\text{solid}}} - \frac{1}{\varepsilon_{\text{int}}} \right) \quad \text{J/mol} \quad (9)$$

where

$$\varepsilon_{\text{int}} = \frac{\varepsilon_{\text{bulk}} - 6}{1 + (1.2 \times 10^{-17}) (d\psi/dx)^2} + 6 \quad \text{C/equiv} \quad (10)$$
\[
\frac{d\psi}{dx} = -2\kappa \frac{RT}{2F} \sinh \frac{ZF\Delta\psi}{2RT} \quad V/m \quad (11)
\]

For these equations, \( N \) is Avogadro's number, \( r_{\text{ion}} \) is the radius of the ion, \( r_w \) is the radius of the water molecule, \( \varepsilon_{\text{solid}} \) is the dielectric constant of the solid, and \( \varepsilon_0 \) equals \( 8.85 \times 10^{-12} \) Farads/m. Thus, the change in the solvation energy for the adsorption of a free metal ion or any of its complexes to some position in the double layer can be calculated knowing: (1) pH, (2) \( \text{pH}_{\text{pzc}} \), (3) the dielectric constant of the solid, (4) the ionic radius and charge of the ion, and (5) the ionic strength of the solution. Consistent with the double layer theory, the James-Healy model also assumes that the adsorbed species are separated from the surface by at least one layer of water molecules, so that the equilibrium distance for adsorption is \( r_{\text{ion}} + 2r_w \).

Chemical Interactions

The chemical free energy term \( \Delta G^\circ_{\text{chem}, j} \) is a term which incorporates all solution species-solid interactions other than the coulombic and solvation energies. Such interactions would include attractive short-range dispersion forces and hydrogen bonding (James and Healy, 1972c). \( \Delta G^\circ_{\text{chem}, j} \) can be evaluated experimentally for mineral oxide
surfaces with moderate to high pH\textsubscript{pzc} such as TiO\textsubscript{2} (pH\textsubscript{pzc} = 5.6) from experimental adsorption data. However, for adsorbents with low pH\textsubscript{pzc} such as $\alpha$-SiO\textsubscript{2} and kaolinite (pH\textsubscript{pzc} < 4.5), $\Delta G^\circ\text{chem,}_j$ can only be determined by fitting the theoretical equations to the experimental adsorption data. In this case, $\Delta G^\circ\text{chem,}_j$ is a model correction factor. The most obvious shortcoming of the James-Healy model, however, is the fact that solution complexes other than hydrolysis products are generally not considered in the adsorption reactions. Additionally, the $\Delta G^\circ\text{chem,}_j$ correction term is considered the same for all complexes of a given metal ion, regardless of their differences.

The Adsorption Isotherm

To obtain the total adsorption density at a given pH due to all the hydrolyzed species, the sum of the individual adsorption densities for each species is computed. In a system in which the aqueous complexes of metal M\textsubscript{e} are distributed according to the general equation

$$Me^{z+} + jH_2O \rightarrow Me(OH)^{z-j}_j + jH^+$$

(12)

the total adsorption density is given by

$$\Gamma_{Me(z)} = \Gamma_{Me^{z+}} + \sum_{j=1}^{Z} \Gamma_{Me(OH)^{z-j}_j}$$

(13)
where \( \beta_j \) is the overall hydrolysis constant, \( j \) is the stoichiometric coefficient of the complex, \( z \) is the charge of the metal ion, and \( \Gamma \) is the adsorption density.

Adsorption of a single metal ion or complex in accordance with the James-Healy model can be described by the equation

\[
Su + Me(OH)^{z-j}_j \xrightarrow{K_{ads,j}} Me(OH)^{z-j}_j S
\]  

(14)

where \( Me(OH)^{z-j}_j \) is the equilibrium concentration of the metal complex, \( Me(OH)^{z-j}_j S \) the concentration of adsorbed species, and \( Su \) is the concentration of unoccupied surface sites. In this equation \( Su \) has units of mol/1, if the total amount of solid (m²/1) dispersed in solution is multiplied by the maximum adsorption density, such that

\[
\Gamma_{max} = \frac{1}{\pi (r_{ion} + 2r_w)^2} \cdot \frac{1}{N} \quad \text{mol/m}^2 \quad (15)
\]

From expression (14):

\[
[Me(OH)^{z-j}_j S] = K_{ads,j}[Me(OH)^{z-j}_j][Su]
\]  

(16)

where the square brackets denote the concentration of species in mol/1, and \( K_{ads,j} \) is the adsorption equilibrium constant for species \( j \), such that
\[ K_{\text{ads},j} = \exp(\Delta G_{\text{ads},j}/RT) \]  
\( \text{(17)} \)

Then, according to the appropriate mass balance equations

\[ [\text{Me}^{\text{TOT}}] = \varepsilon_j [\text{Me(OH)}^{z-j}S] + \varepsilon_j [\text{Me(OH)}^z_j] \]  
\( \text{(18)} \)

and

\[ [S^{\text{TOT}}] = [\text{Su}] + [\text{So}] \]  
\( \text{(19)} \)

where \( \text{Me}^{\text{TOT}} \) is the total metal species both adsorbed and in solution, \( S^{\text{TOT}} \) is the total concentration of surface sites per liter of suspension, and \( \text{So} \) is the concentration of surface sites occupied by adsorbed species. By definition then

\[ [\text{So},j] = [\text{Me(OH)}^{z-j}S] \]  
\( \text{(20)} \)

and

\[ [S^{\text{TOT}}] = [\text{Su}] + \varepsilon_j [\text{Me(OH)}^{z-j}S] \]  
\( \text{(21)} \)

Substituting equation (21) into (16) gives

\[ [\text{Me(OH)}^{z-j}S] = K_{\text{ads},j} [\text{Me(OH)}^z_j] \]

\[ (S^{\text{TOT}} - [\text{Me(OH)}^{z-j}S]) \]  
\( \text{(22)} \)

Dividing both sides by \( [\text{Me(OH)}^{z-j}S] \) yields

\[ \frac{[\text{Me(OH)}^{z-j}S]}{S^{\text{TOT}}} = \frac{K_{\text{ads},j} [\text{Me(OH)}^z_j]}{1 + K_{\text{ads},j} [\text{Me(OH)}^z_j]} \]  
\( \text{(23)} \)
Since

\[ [\text{Me(OH)}^{z-j}_j] = \beta_j (\text{Me}^{z+})(\text{OH})^j \]  \hspace{1cm} (24)

and

\[ \frac{[\text{Me(OH)}^{z-j}_j]}{S_{\text{TOT}}} = \theta_j \]  \hspace{1cm} (25)

where \( \theta_j \) is the fraction of surface sites occupied by the species \( j \), equation (23) can be rewritten as

\[ \theta_j = \frac{K_{\text{ads}},j \beta_j (\text{Me}^{z+})(\text{OH})^j}{1 + \sum_j K_{\text{ads}},j \beta_j (\text{Me}^{z+})(\text{OH})^j} \]  \hspace{1cm} (26)

From this equation it is apparent that the total fraction of surface occupied by all surface species is

\[ \sum_j \theta_j = \frac{\sum_j K_{\text{ads}},j \beta_j (\text{Me}^{z+})(\text{OH})^j}{1 + \sum_j K_{\text{ads}},j \beta_j (\text{Me}^{z+})(\text{OH})^j} \]  \hspace{1cm} (27)

It should be noted that equation (26) is equivalent to the Langmuir Adsorption isotherm equation. The adsorption density of any hydrolyzed species \( j \) can be calculated via expression (27) by multiplying by the maximum adsorption density.

Solution equilibria and adsorption reactions, as described in the above equations, are most conveniently quantified if the surface adsorbed complexes are treated algebraically as if they were solution complexes. James and
Healy (1972a,b,c) employed equations (1-27) to model adsorption of hydrolyzed Fe(III), Cr(III), Co(III), and Ca(II) onto SiO₂ and Co(II) onto TiO₂. MacNaughton and James (1974) expanded the number of solution equations to account for aqueous complexing of Hg(II) by chloride but neglected adsorption of the Hg(II) chloride complexes on α-SiO₂. Most recently, Vuceta (1976) incorporated these equations in the computer program REDEQL (McDuff and Morel, 1973) to examine the effects of organic complexing ligands (citrate and EDTA) on the adsorption of Pb(II) and Cu(II) on α-SiO₂. Vuceta (1976) accounted for the effects of solution complexes on adsorption by incorporating metal ion speciation equations and adsorption equations for each metal complex in the REDEQL program. Additionally, each solution complex (j) was assigned a different ΔG°chem,j term to describe its affinity for the adsorbent surface.

Incorporating these individual chemical free energy correction terms improves the model fit to the experimental adsorption data, but of course increases the number of model-adjustable parameters.

In this study, the James-Healy thermodynamic model has been expanded to account for the formation of metal ligand complexes, other than hydroxy complexes, according to the equation:
where $\beta_i$ is the cumulative formation constant and $i$ is the stoichiometric coefficient of the complex. The formation of surface complexes is described by including additional adsorption reactions in the model calculations of the form:

$$Su + Me_{L_i}^{Z-ik} + Me_{L_i}^{L-ik}$$

(29)

where $Me_{L_i}^{Z-ik}$ is the equilibrium concentration of the metal complex and $Me_{L_i}^{L-ik} S$ is the concentration of adsorbed surface species. By including these reactions in the model calculations, the equation which describes the fractional coverage of the adsorbent surface may be expanded so that:

$$\theta_{ij} = \frac{Me^{Z+]\left[K_{ads,i}^{L_i^i} - K_{ads,j}^{j(OH)}^j\right]}{1 + Me^{Z+]\left[\Sigma_i K_{ads,i}^{L_i^i} + \Sigma_j K_{ads,j}^{j(OH)}^j\right]}$$

(30)

and

$$\Sigma_i \theta_{ij} = \frac{Me^{Z+]\left[\Sigma_i K_{ads,i}^{L_i^i} + \Sigma_j K_{ads,j}^{j(OH)}^j\right]}{1 + Me^{Z+]\left[\Sigma_i K_{ads,i}^{L_i^i} + \Sigma_j K_{ads,j}^{j(OH)}^j\right]}$$

(31)

where $\Sigma_i \theta_{ij}$ is the total fractional surface coverage of the sorbent. These equations are solved by computing the equilibrium free metal ion concentration from the expanded mass balance equation.
\[ M_{TOT} = M^{2+} (\sum_i \beta_i (L)^i + \sum_j \beta_j (OH)^j + \]

\[ S_{TOT} \left[ \frac{\sum_i K_{ads, i} \beta_i (L)^i + \sum_j K_{ads, j} \beta_j (OH)^j}{1 + M^{2+} (\sum_i K_{ads, i} \beta_i (L)^i + \sum_j K_{ads, j} \beta_j (OH)^j)} \right] \]

(32)

where \( S_{TOT} \) is the total number of adsorption sites per liter of suspension. \( S_{TOT} \) may be estimated from the cross sectional area of the hydrated metal ion as with the maximum adsorption density described above, or may be estimated by assuming a specific surface coverage per adsorbed molecule. In this study, it was assumed that each adsorbed molecule occupies approximately 40 \( \text{Å}^2 \).

The above solution speciation and adsorption equations were solved using the computer program SORSE developed for this study. This program quantitatively calculates the percent adsorption and surface coverage of adsorbed metal ions and complexes as a function of solution pH. Further, it accounts for the increased or decreased adsorption of the metal brought about by hydrolysis and complexation. The chemical free energy correction term was assumed a constant for adsorption of the free metal ion, hydroxy complexes and ligand complexes in order to minimize the number of model-adjustable parameters. The model was formulated to describe the adsorption of a trace metal onto a variable charge, variable potential surface. No provision was made to describe adsorption onto a constant charge surface.
Input parameters to the model include: (1) total metal and ligand concentrations, (2) cumulative formation constants for the metal complexes, (3) the ionic strength of the solution, (4) the charge and radius of the metal ion, (5) the dielectric constant and $\text{pH}_{\text{pzc}}$ of the adsorbent, and (6) the chemical free energy of adsorption, $\Delta G^\circ_{\text{chem}}$.

The Surface Complexation Site-Binding Model

The surface complexation site-binding model proposed by Davis and others (Davis et al., 1978; Davis and Leckie, 1978, 1980) is the product of several earlier double layer adsorption models including the thermodynamic approach described in the previous section (James and Healy, 1972c; Yates et al., 1974; Stumm et al., 1976). The model is reasonably complete in that both physical and chemical interactions are accounted for in its development. The model can simultaneously predict the adsorptive behavior of dissolved species and the development of surface charge and potential at the oxide-water interface. Further, the equilibrium constants determined by the model are applicable over a wide range of ionic strengths since the specific adsorption of electrolyte ions is considered.

The Electrical Double Layer

The site-binding model assumes that the oxide-water interface is composed of three layers of charge as depicted
in Figure 6. The charge at the oxide surface, \( \sigma_o \), is caused by the presence of potential determining ions \( \text{H}^+ \) and \( \text{OH}^- \), which are subject to the potential, \( \sigma_o \). The charge, \( \sigma_\beta \), in the plane of adsorbed ions (Inner Helmholtz Plane) corresponds to the potential \( \psi_\beta \). At the diffuse layer (Outer Helmholtz Plane), the charge is \( \sigma_d \) and the potential \( \psi_d \). Electroneutrality within the double layer requires that

\[
\sigma_o + \sigma_\beta + \sigma_d = 0
\] (33)

The planes of charge are separated by regions assumed to have constant capacitances such that the charges and potentials are related through those capacitances as follows:

\[
\sigma_o = C_1(\psi_o - \psi_\beta)
\] (34)

and

\[
\sigma_\beta = C_2(\psi_\beta - \psi_d)
\] (35)

where \( C_1 \) and \( C_2 \) are the integral capacitances of the inner and outer regions, respectively. In addition, the charge at the diffuse layer is defined by Gouy-Chapman diffuse layer theory through the equation
\[ \sigma_0 = [\text{SOH}_2^+] + [\text{SOH}_2^--\text{NO}_3^-] - [\text{SO}^-] - [\text{SO}^-\text{Na}^+] \]
\[ \sigma_\beta = [\text{SO}^-\text{Na}^+] - [\text{SOH}_2^--\text{NO}_3^-] \]
\[ \sigma_0 + \sigma_\beta + \sigma_d = 0 \]

Figure 6. Schematic representation of an oxide-solution interface showing possible locations of molecules occupying the hypothetical planes of charge (Davis et al., 1978).
\[
\sigma_d = -11.74 C^{1/2} \sinh \left( \frac{ze_0}{2kT} \right) \quad \mu C/cm^2 \quad (36)
\]

where \(C\) and \(z\) are the bulk concentration and charge of the supporting electrolyte counterion in the diffuse layer, and \(e, k,\) and \(T\) have their usual meaning.

Amphoteric Surface Sites

The site-binding model assumes that the charge at the oxide surface, \(\sigma_o\), originates from two processes (Yates et al., 1974; Davis et al., 1978). The first is due to amphoteric ionization reactions of the surface hydroxyl groups

\[
K_{a1}^{int} \quad \text{SOH}_2^+ + \text{SOH} + H_s^+ \quad (37)
\]

and

\[
K_{a2}^{int} \quad \text{SOH} + \text{SO}^- + H_s^+ \quad (38)
\]

where \(\text{SOH}_2^+\) and \(\text{SO}^-\) are ionized surface species, \(\text{SOH}\) is a neutral surface species, \(H_s^+\) denotes activities of protons on the surface, and \(K_{a1}^{int}\) and \(K_{a2}^{int}\) are so called intrinsic acidity constants.

In addition to these reactions, the interaction of supporting electrolyte ions with the oxide-water interface
can provide surface charge effects through surface complexation reactions

\[
\text{SOH} + C_s^+ \overset{\text{int}}{\rightleftharpoons} \text{SO}^-C^+ + H_s^+ \quad (39)
\]

and

\[
\text{SOH} + H_s^+ + A_s^- \overset{\text{int}}{\rightleftharpoons} \text{SOH}_2^+A^- \quad (40)
\]

where \(A^-\) represents an anion and \(C^+\) a cation, and the symbols \(\text{int}_\text{cation}^*\) and \(\text{int}_\text{anion}^*\) denote intrinsic complexation constants. The subscripts, \(s\), in the above equations denote ions that are very near the surface, either in the \(\psi_o\) or \(\psi_a\) plane. The charge at the oxide surface, \(\sigma_o\), is defined as the sum of positive charges minus the sum of negative charges in that plane. This is mathematically expressed as

\[
\sigma_o = \frac{10^6 F}{A} \left( [\text{SOH}_2^+] + \Gamma_n [\text{SOH}_2^+A_n^-] - [\text{SO}^-] - \Gamma_k [\text{SO}^-C_k^+] \right) \quad (41)
\]

where the square brackets indicate mol/l, \(A\) is the surface area of oxide available in solution in cm\(^2\)/l, and \(F\) is the Faraday constant (96,500 C/mol). Similarly, the charge, \(\sigma_a\), in the plane of the adsorbed ions is defined as the sum of the positive charge due to the presence of cations minus the sum of negative charge due to the presence of anions. Thus,
\[ \sigma_B = \frac{10^6 F}{A} (\sum_k Z^+_k [SO^-_C^+] - \sum_n Z^-_n [SOH^+_A^-_n]) \] (42)

where \( Z^+ \) and \( Z^- \) are the charge of the adsorbed cation and anion, respectively. The mean surface plane for the ionized surface and secondary plane of adsorbed ions are depicted in Figure 7. Since the ions near the surface are under the influence of the charged surface, their activities in the double layer are different from their activities in the bulk solution. These activities differ by the electrical work necessary to bring the ions from the bulk solution to some position in the double layer. Therefore, the activity of protons at some location, \( i \), in the double layer is related to the activity in the bulk solution by a Boltzmann distribution function

\[ (H^+)_i = (H^+)_{aq} \exp(-ze\psi_i/kT) \] (43)

The intrinsic constants are assumed independent of the surface environment so that the distribution of surface species can be expressed in terms of the intrinsic equilibrium constants, the bulk solution concentrations, and Boltzmann distribution functions as follows:

\[ [SOH^+_2] = \frac{\text{[SOH]}(H^+) \exp(-e\psi_o/kT)}{K_{al}^{\text{int}}} \] (44)

\[ [SO^-] = \frac{K_{al}^{\text{int}} \text{[SOH]} \exp(e\psi_o/kT)}{[H^+]} \] (45)
Figure 7. Schematic representation of the charge distribution at an idealized planar surface and the potential decay away from the surface in aqueous solution (Davis et al., 1978).
\[
[\text{SOH}_2^+\text{A}^-] = \frac{[\text{SOH}][\text{A}](\text{H}^+)}{K_{\text{anion}}^{\text{int}}} \exp[(ze/kT)(\psi_\beta - \psi_\alpha)] 
\]

and

\[
[\text{SO}^-=\text{C}^+] = \frac{K_{\text{cation}}^{\text{int}} [\text{SOH}][\text{C}^+] \exp[(ze/kT)(\psi_\alpha - \psi_\beta)]}{(\text{H}^+)} 
\]

In addition, the total number of surface species and complexes must be constrained by the total number of surface sites, \( N_s \), through the mass balance equation

\[
N_s = [\text{SOH}_2^+] + [\text{SOH}] + [\text{SO}^-] + \sum_n [\text{SOH}_2A_n^-] + \sum_k [\text{SO}^-=\text{C}_k^+] 
\]

Mixed Site Surfaces

James et al. (1978) have shown that the surface complexation site-binding model can be generalized to surfaces with several types of functional groups. This can be done by defining additional surface reactions and intrinsic equilibrium constants. For a clay mineral with two types of amphoteric surface sites, represented by the symbols SOH and TOH, an additional set of surface reactions can be defined for TOH sites

\[
\text{TOH}_2^+ \leftrightarrow \text{TOH} + \text{H}^+_s, \quad K_{\text{al},\text{TOH}}^{\text{int}} 
\]

\[
\text{TOH} \leftrightarrow \text{TO}^- + \text{H}^+_s, \quad K_{\text{a2},\text{TOH}}^{\text{int}} 
\]
\[ \text{TOH} + C^+_s \leftrightarrow \text{TOH}^+ + C^+_s, \quad \frac{1}{K_{\text{int}, \text{TOH}}} \]

and

\[ \text{TOH} + H^+_s + A^-_s \leftrightarrow \text{TOH}^+_2A^-_2, \quad \frac{1}{K_{\text{anion}, \text{TOH}}} \]

These reactions have intrinsic constant expressions with the same form as equations (44) through (47). Equations (49-52) are then coupled with the SOH equilibria through the following mass balance and charge balance equations

\[ [\text{TOH}]_T = [\text{TOH}] + [\text{TOH}^-] + [\text{TOH}^+_2A^-] \]  

(53)

\[ [\text{SOH}]_T = [\text{SOH}] + [\text{SOH}^-] + [\text{SOH}^+_2A^-] \]  

(54)

\[ [C]_T = [C^+] + [\text{SOH}^-] + [\text{TOH}^-] \]  

(55)

\[ [A]_T = [A^-] + [\text{SOH}^+_2A^-] + [\text{TOH}^+_2A^-] \]  

(56)

and

\[ [H^+] + [C^+] = [OH^-] + [\text{SOH}^-] + [\text{TOH}^-] + [A^-] \]  

(57)

Recently, Davis et al. (1978) added these surface equations to the solution-mineral equilibrium program MINEQL, which was originally developed by Westall et al. (1976). This program simultaneously solves the electrical double layer equations described above, the mass and charge balance equations for mineral oxide surfaces, including
clays, and the solution equilibria equations. Required
input data for the model are: (1) the total concentrations
of all the ions in solution and on surface sites, (2)
surface area of the solid, (3) values for the intrinsic and
solution equilibrium constants, and (4) integral
capacitances for the inner and outer regions of the double
layer. Where more than one type of surface site is present,
the total number of sites of each type must be specified
(e.g., N_S,SOH and N_S,TOH).

The Power Exchange Function Model

The power exchange function model, recently proposed by
Ozsvath (1979) and Langmuir (1981) is a simple two-parameter
function which can accurately model the exchange behavior of
major and minor cations on sorbent surfaces. It is a semi-
empirical, modified mass-action expression which thus far in
its development lacks a theoretical basis over the full
range of adsorbate concentrations to which it has been
applied. In spite of this, the power exchange function has
been useful in modeling alkali metal and trace metal
adsorption on a variety of adsorbents, over a wide range of
concentrations and pH values at different temperatures. The
utility of this function for modeling natural systems lies
in its mathematical simplicity and the limited number of
parameters required to apply it.
According to Langmuir (1981), empirical data on the adsorption of metal cations by naturally occurring geologic materials can be systematized in terms of power exchange functions. Literature surveys combined with laboratory studies reported by Garrels and Christ (1965), Ozsvath (1979), Langmuir (1981), and Hsi (1982) show that the exchange behavior of $H^+$, $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Ca^{2+}$, $Mg^{2+}$, $Cd^{2+}$, $Ag^+$, $Ni^{2+}$, $Pb^{2+}$, $UO_2^{2+}$, and $Zn^{2+}$ and their hydroxy complexes can be successfully modeled over a wide cation concentration range on a variety of adsorbents including montmorillonites, beidellite, illite, ferric oxyhydroxides, zeolites, and humic materials using up to three power exchange expressions for a given sorbent and competing cation pair.

For the homovalent binary exchange reaction given by

$$A + BX = B + AX$$

(58)

The empirical exchange constant expression is

$$K_{ex} = \frac{[B]}{[A]} \frac{(AX)^n}{(BX)}$$

(59)

where the square brackets denote activities of species A and B, AX and BX are the mole fractions of A and B on the adsorbent, $n$ is a constant, and $K_{ex}$ is the equilibrium exchange constant.
The corresponding theoretical expression is

\[ K_{ex} = \frac{[B]^{\lambda_{AX}} (AX)}{[A]^{\lambda_{BX}} (BX)} \]  

(60)

where \( \lambda_{AX} \) and \( \lambda_{BX} \) are the rational activity coefficients of A and B on the sorbent surface.

Using plots of rational activity coefficients versus mole fraction, Langmuir (1981) has shown that the power exchange function is mathematically equivalent to the regular solution exchange model of Garrels and Christ (1965) and Truesdell and Christ (1968) when the mole fractions of the adsorbed cations lie between 0.25 and 0.75, and to the Freundlich isotherm equation when the mole fraction of the minor component is less than 0.05. In addition, the power exchange function is identical to the Ion Exchange - Surface Complexation model of Dugger et al. (1964) when \( n = 1 \), which corresponds to simple ion exchange.

Log-linearization of the power exchange function for A-B exchange gives

\[ \log \frac{[A]}{[B]} = -\log K_{ex} + n \log \frac{(AX)}{(BX)} \]  

(61)

so that a plot of \( \log ([A]/[B]) \) versus \( \log (AX/BX) \) has a slope of \( n \) and an intercept of \( -\log K_{ex} \). Using published adsorption data, Langmuir (1981) found that the adsorption of alkali metal and alkaline earth metal cations on pure
clays and whole soils at cation concentrations of $10^{-4}$ to $10^{-2}$m can be described by power exchange functions with $n = 1$, corresponding to simple ion exchange. Adsorption of heavy metal cations from solutions of $10^{-7}$ to $10^{-3}$m was described by the exchange functions with $n = 0.8$ to 2.0. Correlation coefficients obtained for the power exchange function model fits generally exceeded 0.98.

Application of the n-power exchange function to trace metal adsorption data requires information on: (1) the equilibrium trace metal solute activities, (2) the cation exchange or base exchange capacity of the adsorbent material as a function of pH, and (3) the mole fractions of the adsorbed species.
EXPERIMENTAL METHODS AND MATERIALS

Chemical Reagents

All chemical reagents used in this study were of analytical reagent (AR) grade or better. All solutions were made with doubly deionized water with a conductivity of less than 1.0 \( \mu \text{mho/cm} \) at 25\(^\circ\)C. Ionic strength in the adsorption studies was adjusted primarily by the addition of 0.1m NaNO\(_3\) solution. The pH was adjusted with 0.1N HNO\(_3\) or 0.1N NaOH. In some experiments with Th(IV), Na\(_2\)SO\(_4\) was used to adjust the ionic strength in order to investigate the influence of SO\(_4^{2-}\) on the adsorption of Th(IV). For these experiments, pH was adjusted with 0.1N H\(_2\)SO\(_4\) and 0.1N NaOH.

Trace metal stock solutions for thorium were prepared from the nitrate salt. Solutions of radium were prepared from a National Bureau of Standards standard reference material (No. 4963). The standard consisted of radium-226 in approximately 5 ml of 5 weight percent HNO\(_3\) solution in a flame-sealed glass ampoule. As of September 1, 1967, there was 49.43± 1.06 \( \mu \text{g} \) of Ra-226 in the ampoule. All stock solutions were stored in polyethylene containers.
Sorbent Preparation

Quartz and kaolinite sols of a narrow particle size distribution comprised of particles having reasonably uniform shape were used in the adsorption studies. The surface preparation and bulk chemical analysis of these phases are described below.

Quartz

$\alpha$-SiO$_2$ (quartz) is commercially available from the Pennsylvania Sand and Glass Corporation in the form of a fine powder (nominal 5 $\mu$m particle size) under the trade name "Min-u-Sil 5". It was prepared from natural quartz sand from Berkeley Springs, West Virginia, by grinding in a silica-lined ball mill using silica pebbles. Selection of particle size was accomplished by air separation in a cyclone separator. The silica was first boiled twice in a 6M HNO$_3$-HCl mixture to dissolve and remove any iron contaminants introduced in the manufacturing process. After settling each time, the finely-suspended material was decanted off. The remaining leached material was centrifuged and washed repeatedly, first with 0.1M HCl (3 times) and then with doubly deionized water (3 times). The quartz was then washed with 2M NaOH to remove amorphous silica and repeatedly washed with deionized water to remove
the excess base. At this point, half of the leached quartz was washed (3 times) with 0.5M NaCl to produce the sodium surface form and then washed again (3 times) with deionized water to remove excess salt. Each final water wash was tested for residual chloride by addition of AgNO₃. The washing was continued by dialysis (approximately 1 week) until no AgCl precipitate formed. The purified silica was then dried in an oven at 110°C, heated to 450°C for 12 hrs in a muffle furnace to destroy organic material, and stored in a desiccator.

Kaolinite

Kaolinite clay (KGa-1) from Washington County, Georgia, was obtained from The Source Clays Repository at the University of Missouri, Columbia, Missouri. Approximately 100 grams of clay were first soaked in 2 liters of deionized water for 1 week with gentle stirring using an electric stirrer. The clay suspension was then allowed to stand undisturbed for 48 hrs. Settling velocity (approx. 2 cm/50 min) observed during this time indicated that the clay particles were approximately 2 μm in diameter (Folk, 1969). At the end of 48 hrs, the unsettled clay suspension was decanted and discarded. The settled clay suspension was then placed in 250 ml plastic centrifuge bottles and
centrifuged at 5,000 rpm for 15 min. Particles less than 0.1 μm which remained in the supernatant were discarded.

To remove iron and aluminum oxides in the clay, extraction with acid ammonium oxalate was employed (McKeague and Day, 1966). This method was chosen in preference to the citrate-dithionite method of Mehra and Jackson (1960) because of less possible structural alteration of the kaolinite. The clay particles were stirred in 2 liters of 0.2M ammonium oxalate solution and the pH adjusted to 4.0 using 1.0N HCl. At the end of 48 hours, the clay suspension was centrifuged and rinsed twice with deionized water.

To remove amorphous silica embedded between the layers of the clay particles, the hot caustic extraction method of Jones and Bower (1977) was employed. To each of the centrifuge bottles containing the clay, 0.5M NaOH was added. The mixture was shaken and placed in a 95°C water bath for 1 hr. At the end of the extraction period, the suspensions were centrifuged and washed with deionized water. To convert the kaolinite surface to the sodium form, the solid phase was rinsed twice with 0.5M NaCl and then three times with deionized water to remove the excess salt prior to dialysis. The sodium kaolinite was placed in a cellulose acetate dialysis bag and dialyzed against deionized water in a 4-liter bleaker with constant
stirring. To shorten the dialysis time, several 1-hr water changes were made. The silver nitrate precipitation method was used to monitor the progress of dialysis. When no cloudy precipitate was formed on addition of 0.1N AgNO₃ to the dialysate, and the pH of the water was near neutral, dialysis was considered complete. The purified clay suspension was then removed from the dialysis bag, dried in a 60°C oven, and stored in a desiccator.

Chemical Analysis of Sorbents

In order to verify the purity of the samples, both the α-SiO₂ and kaolinite were subjected to chemical analysis by X-ray fluorescence and emission spectrometry. Results of these analyses are presented in Table 6.

The prepared α-SiO₂ contained several impurities, most notably Na, K, Fe, and Cl, but not in excess of amounts usually found in pure quartz (Deer et al., 1963). It is possible that the Na and Cl are artifacts of the sodium preparation step. Nevertheless, these results indicate a significantly cleaner phase than the starting material supplied by the manufacturer. The Pennsylvania Sand and Glass Corporation report weight percent impurities of 0.10 for Al₂O₃, 0.019 for TiO₂, and 0.023 Fe₂O₃. Apparently, most of the contaminants occur as surface coatings or
Table 6. Chemical analysis of sorbents

<table>
<thead>
<tr>
<th>Sample Method</th>
<th>Quartz</th>
<th>Kaolinite</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>XRF</td>
<td>Emission Spec</td>
</tr>
<tr>
<td>Element</td>
<td>Wt%</td>
<td></td>
</tr>
<tr>
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<td>0.05</td>
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<tr>
<td>As</td>
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</tr>
<tr>
<td>Ba</td>
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<td></td>
</tr>
<tr>
<td>Ca</td>
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<td></td>
</tr>
<tr>
<td>Ce</td>
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</tr>
<tr>
<td>Cr</td>
<td>ND</td>
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</tr>
<tr>
<td>Cu</td>
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</tr>
<tr>
<td>Cl</td>
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</tr>
<tr>
<td>Fe</td>
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<td></td>
</tr>
<tr>
<td>Mg</td>
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<td>0.006</td>
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<td>Mn</td>
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</tr>
<tr>
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<tr>
<td>Ni</td>
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</tr>
<tr>
<td>K</td>
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<tr>
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<tr>
<td>Sr</td>
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<tr>
<td>Th</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>U</td>
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</tr>
<tr>
<td>V</td>
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</tr>
<tr>
<td>Zn</td>
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</tr>
<tr>
<td>La</td>
<td>&lt;0.002</td>
<td></td>
</tr>
</tbody>
</table>
particulates and were removed by the surface preparation procedure. The total concentration of contaminants found in the α-SiO₂ used here was approximately 0.095 weight percent.

The chemical composition of the kaolinite was typical for a kaolin-type clay and very similar to results reported in the Data Handbook for Clay Minerals (1980). Presumably, the various trace element contaminants are incorporated in the kaolinite structure, isomorphously substituted for aluminum and silicon in the octahedral or tetrahedral layers. In spite of these trace contaminants, results of the chemical analysis indicate a relatively pure kaolinite. Further, there is no evidence for thorium of sufficient concentration to interfere with subsequent adsorption experiments. Total concentration of trace contaminants was approximately 1.22 weight percent.

**Characterization of Sorbents**

Mineral adsorbent properties such as particle size, morphology, chemical composition, surface area, surface charge, electrophoretic mobility, and surface site density of functional groups are necessary parameters for interpreting experimental adsorption data, and the development or application of sophisticated adsorption
models. A discussion of the various experimental methods used to characterize these properties is given below.

Scanning Electron Microscopy and Particle Size Analysis

A scanning electron microscope equipped with a Le Mont image analyzer was used to determine the particle size and morphology of the $\alpha$-SiO$_2$ and kaolinite. Samples of the colloids were mounted on stainless steel disks and coated with a thin film of evaporated Au/Pd alloy. The samples were then examined under the electron microscope. Results of the electron microscopy studies are depicted as photomicrographs of the colloids shown in Figures 8-11. Output from the image analyzer provided statistical information on particle dimensions. Electron photomicrographs of the $\alpha$-SiO$_2$ (Figures 8 and 9) show elongated irregularly shaped particles of 1-10 $\mu$m in length. Data from the image analyzer indicate an average diameter of 2.5 $\mu$m with a length-to-width ratio of 4.9. The diameter of the particles was bimodally distributed with population densities centered at 1.25 and 2.80 $\mu$m. Particles of the $\alpha$-SiO$_2$ also show sharp edges indicating minimal dissolution during sample preparation.

Electron photomicrographs of the kaolinite show hexagonally shaped platelets, as well as "kaolinite worms" consisting of regularly ordered stacks of individual
Figure 8. Electron photomicrograph of α-SiO$_2$ (quartz) particles magnified 5000X.
Figure 9. Electron photomicrograph of α-SiO₂ (quartz) particles magnified 5000X.
Figure 10. Electron photomicrograph showing hexagonally shaped kaolinite platelets magnified 5000X.
Figure 11. Electron photomicrograph showing stacks of kaolinite platelets magnified 5000X.
particles. Image analysis of the particles indicated a size variation of 0.2-2.5 μm, with an average diameter of 1 μm.

X-ray Diffraction Analysis

X-ray diffraction analysis was used to check the surface composition and crystallinity of the starting materials. The line broadening effect observed from the x-ray diffraction patterns provided information about particle thickness (Cullity, 1956), which could not be obtained directly from electron microscopy studies.

The x-ray diffraction pattern of the α-SiO₂ showed it to be pure quartz with an average particle thickness of 0.1 μm. Similarly, the x-ray diffraction patterns for the kaolinite identified it as pure kaolinite with an average particle thickness of 0.085 μm. Back scatter x-ray dot patterns gave no indication of surface contamination for either sample.

Surface Area Measurement

Specific surface area measurements of the colloidal particles are required for calculations of surface charge density as well as surface concentration of ionizable functional groups from isotopic exchange measurements. The surface areas of the α-SiO₂ and kaolinite were measured by the 4-point BET nitrogen gas adsorption method (ASTM No.
This method is discussed in detail by Gregg and Sing (1967). Prior to analysis, the samples were outgassed at 150°C for 24 hrs. The BET surface area of α-SiO₂ was measured as 4.15 m²/g. Other reported values for BET surface areas of α-SiO₂ prepared in a similar manner are 5.0 ± 1.0 m²/g (MacNaughton and James, 1974), 4.56 m²/g (Basset, 1976), and 3.03 m²/g (Silva et al., 1979). The BET surface area of kaolinite was measured as 12.3 m²/g. Thomas et al. (1979) and Wilson (1979) reported a N₂-BET surface area of 8.75 m²/g and 10.05 m²/g, respectively, on the same kaolinite with no pretreatment. Madsen (1979) reported both a N₂-BET surface area of 10 m²/g and a glycerol surface area of 16 ± 2 m²/g on a kaolinite which was pretreated according to the method of Mehra and Jackson (1960).

Specific surface area measurements of suspended, charged colloids can also be derived from determination of the negative adsorption of co-ions (Van Den Hul and Lyklema, 1967). Advantages of this method are that no drying of the samples is required and that the surface area is not dependent on the cross-sectional area or orientation of the adsorbing molecule. However, the sensitivity of the approach is strongly limited by the precision of the method used to chemically analyze the solution for remaining
sorbate since the changes in the bulk concentration due to negative adsorption are generally very small. In this study surface areas for the \( \alpha \)-SiO\(_2\) and kaolinite could not be determined by negative adsorption due to the poor analytical precision for Na\(^+\) and Ca\(^{2+}\).

Surface Charge Density and P.Z.C. Determination by Potentiometric Titration

The surface charge as a function of pH and electrolyte concentration for the \( \alpha \)-SiO\(_2\) and kaolinite was determined by potentiometric titration according to the method of Bolt (1957), Parks and DeBruyn (1962), and Yates and Healy (1976). The principle of the technique is that the adsorption densities of the potential determining ions (p.d.i.) \( H^+ \) and \( OH^- \) for hydrous oxides are calculated from the amount of acid or base added to the suspension and the equilibrium concentration determined potentiometrically. The surface charge, \( \sigma_0 \), can then be calculated from the general equation

\[
\sigma_0 = F(\Gamma_H^+ - \Gamma_{OH^-})
\]  

(62)

where \( F \) is the Faraday constant and \( \Gamma_H^+ \) and \( \Gamma_{OH^-} \) are the number of moles of \( H^+ \) and \( OH^- \) adsorbed per cm\(^2\). The titrations are performed in the presence of a constant electrolyte concentration in order to fix the activity
coefficients for each titration and to ensure that the p.d.i. do not contribute significantly to the diffuse layer charge (Yates, 1975).

In this study, surface charge was calculated for each point in the titrations according to the equation (Silva, et al., 1979)

$$
\sigma_o = \frac{F}{A} \left[ (H^+)_i - (OH^-)_i \right] \frac{V_i}{\gamma_i} + C_a V_a - C_b V_b - \\
\left[ (H^+)_j - (OH^-)_j \right] \frac{V_j}{\gamma_j}
$$

(63)

where

- $\sigma_o$: surface charge density, (C/cm$^2$)
- $A$: surface area of sample, (cm$^2$)
- $(H^+)_i, (OH^-)_i$: measured $H^+$ and $OH^-$ ion activities of the starting electrolyte solution, (m)
- $V_o$: initial volume of electrolyte solution, (l)
- $C_a, C_b$: concentration of acid and base used for titration, (M)
- $V_a, V_b$: volume of acid or base used to a given point on the titration curve, (l)
- $(H^+)_j, (OH^-)_j$: measured $H^+$ and $OH^-$ ion activities at a given point on the titration curve
- $V_j$: total volume at a given point on the titration curve, $V_a + V_b + V_i$, (l)
\( \gamma_i, \gamma_j \): activity coefficients of \( \text{H}^+ \) and \( \text{OH}^- \), respectively, used to convert activities to concentrations.

The point of zero charge (p.z.c.), the pH at which the surface charge (\( \sigma_0 \)) is zero, was determined from the point of intersection of titration curves at different concentrations of indifferent electrolytes. Indifferent electrolytes are defined here as salt solutions in which the positive and negative ions of the supporting electrolyte have equal or no specific affinity for the surface. In an electrolyte where one of the ions is specifically adsorbed, the p.z.c. varies with the concentration of the electrolyte. In such cases, the net adsorption density and the surface charge are taken relative to the intersection point of the titration curves for the two lowest electrolyte concentrations.

Titrations were carried out on the acid forms of the \( \alpha-\text{SiO}_2 \) and the kaolinite. Preparation of the acid form of the quartz is described under the section entitled "Sorbent Preparation". In the case of the kaolinite, it has been reported by Paver and Marshall (1934), Chatterjee and Paul (1942), and Mukerjee et al. (1942) that hydrogen kaolinites are in reality hydrogen-aluminum systems. Grim (1968) reported that it is essentially impossible to prepare a clay
in which all the exchange positions are occupied by H⁺, since Al³⁺ moves from the lattice to exchange positions before saturation with H⁺ is complete. These conclusions are probably most applicable to other expanding clay minerals such as montmorillonites, with kaolinite affected to the least degree at a given pH. Harwood and Coleman (1954) and Ojea and Taboadela (1959) suggested preparing the hydrogen form of the clay by cation exchange with an ion exchange resin. For these experiments, an aqueous suspension of the kaolinite (0.05 g/ml) was passed through a 2.5 cm by 15.25 cm long column of 100 Mesh Dowex HCH-50 strong acid cation exchange resin. The acid form of the kaolinite was then redried in a 60°C oven and stored in a desiccator for subsequent titrations.

The titration vessel was filled with 100 ml of doubly deionized water and enough electrolyte added to bring the total ionic strength to 10⁻⁴m. The solution was then purged of CO₂ by bubbling nitrogen through it until the pH remained constant. Enough solid oxide was added to give at least 20 m² of surface. The suspension was then equilibrated by stirring under nitrogen at its natural pH for at least 24 hrs before titrating.

The acid-base titration of the suspensions was carried out by adding small volumes of 0.100N standard acid or base
using a Brinkman–Metrohm automatic titrator. Each
supporting electrolyte used for ionic strength adjustment
was titrated with its corresponding strong acid and base.
Following the addition of titrant, the pH of the suspension
was measured after approximately 2 min when the pH drift was
less than 0.01 units/min. The pH was measured with a
Brinkman glass electrode and Metrohm digital pH meter. The
titration sequence was generally as follows: starting at
the natural suspension pH, the oxide was titrated with acid
to pH 3, then with base to pH 9–10 and back to about the
starting pH with acid. The ionic strength of the suspension
was increased to $10^{-3}$ m by adding solid salt and the
titration sequence repeated. The same procedure was
repeated for higher electrolyte concentrations as
required. The suspensions were allowed to stand for long
times (sometimes overnight) only at near neutral pHs.

Blank titrations were similarly carried out on the
appropriate concentrations of the electrolyte solutions.
The blank titrations did not agree exactly with
 corresponding curves calculated using mean ion activity
coefficients for the background electrolytes, but the
difference was usually small and can probably be attributed
to the liquid junction potential.
Ideally, the blank titrations should be carried out on solutions containing the same concentrations of soluble species present in solution as would be present in contact with the suspensions (Bolt, 1957; Huang, 1981). This procedure was applied to the silica titrations, since quartz has a significant solubility and corrections for the hydrolysis of soluble species were necessary. Titrations with acid and base were performed on supernatants removed from a silica suspension which itself had been equilibrated for the same length of time as had the quartz suspensions titrated for surface charge determinations. These titrations indicated that a significant amount of hydroxide was consumed in the formation of silicic acid species at increasing pH.

For the silica titrations, the consumption of hydroxide due to aqueous silica speciation was also determined by measuring the concentration of total aqueous silica and calculating the hydroxide loss from the known dissociation constants of silicic acid (Morey et al., 1962; Busey and Mesmer, 1977). The concentration of soluble silica was determined by removing 5 ml aliquots from the supernatant of a silica suspension equilibrated as described above. The supernatants were filtered through a 0.45 μm millipore filter and analyzed by atomic absorption spectroscopy.
These samples indicated that the suspensions were slightly supersaturated with respect to $\alpha$-SiO$_2$. This rapid equilibration and supersaturation is not surprising considering the large available surface area of the silica and a probable dissolution rate of greater than $10^{-6}$ moles/m$^2$ hr (Stober, 1967). The presence of soluble silica does not affect the titrations below pH 7 since the neutral species $H_4SiO_4^0$ predominates; however, above about pH 7.8, the formation of $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ consume OH$^-$ so that it is necessary to know their concentrations.

For any pH, the number of moles of OH$^-$ ions adsorbed on the $\alpha$-SiO$_2$ surface can be calculated from the total number of moles consumed minus the number of moles consumed by the soluble silica. It should be noted that at high solid to solution suspension ratios, the consumption of hydroxide by the soluble species is a much smaller proportion of the total uptake of hydroxide, so that the correction for the dissolution is less important.

In the case of the clay, surface charge curves for kaolinite were calculated by subtracting blank electrolyte titration curves from the potentiometric titrations of the suspensions. It was not possible to account for the consumption of titrant due to soluble species of both silica and aluminum in a solution from which the kaolinite itself
had been removed. In such a complex system, titrant can be consumed or released by the incongruent dissolution of the kaolinite surface, reprecipitation of aluminum species as amorphous aluminum hydroxide (Schofield and Samson, 1953), and by the hydrolysis of the soluble alumina and silica. These reactions are further complicated by the potential for specific adsorption of the hydrolyzed aluminum ions by the negative surface (Smith and Emerson, 1976), with subsequent release of protons to the bulk solution. Consequences of these reactions can be minimized at pHs above 6 by employing large solid to solution ratios in the potentiometric titrations.

Figures 12 to 15 show the surface charge titration curves of $\alpha$-SiO$_2$ in NaCl, NaNO$_3$, Na$_2$SO$_4$, and CaCl$_2$. In each plot, the p.z.c. of the quartz is located at the intersection of all the titration curves. Close examination of the curves reveals no unique crossover point; the precise value of the p.z.c. is uncertain due to the low accuracy and low slope of the isotherms in the acid region. Accurate calculation of the p.z.c. was confounded by the overlap of the blank electrolyte titrations and the potentiometric titrations of the suspensions at acid pHs of 3 to 4.5. Fortunately, this uncertainty is not critical in calculating the surface charge because around the p.z.c. the isotherms
Figure 12. Surface charge development of α-SiO$_2$ as a function of pH and ionic strength in NaCl electrolyte solutions.
Figure 13. Surface charge development of $\alpha$-SiO$_2$ as a function of pH and ionic strength in NaNO$_3$ electrolyte solutions.
Figure 14. Surface charge development of $\alpha$-SiO$_2$ as a function of pH and ionic strength in Na$_2$SO$_4$ electrolyte solutions.
Figure 15. Surface charge development of α-SiO₂ as a function of pH and ionic strength in CaCl₂ electrolyte solutions.
are horizontal. For this study, the surface charge curves for $\alpha$-SiO$_2$ are based on a pH$_{pzc}$ of 3.0 $\pm$ 0.5. Earlier titration studies of silica have been made by Bolt (1957), Li and DeBruyn (1966), Tadros and Lyklema (1968, 1969), Abendroth (1970), Yates and Healy (1976), and Smith et al., (1978); however, most of this work has been with precipitated amorphous silicas. These studies indicate the p.z.c. of SiO$_2$ is highly variable, but usually less than 4.0 (Parks, 1965; Schwertman and Taylor, 1972).

As shown in Figure 16, values for the $\alpha$-SiO$_2$ (in 0.1m NaNO$_3$) are similar to those determined by Bolt (1957), Tadros and Lyklema (1968), Abendroth (1970), and Yates (1975) on precipitated pyrogenic silicas in various 1:1 electrolytes. Surface charge values reported by Tadros and Lyklema are comparatively high (150 $\mu$C/cm$^2$ at pH 10) and may at least partly reflect the presence of soluble silica for which they did not make a correction.

Titration curves for the kaolinite are shown in Figures 17, 18, and 19 for the electrolytes NaNO$_3$, Na$_2$SO$_4$, and CaCl$_2$, respectively. These curves, unlike those for $\alpha$-SiO$_2$, depict only the relative charge of the surface as a function of pH and electrolyte concentration, since they are not corrected for kaolinite dissolution or aqueous aluminum precipitation. The importance of these processes during the
Figure 16. Surface charge development of $\alpha$-SiO$_2$ as a function of pH in 0.1m NaNO$_3$ solution. Corresponding surface charge values for SiO$_2$ obtained by other workers are included for comparison.
Figure 17. Surface charge development of kaolinite as a function of pH and ionic strength in NaNO₃ electrolyte solutions.
Figure 18. Surface charge development of kaolinite as a function of pH and ionic strength in Na$_2$SO$_4$ electrolyte solutions.
Figure 19. Surface charge development of kaolinite as a function of pH and ionic strength in CaCl₂ electrolyte solutions.
potentiometric titration of the clay is apparent from the rapid increase in surface charge, translated as the tremendous consumption of titrant by the system at pHs below 5 to 6. At higher electrolyte concentrations (I = 10^{-2} to 10^{-1}), the titrant consumption is dramatically increased as a result of longer residence times for the kaolinite in the titration vessel and repeated equilibration at acid pH prior to the next titration cycle. At neutral and alkaline pHs, above the point of precipitation for amorphous aluminum hydroxide, charge development of the kaolinite surface is more typical of mineral oxides. It is the upper portion of these curves which is used subsequently for the determination of surface equilibrium constants.

The pH_{PZC} of the kaolinite was determined from uncorrected potentiometric titration curves performed consecutively on suspensions of clay in NaNO₃, Na₂SO₄, and CaCl₂ electrolytes. Results of these titrations are shown in Figures 20, 21, and 22. The pH–acid/base curves for NaNO₃ and Na₂SO₄ were obtained over a two-day period following the onset of the titrations, while those for CaCl₂ were obtained from rapid titrations (8 hrs) in order to minimize hysteresis in the titrations possibly resulting from surface dissolution and aluminum hydroxide precipitation. The point of intersection of the pH–
Figure 20. Experimental potentiometric titration curves for kaolinite as a function of ionic strength in NaNO₃ electrolyte solutions.
Figure 21. Experimental potentiometric titration curves for kaolinite as a function of ionic strength in Na$_2$SO$_4$ electrolyte solutions.
Figure 22. Experimental potentiometric titration curves for kaolinite as a function of ionic strength in CaCl$_2$ electrolyte solutions.
acid/base titrations for different electrolyte
concentrations defines the p.z.c. at pH = 4.6 ± 0.3 in all
three electrolytes. This value agrees reasonably well with
the isoelectric point obtained for the same sample in NaNO₃
using microelectrophoresis described in the following
section. However, the results for the NaNO₃ and Na₂SO₄
titrations show several additional features. For
electrolyte concentrations of 0.01M and higher, the pHₚzc
shifts significantly to higher values, approaching 7.5 to
8.2. Furthermore, these same curves show a pronounced
inflection in the titration long before the endpoint is
reached, not evidenced at lower electrolyte concentrations.
It has been hypothesized by Low (1955) and Cabrera and
Talibudeen (1978) that this initial inflection point
represents the point at which the titration of exchangeable
hydrogen on the surface of the clay is completed and the
titration of exchangeable aluminum begins, and that the
exchangeable aluminum results from the replacement of
crystal lattice aluminum by exchangeable hydrogen as
postulated by Paver and Marshall (1934). It is further
proposed that during the consecutive titrations of the
kaolinite surface, sufficient aluminum is liberated to the
solution to be reprecipitated or adsorbed and to form an
aluminum hydroxide or gibbsite coating on the kaolinite.
Such a process would be consistent with the $pH_{pzc}$ values observed by Kinneburgh et al. (1975) ($pH_{pzc} = 8.3$) for gibbsites, and the trend of increasing $pH_{pzc}$ observed in this study.

In order to further test the validity of the $pH_{pzc}$ value for kaolinite, individual titrations at $10^{-4}$ and $10^{-1}$M NaNO₃ were performed on separate aliquots of kaolinite suspension. These experiments were made in order to reduce the residence time for the clay in solution and minimize its exposure to strong acid solutions. Results of these titrations are superimposed in Figure 23 and clearly indicate a crossover point $pH_{pzc}$ value of 4.6.

Electrophoretic Mobility

In this study, microelectrophoresis was used to determine the isoelectric point and $pH_{pzc}$ for the mineral oxides. According to Lyklema (1971), the point of zero charge of a surface is defined as the concentration of potential determining ions for which the surface charge $\sigma_o$ is zero. For oxides, it is the pH value ($pH_{pzc}$) at which $\Gamma_{H^+} = \Gamma_{OH^-}$. The isoelectric point (i.e., p.) of the surface is defined as the concentration of p.d.i. at which the electrokinetic potential or zeta potential ($\zeta$) is zero. The zeta potential is the potential at the shear plane between two charged phases. In many previous articles (e.g., Parks,
Figure 23. Experimental potentiometric titration curves for kaolinite in $10^{-4}$m and $10^{-1}$m NaNO₃ solutions. The curves show a cross-over point at pH$_{PZC} = 4.6$. 
1965), the p.z.c. and i.e.p. have been used interchangeably. However, the p.z.c. generally refers only to the surface charge and the i.e.p. to the diffuse layer charge. In the absence of specific adsorption, then, the pH_{pzc} = pH_{iep}.

The measurement and significance of electrokinetic potentials has been reviewed by Shaw (1969) and Smith (1973). The determination of zeta is important from a theoretical standpoint since knowledge of the potential in the diffuse layer (\psi_d) allows model calculations of the electrical double layer to be more rigorously tested. In general, the exact location of the shear plane is not known because some unknown amount of solvent and adsorbed ions probably remain attached to the solid surface during shear. It is likely that the shear plane is located at a small distance further from the surface than the Outer Helmholtz Plane (O.H.P.) so that z < \psi_d. In fact, Li and DeBruyn (1966) and Smith (1973) found good agreement between measured zeta potentials and calculated values of \psi_d for quartz and silver halides in 10^{-2}M 1:1 electrolytes at low potentials.

According to Yates (1975), the electrophoretic mobility of a charged colloidal particle can be measured with considerable accuracy but the calculation of zeta potentials is difficult, particularly at high potentials. As a result
of retardation and relaxation of the ion-atmosphere, the relationship between mobility and \( \zeta \)-potential depends on the magnitude of \( \zeta \), the radius of the particle, \( a \), and on the Debye-Huckel double layer thickness \( 1/\kappa \). To calculate \( \zeta \) from mobilities, this relationship must be known. At present, the mobility -\( \zeta \) relationship is only known for irregularly shaped particles at small \( \kappa a \) (<0.02) or large \( \kappa a \) (>200), although for uniformly charged spheres, it is known for all \( \kappa a \). Unfortunately, most colloidal oxide systems do not meet these criteria. Kaolinite particles in particular are irregularly shaped and even the large \( \kappa a \) condition is satisfied only under conditions of large \( a \), or high ionic strength, where measurement of the particle mobility is difficult. Zeta potentials in this study were calculated by a rationalized form of the Smoluchowski equation such that

\[
\zeta = 12.83 \, u
\]  

(64)

where \( u \) is the mobility in \( \mu m \) per second under 1 volt per cm.

A single-particle microelectrophoresis apparatus (Rank Brothers, Ltd., Bottisham, Cambridge, Mark II) was used for electrophoretic mobility measurements. The instrument was fitted with cylindrical platinum electrodes for use with
either cylindrical glass or rectangular cells. The cells used in this study were of the Van Gils (internal electrode) thin-walled cylindrical-glass type. Blackening of the electrodes to minimize polarization effects was performed as necessary during the course of investigation. Details of this instrument and the microelectrophoresis technique are given by Parfitt (1973). Mineral oxide dispersions were prepared in separate equilibration vessels at 25°C under a circulating purified nitrogen atmosphere. The solids concentration in the suspensions was high enough to allow quick location of the particles in the instrument, yet low enough to avoid problems associated with sedimentation and particle-particle interactions. Adjustment of pH and ionic strength, and pH measurement were carried out in the equilibration vessel. For each electrolyte concentration, measurements were made with decreasing pH. Mobility measurements were made by timing 10 particles at both stationary levels in the cell with the polarity of the platinum black electrodes reversed between successive observations, in order to further minimize polarization effects. The mean of the reciprocal times was used to calculate electrophoretic mobility. The average error of a single mobility determination was less than ±10 percent for mobilities greater than 1 μm/sec/V/cm; however, errors were
larger for low mobilities, approaching ±0.25 μm/sec/V/cm for mobilities close to zero.

Figures 24 and 25 show the electrophoretic mobilities and zeta potentials determined for α-SiO₂ and kaolinite as a function of pH for three concentrations of NaNO₃. Extrapolation of the curves shows that the pH for which the mobility is zero is the same for each electrolyte concentration. This result indicates that the NaNO₃ behaves indifferently with respect to both α-SiO₂ and kaolinite. Thus, pH_{iep} is equivalent to pH_{pzc}. For α-SiO₂, the measured isoelectric point is 3.0 ± 0.1 which agrees well with values recorded in the literature (Parks, 1965; Wiese et al., 1971) for quartz and amorphous silica. Published data on the electrokinetic properties of kaolinite, however, are relatively scarce (Street and Buchanan, 1956; Packham, 1965; Nicol and Hunter, 1970; Ferris and Jepson, 1975; Williams and Williams, 1978) and such data differ considerably reflecting the source of the clay, surface preparation, and experimental technique. The pH_{iep} for the kaolinite used in this study was 4.0 ± 0.1.

Cation Exchange Capacity

Cation Exchange Capacities (CEC) were determined for α-SiO₂ and kaolinite as a measure of surface site density. CECs were measured both in batch and by titration with
Figure 24. Electrophoretic mobility and zeta potential for $\alpha$-$\text{SiO}_2$ as a function of pH and ionic strength in NaNO$_3$ electrolyte solutions.
Figure 25. Electrophoretic mobility and zeta potential for kaolinite as a function of pH and ionic strength in NaNO₃ electrolyte solutions.
Ca(OH)$_2$ in order to illustrate the dependence of exchange capacities on pH. For the kaolinite clay, where surface charge is assumed to be largely controlled by broken bonds and non-stoichiometric substitution within the clay mineral lattice (Schofield and Samson, 1953), such CEC measurements by titration were considered important in determining the relative contribution of pH-dependent surface ionization reactions to surface charge.

Cation exchange capacities for Na, K, NH$_4$, and Ca were determined in batch for both the α-SiO$_2$ and kaolinite, according to the procedure of Jackson (1975). The method involved washing an accurately weighed sample in a tared centrifuge tube with a 0.5M solution of the chloride salt of the cation to be loaded on the clay. This was followed by five washings with 0.1M salt solution. After centrifugation and removal of the aqueous phase, the excess 0.1M solution remaining with the sample was determined by again weighing the tube. To desorb Na or K, the sample was rinsed five times with 0.5M NH$_4$Cl. For Ca and NH$_4$ desorption, 0.5M MgCl$_2$ and 0.5M NaCl solutions, respectively, were used. The combined rinses were diluted and the concentration of Na, K, and Ca determined by atomic absorption spectroscopy. To determine NH$_4$, samples were analyzed by Nessler's method (Hawk et al., 1965). Nessler's method involves the
formation of a colored complex which can be detected spectrophotometrically. Results of the batch cation exchange measurements are given in Table 7.

To determine the CEC of the α-SiO₂ and kaolinite over a wide pH range (4-9), the titration procedure of Ozsvath (1978) was employed. One gram of prepared solid was suspended in deionized water and enough 0.1M HNO₃ was added to bring the pH to 3.7. The solid suspension was then titrated with 0.1N Ca(OH)₂ up to pH 9. At approximately each half pH unit increase during the titration, a small sample was withdrawn and the calcium concentration measured. The difference between the calculated calcium concentration and the measured calcium concentration was taken as the calcium adsorbed by the sorbent. The calcium concentration in solution was measured by atomic absorption spectroscopy, and the pH was measured with an Orion 901 microanalyzer. Results of the CEC titrations for α-SiO₂ and kaolinite are presented in Figures 26 and 27, respectively.

Cation exchange capacities for a given mineral generally vary with the source, chemical pretreatment, crystalinity, degree of lattice distortion, and particle size. Grim (1968) reports a range of 3-15 meq/100g for typical kaolinites, while the Data Handbook for Clay Materials and Other Non-Metallic Minerals (1979) gives a
Table 7. Cation exchange capacities for $\alpha$-SiO$_2$ and kaolinite (meq/100g)

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>NH$_4$</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-SiO$_2$</td>
<td>0.38</td>
<td>0.86</td>
<td>1.16</td>
<td>1.65</td>
</tr>
<tr>
<td>$\alpha$-SiO$_2^*$</td>
<td>0.22</td>
<td>0.26</td>
<td>0.95</td>
<td>1.25</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>8.1</td>
<td>2.7</td>
<td>3.2</td>
<td>9.6</td>
</tr>
</tbody>
</table>

*From Silva, et al., 1979
Figure 26. Cation exchange capacity (CEC) vs pH for α-SiO$_2$. CEC determined by Ca(OH)$_2$ titration.
Figure 27. Cation exchange capacity (CEC) vs pH for kaolinite. CEC determined by Ca(OH)$_2$ titration.
mean CEC of 2.0 for the same well crystallized kaolinite used in this study. CEC values obtained using Na, K, NH₄, and Ca salts as given in Table 7 show considerable scatter with only the K and NH₄ results (2.7 and 3.2, respectively) comparable to the value reported here. Evidence that the Na and Ca CEC determinations are in error is provided by the plot of CEC versus pH for the titration. Figure 27 shows a CEC of 2.6 for the kaolinite at pH 7. For α-SiO₂, the batch CEC and calcium titration measurements are in good agreement with values reported by Silva et al. (1979). CEC measurements for both solid phases as a function of pH indicate very little exchange capacity or surface charge exists at pH's less than 4.

In the case of clays, experimentally determined CEC is generally taken as a good measure of surface site density, Nₛ (James and Parks, 1981). However, for silica, standard methods for measuring CEC underestimate the total number of sites considerably (Allen et al., 1971). Calculated site densities based on measured surface areas, or site densities from isotopic exchange measurements, appear to be more reliable (Yates, 1975) and were, therefore, used as input parameters for model calculations in this study.
Tritium Exchange Determination of Surface Site Density

The tritium exchange method of Berube et al. (1967) and Yates (1975) was used to determine the surface site densities ($N_s$) of the $\alpha$-SiO$_2$ and kaolinite. The objective of the method is to measure the amount of hydrogen-tritium exchange between liquid water and the tritium labeled mineral oxide. The frequently used method for estimating surface hydroxyl group concentrations from the weight loss on heating to 800 - 1000°C (Kellum and Smith, 1967) was rejected since it provides no evidence concerning the surface accessibility of the water removed by heating and also measures water within the bulk mineral.

The $\alpha$-SiO$_2$ and kaolinite samples were labeled with tritium by taking enough sample to give about 30 m$^2$ of surface and dispersing them in tritiated water of known activity ($4.45 \times 10^6$ cpm/ml). The suspensions were then sealed in polycarbonate centrifuge tubes and shaken continuously for four days.

Following labeling, the suspensions were centrifuged and the excess water removed by decanting. The centrifuge tubes containing the wet oxides were then outgassed in a vacuum at room temperature for four days. The water retained after evacuation is considered to be present as
surface hydroxyl groups and other forms of chemically bound water.

After the outgassing step, dry nitrogen gas was let into the vacuum line, the tubes containing the samples removed, 20.0 cm$^3$ of distilled water added immediately, and the tubes again sealed. The solids were redispersed with ultrasonic irradiation and continuous shaking. After the desired equilibration time, the suspensions were centrifuged and 0.5 ml samples were removed from the clear supernatant. The radioactivity of these samples was determined by conventional liquid scintillation counting methods. For both the $\alpha$-SiO$_2$ and kaolinite, an equilibration time of seven days was allowed.

The number of exchangeable proton sites or site density ($N_s$) on the mineral oxide surfaces were calculated according to the following equation (Yates and Healy, 1975):

$$N_s = \frac{A_t}{A_L S_{BET} M} \text{ mol/m}^2$$

(65)

where $A_t$ is the total activity (in cpm) removed from the surface, $A_L$ is the activity per mole H (cpm/mol) of the labeling solution, $S_{BET}$ is the BET surface area (m$^2$/g), and $M$ is the mass (g) of the solid sample. To obtain $A_t$ from the measured activity of the supernatants, it was necessary
to determine and correct for the activity removed from the walls of the centrifuge tube.

The surface site density determined for α-SiO₂ was 4.5 sites/nm² which is in good agreement with the commonly accepted value of 5 sites/nm² reported by Armstead and Tyler (1969) and Yates and Healy (1975). The surface density of hydroxyls (Nₛ) on silica is reasonably well established, although some disagreement exist, probably due to the effects of surface impurities and differences in the various experimental techniques. In any case, it is apparent that nearly all experimentally determined Nₛ values lie between 3 and 6 hydroxyls per nm² (Peri and Hensley, 1968; Snoeyink and Weber, 1972); Iler, 1973). Hockey (1967) concluded that the most reliable value for fully rehydrated, well annealed SiO₂ is 4.6 hydroxyls/nm², while slightly higher values occur for freshly prepared, nonannealed surfaces.

In situations where information is available concerning the distribution of total surface area per gram among the various crystal faces for the oxide, theoretical calculations can be made estimating Nₛ. Iler (1979) reports a surface site density of 4.6 sites/nm² for a tridymite surface and 8 hydroxyls per nm² for the (100) crystal plane of beta cristobalite. Similar calculations by DeBoer and Vleeskens (1958) give 4.55 hydroxyls per nm² for the (111)
octahedral face of beta cristobalite. It is clear from these values that the experimentally determined hydroxyl densities are in reasonable agreement with the calculated values.

The surface site density, \( N_s \), determined for kaolinite was 6.0 sites \( \text{nm}^2 \). Currently, there are no isotopic exchange data available in the literature for comparison, but it is apparent that this value is higher than would be expected from cation exchange capacity measurements alone. The isotopically measured site density is presumed equivalent to the sum of the hydroxyl surface sites available by ionization, and the net deficit of positive charge due to isomorphous substitution characteristic of all clay minerals. The surface site density determined by tritium exchange was adopted for subsequent modeling in this study because of the poor reproducibility of the cation exchange measurements.

Future measurements of surface site density by tritium exchange may require dehydration of the surface by evacuation at elevated temperatures following labeling, in order to reduce the surface site contribution of physically adsorbed molecular water to the measurement. However, it may be exceedingly difficult or impossible to prepare a
fully hydroxylated surface which is devoid of molecular water.

Water Content and Surface Hydration

The surface site density of hydroxyl groups on both the $\alpha$-SiO$_2$ and kaolinite was determined by the tritium exchange technique described in the previous section. The tritium exchange technique requires that physically adsorbed water be removed from the surface without removing the chemically adsorbed water. To establish that outgassing at room temperature accomplishes this and in order to determine the total water content of the sample, the weight loss during outgassing was determined as a function of temperature. The percentage weight lost by the $\alpha$-SiO$_2$ and kaolinite on outgassing was determined by thermal gravimetric analysis using a Mettler Thermoanalyzer. Both samples were heated at a rate of $2^\circ$C/min. Both the $\alpha$-SiO$_2$ and kaolinite showed negligible weight loss between 50 and $150^\circ$C which suggests that all physically adsorbed water was removed by evacuation below $50^\circ$C or at room temperature. This agrees with the conclusions of other workers based on water vapor adsorption-desorption studies (cf. Young, 1958; Basset et al., 1968). Additionally, removal of surface hydroxyl groups by condensation to form silica-oxygen bonds and water does not usually occur below $180^\circ$C so that it is unlikely
that chemisorbed water is significantly removed by outgassing at room temperature (Young, 1958; Iler, 1979). Therefore, it is safe to conclude that outgassing to constant weight at 25°C removed all physically adsorbed water without condensing surface hydroxyl groups.

The physical and surface properties of the α-SiO₂ and kaolinite are summarized in Table 8.

**Adsorption Experiments**

Preparation and characterization of the α-SiO₂ and kaolinite for radium and thorium adsorption studies were discussed under the sections "Sorbent Preparation" and "Characterization of Sorbents". Adsorption experiments were conducted in batches as follows. Measured amounts of α-SiO₂ (5.00 g/l) and kaolinite (2.50 g/l) were each equilibrated in 1 liter of CO₂-free deionized water. The suspensions were added to centrifuge tubes and the ionic strength adjusted by the addition of 4.0 ml of 0.1M NaNO₃ solution. The pH was adjusted primarily by addition of 0.1N HNO₃ or 0.1N NaOH. In some experiments with Th(IV), Na₂SO₄ was used to adjust the ionic strength in order to investigate the influence of SO₄²⁻ on the adsorption of Th(IV). For these experiments, pH was adjusted with 0.1N H₂SO₄ and 0.1N NaOH. The desired amount of thorium or
Table 8. Physical and surface properties of the sorbents. Surface areas have been determined by the BET method. Particle sizes are as diameters.

<table>
<thead>
<tr>
<th>Composition and Particle Shape</th>
<th>Particle size (m)</th>
<th>Surface area (m²/g)</th>
<th>Sites per nm²</th>
<th>pH_Pzc</th>
<th>pH_Iep</th>
<th>Water Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-SiO₂</td>
<td>2.5</td>
<td>4.15</td>
<td>4.5</td>
<td>3.0</td>
<td>3.0 ± 0.2</td>
<td>0.5</td>
</tr>
<tr>
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<td>6.0</td>
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<td>4.0 ± 0.3</td>
<td>12.8</td>
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radium was then added to the solution from $10^{-3}$ m Th and $10^7$ pCi Ra/l stock solutions. Kaolinite and $\alpha$-SiO$_2$ were added to the centrifuge tubes as 10.0 ml aliquots from the previously prepared suspensions. Enough CO$_2$-free deionized water was added to bring the total volume of the suspension to 40.0 ml. The centrifuge tubes were shaken continuously for one week at room temperature. No pH measurements were made during the adsorption reaction. After the desired reaction period, the suspensions were centrifuged at 12,000 rpm for 90 min in a Damon-IEC refrigerated centrifuge. After centrifugation, the clear supernatant was analyzed for thorium or radium. Final pH measurements were made on the remaining suspension after samples were removed.

Thorium concentration was determined by Instrumental Neutron Activation Analysis (INAA). Thorium aliquots of 4 ml were evaporated in 0.4g vials, heat sealed, and irradiated for three hours at the University of California at Los Angeles nuclear reactor with a thermal neutron flux of $2 \times 10^{12}$ neutrons/cm$^2$/sec. After irradiation, the samples were allowed to cool for two weeks and then counted on a Ge-Li gelly detector for Pa-233. Counting peaks were integrated and compared to standards.

Radium was determined by high resolution alpha spectrometry using Ba-133, a gamma emitter, as a tracer.
Radium was isolated by coprecipitation with barium sulfate, preceded by complexation of thorium with DTPA (Sill, 1969, 1980).
RESULTS OF ADSORPTION EXPERIMENTS

Effect of pH on Adsorption

In order to examine the effect of pH on the adsorption of dissolved Th(IV) species and Ra(II), 0.1N HNO₃ or NaOH solutions were used to adjust the pH of the suspensions. For radium solutions with NaCl as the background electrolyte, 0.1N HCl and 0.1N NaOH solutions were used. Enough thorium or radium was added to each suspension from their stock solutions to give an initial total thorium concentration of $10^{-5}$m (2.32 ppm), and an initial radium concentration of 1000 pCi/l. Figures 28 to 31 show the percentage of thorium and radium adsorbed at different pHs by α-SiO₂ and kaolinite. Figure 28 also shows the effect of reduced thorium concentration on adsorption with α-SiO₂ as a function of pH. The results suggest that thorium is strongly adsorbed on α-SiO₂ at pH 3 and above, and on kaolinite at pHs above 2. This is in spite of the fact that both the dissolved thorium species present and mineral oxides have a net positive charge at pH values below the p.z.c. values of the oxides ($pH_{pzc} = 3$ for α-SiO₂ and 4.6 for kaolinite). Radium on the other hand, is not as strongly adsorbed as thorium. Radium is 50% adsorbed by α-SiO₂ at pH 6, and 50% adsorbed by kaolinite at pH 5.
Figure 28. Adsorption of thorium (IV) vs pH onto α-SiO₂ at 25°C in NaNO₃ electrolyte solution (I = 0.01 m). Data are for ∑Th = 10⁻⁵.85 and 10⁻⁵ m.
Figure 29. Adsorption of thorium (IV) vs pH onto kaolinite at 25°C in NaNO₃ electrolyte solution (I = 0.01 m).
Figure 30. Adsorption of radium (II) vs pH onto α-SiO$_2$ at 25°C in NaCl electrolyte solution ($I = 0.01$ m).
Figure 31. Adsorption of radium (II) vs pH onto kaolinite at 25°C in NaNO₃ electrolyte solution (I = 0.01 m).
The results depicted in Figure 31 also suggest that some radium may be specifically adsorbed on kaolinite at pHs below 4.5, or that some residual negative charge exists on the surface of the kaolinite at this pH. Because of the extremely small concentration of radium in the suspensions (approximately $10^{-11} \text{m}$), only a small fraction of the number of surface sites on the kaolinite need to be ionized to adsorb all of the radium from solution. For example, to adsorb 25% of the dissolved radium at pH 4 requires ionization of only $8.8 \times 10^{-10}$ percent of the kaolinite surface sites or a cation exchange capacity of $10^{-9}$ equivalents per 100g. Cation exchange capacity measurements described in a previous section show a kaolinite exchange capacity of approximately 0.1 meq/100g at pH 4. Similarly, Figure 29 shows that 80% of the dissolved thorium is removed by kaolinite at pH 3. Under these strongly acid conditions, we can only speculate that the thorium is either specifically adsorbed or Th$^{4+}$ diffuses into the crystal lattice and replaces Al$^{3+}$ or Si$^{4+}$ in the octahedral or tetrahedral positions.

Adsorption data presented as percent metal ion adsorbed versus pH are most useful for illustrating the adsorption edge and defining the pH at which metal ion adsorption begins. However, because total dissolved thorium
concentrations in groundwaters or waste-waters are usually
in the parts per billion range, and radium concentrations
are seldom higher than a few hundred picocuries, even in
waters associated with uraniferous rocks, the adsorption
data are also presented to indicate solution concentrations
remaining. In Figures 32 to 35, thorium and radium
concentrations in the solution phase after centrifugation
are plotted as a function of pH. In these and subsequent
figures, the analytical error of the experimental data is
represented by the vertical bars through the data points.
The plots again show that thorium is strongly adsorbed by
\( \alpha\text{-SiO}_2 \), but even more so by kaolinite. Radium is also more
strongly adsorbed by kaolinite than \( \alpha\text{-SiO}_2 \). The dotted line
shown in Figures 32 and 33 represents the observed
precipitation of thorium in blank experiments without
mineral oxide present. Precipitation of the thorium is
presumably as amorphous thorium (IV) hydroxide, \( \text{Th(OH)}_4 \).
While the pH for precipitation for thorium hydroxide
represented in these figures is considerably higher than
expected from the thermodynamic data, it was evident from
the blank adsorption experiments that precipitation of more
crystalline thorium hydroxide is kinetically hindered. This
observation is consistent with the findings of Matijevic et
al. (1961). Because most of the data points are at least
Figure 32. Adsorption of thorium (IV) vs pH onto α-SiO$_2$ at 25°C in NaNO$_3$ electrolyte solution ($I = 0.01$ m). The dotted line represents the apparent solubility of thorium hydroxide. (See text).
Figure 33. Adsorption of thorium (IV) vs pH onto kaolinite at 25°C in NaNO$_3$ electrolyte solution (I = 0.01 m). The dotted line represents the apparent solubility of thorium hydroxide. (See text).
Figure 34. Adsorption of radium (II) vs pH onto $\alpha$-SiO$_2$ at 25°C in NaCl electrolyte solution ($I = 0.01m$).
Figure 35. Adsorption of radium (II) vs pH onto kaolinite at 25°C in NaNO₃ electrolyte solution (I = 0.01 m).
one order of magnitude lower than the observed precipitation curve, it is clear that they are controlled by adsorption reactions rather than by precipitation of thorium hydroxide or thorianite. It is also evident in Figure 32, and in several subsequent figures, that a few data points exceed the apparent solubility of the thorium hydroxide. The thorium analyses yielding these data points most likely include Th associated with minute quantities of sorbent which adhered to the meniscus of the solution and could not be centrifuged out.

Initial radium concentrations employed in the adsorption reactions are several orders of magnitude undersaturated with respect to radium carbonate, radium chloride, or radium nitrate. As a result, the dissolved radium concentrations shown in Figures 34 and 35 are exclusively controlled by radium adsorption reactions.

**Reversibility of Adsorption**

Abramson et al. (1964) reported that the adsorption of thorium onto a silver iodide sol was reversible but that the rate of desorption was slow. In this study, the reversibility of Th(IV) adsorption onto α-SiO₂ and kaolinite was investigated over the pH range 2.5 to 6.0. The dark circles in Figures 36 and 37 represent data points for
Figure 36. Reversibility of thorium (IV) adsorption onto α-SiO₂ at 25°C in NaNO₃ electrolyte solution (I = 0.01m).
Figure 37. Reversibility of thorium (IV) adsorption onto kaolinite at 25°C in NaNO₃ electrolyte solution (I = 0.01m).
thorium (IV) adsorption experiments conducted in exactly the same fashion as described in the previous section. After the adsorption reaction was complete, a 5 ml sample of the suspension was withdrawn for thorium analysis. Then, the pH of the remaining suspension was readjusted with 0.1N HNO₃ or 0.1N NaOH to a different pH value. These values are represented by the open circles in Figures 36 and 37. After allowing one week for re-equilibration, the suspensions were centrifuged and the supernatants analyzed for thorium and pH. The final pH and thorium concentrations are plotted as inverted triangles on the figures. The figures show that the re-equilibrated suspensions returned to the initial adsorption curve following pH adjustment. These data indicate that the thorium (IV) adsorption is reversible over the period of one week.

The reversibility of radium (II) adsorption was not tested in this study.

**Effect of Surface Area on Adsorption**

To examine the effect of surface area or sorbent-solution ratio on the adsorption of radium and thorium, experiments were conducted as a function of pH at increased suspension concentrations. Thorium (IV) adsorption experiments were performed with α-SiO₂ and kaolinite at a
sorbent-solution ratio three times higher than that described in the previous sections. Radium (II) adsorption experiments with kaolinite were conducted at suspension concentrations three times higher, while those with $\alpha$-SiO$_2$ were made in the presence of $10^{-4}$m calcium at a sorbent-solution ratio twice that employed throughout the remainder of this study. These later experiments were performed to simultaneously determine the effects of surface area and competitive adsorption. All suspensions were adjusted with 0.1m NaNO$_3$ to an ionic strength of 0.01m. Figures 38 and 39 present the results for thorium (IV) adsorption on $\alpha$-SiO$_2$ and radium adsorption on kaolinite, respectively. For comparison, the experimental results are plotted along with the data from Figures 32 and 35. The plots show that the adsorption isotherms are shifted to lower pH with increasing sorbent-solution ratio, thus the specific surface area is an important factor in determining the position of the adsorption isotherms. Other adsorption experiments involving thorium and kaolinite and radium and $\alpha$-SiO$_2$ (not shown) provided similar results.

Effect of Sulfate Complexing on Thorium Adsorption

In order to examine the effect of sulfate complexing on Th(IV) adsorption, enough Na$_2$SO$_4$ salt was added to the
Figure 38. Effect of surface area on adsorption of thorium (IV) by α-SiO$_2$ at 25°C as a function of pH.
Figure 39. Effect of surface area on adsorption of radium (II) by kaolinite at 25°C as a function of pH.
suspensions to bring the total ionic strength in the suspensions to 0.001, 0.01, and 0.1M. Other conditions of the experiments were the same as reported in previous sections. Figures 40 to 42 describe Th(IV) adsorption on α-SiO₂ in Na₂SO₄ salt solutions at ionic strengths of 0.001, 0.01, and 0.1M, respectively. The plots indicate that the point of 50% adsorption increases from pH 4.0 through 4.5 to 4.75 as the ionic strength is progressively increased.

Shown with the data for comparison are calculated distribution curves for aqueous thorium hydroxide (Th(OH)₄⁰). These curves illustrate the percentage of Th(IV) in solution which exists as the neutral thorium hydroxide complex. Blank adsorption experiments conducted at corresponding ionic strengths indicated that thorium precipitation occurred at pHs close to the Th(OH)₄⁰ curve.

Figures 43 to 45, plotted as Th(IV) in solution versus pH, following centrifugation compare the adsorption from the same sodium sulfate solutions to adsorption from sulfate-free solutions. The plots indicate that sulfate complexing inhibits adsorption and favors desorption of Th(IV) by α-SiO₂. It is also clear that adsorption inhibition is proportional to the total sulfate concentration. The dotted lines in these figures correspond to the appearance of Th(IV) precipitation in the sulfate suspensions.
Figure 40. Effect of sulfate complexing on the adsorption of thorium (IV) by α-SiO₂ at 25°C in Na₂SO₄ electrolyte solution (I = 0.001 m). The calculated distribution curve for dissolved Th(OH)₄ is shown for comparison.
Figure 41. Effect of sulfate complexing on the adsorption of thorium (IV) by α-SiO₂ at 25°C in Na₂SO₄ electrolyte solution (I = 0.01m). The calculated distribution curve for dissolved Th(OH)₄⁺ is shown for comparison.
Figure 42. Effect of sulfate complexing on the adsorption of thorium (IV) by α-SiO₂ at 25°C in Na₂SO₄ electrolyte solution (I = 0.1m). The calculated distribution curve for dissolved Th(OH)₄ is shown for comparison.
Figure 43. Effect of sulfate complexing on the adsorption of thorium (IV) by α-SiO₂ at 25°C in Na₂SO₄ electrolyte solution (I = 0.001m). Adsorption data from NaNO₃ solution (I = 0.01m) are shown for comparison.
Figure 44. Effect of sulfate complexing on the adsorption of thorium (IV) by $\alpha$-SiO$_2$ at 25°C in Na$_2$SO$_4$ electrolyte solution (I = 0.01m). Adsorption data from NaNO$_3$ solutions (I = 0.01m) are shown for comparison.
Figure 45. Effect of sulfate complexing on the adsorption of thorium (IV) by α-SiO$_2$ at (I = 0.01m). Adsorption data from NaNO$_3$ solution (I = 0.01m) are shown for comparison.
The percentage distribution diagrams of the thorium (IV)-hydroxy-sulfate complexes in Figures 2-4 suggest that the thorium mono-, di-, and tri-sulfate complexes are very weakly adsorbed, if at all, relative to strong adsorption of the hydroxyl complexes ThOH$^{3+}$, Th(OH)$_2^{2+}$, Th(OH)$_3^+$, and possibly Th(OH)$_4^0$. Th$^{4+}$ ion is apparently not strongly adsorbed onto $\alpha$-SiO$_2$ consistent with the results of Matijevic et al. (1961) and Abramson et al. (1964) on silver iodide. Vydra and Galba (1967) found that only minor adsorption of thorium occurred onto silica gel at pHs below 2 but increased steadily with pH. In addition, it is apparent from these figures that ThSO$_4^{2+}$ is not strongly adsorbed on $\alpha$-SiO$_2$ in spite of its net negative charge at pHs above 3. It is possible that the presence of large sulfate ions complexed with the thorium sterically hinders the adsorption of Th(IV). Formation of these extremely large complexes may not permit close enough approach of the thorium ion to the surface for electrostatic adsorption.

Figure 46 shows the percentage of Th(IV) adsorbed onto kaolinite as a function of pH from Na$_2$SO$_4$ salt solutions having ionic strengths of 0.001, 0.01, and 0.1m. The plot shows that the presence of sulfate strongly inhibits adsorption on kaolinite, similar to the results obtained for the quartz suspensions. However, because of the increased
Figure 46. Effect of sulfate complexing on the adsorption of thorium (IV) by kaolinite at 25°C in Na₂SO₄ electrolyte solutions (I = 0.001, 0.01, and 0.1m).
adsorption at low pH (below pH 4) compared with the results obtained in the α-SiO₂ system, some adsorption of thorium sulfate complexes must be invoked. The most likely sulfate complexes adsorbed are ThSO₄²⁺ or Th(SO₄)₂⁻. For these suspensions, particularly at low pH where aluminum is liberated from the lattice to edge exchange positions, it is conceivable that the sulfate ions are bonded directly to the aluminum, resulting in coupled adsorption of the thorium. Davis and Leckie (1978, 1979) made a similar assumption to explain the enhanced adsorption of silver thiosulfate complexes on ferric hydroxide. In any case, the increased importance to Th(IV) adsorption of the hydroxyl complexes relative to the sulfate complexes is evident from the increased slopes of the percentage curves at higher pHs where the thorium hydroxyl complexes predominate.

The distribution coefficient (Kd) and enrichment factor (EF) concepts are two approaches commonly used by chemical engineers, soil scientists, and environmental geochemists to define the sorptive behavior of dissolved trace elements onto geologic materials (cf. Ames and Rai, 1978). For thorium, Kd is defined as the weight of sorbed Th per weight of sorbent divided by the mass in grams of Th per milliliter of solution. EF is defined as the weight of sorbed Th per weight of sorbent plus Th, divided by the weight of
dissolved Th per weight of solution. The EF is dimensionless and can be converted to Kd (in ml/g) by division by the solution density. Using the data shown in Figures 43 to 45, Kd values for adsorption of Th by α-SiO₂ were calculated and are plotted in Figure 47. From this plot, it is evident that Kd values depend on pH and total sulfate or ionic strength, and vary by several orders of magnitude. This suggests that attempts to model and predict the transport of thorium in natural or waste-waters based on Kd values alone is unreliable at best. In general, distribution coefficients have no accurate predictive value outside the laboratory systems used for their determination, particularly for elements that form strong complexes. A comprehensive, thermodynamically meaningful model is required to simultaneously account for pH, ionic strength, complexation, precipitation, and surface properties of the sorbent phases in order to predictively model trace metal transport.

Effect of Calcium Competition on Radium Adsorption

Since most radium-bearing natural waters or waste-waters contain calcium concentrations in excess of 10⁻⁴ m, and both ions behave similar chemically, it was decided to investigate the competitive effect of Ca(II) on Ra(II)
Figure 47. Effect of pH and sulfate complexing on the distribution coefficient (Kd) for thorium (IV) adsorption by α-SiO₂.
adsorption. For this purpose, 0.1m Ca(NO$_3$)$_2$ solution was added to the suspensions to give a total calcium concentration of $10^{-4}$ or $10^{-3}$m. Figures 48 and 49 compare the effects of calcium on radium adsorption with adsorption from calcium-free NaCl solutions. The plots show that Ra(II) adsorption is inhibited by the presence of Ca(II) for both the α-SiO$_2$ and kaolinite, and that the extent of inhibition is proportional to the total calcium concentration. This suppression of radium adsorption is most certainly the result of competition with the sorbent surface for available adsorption sites. From this result, it is likely that radium adsorption is dependent on all major cation concentrations, but particularly on divalent cations.

In order to more accurately define the pH range over which Ca(II) has the greatest competitive effect on Ra(II) adsorption, experiments were conducted to investigate Ca(II) adsorption on the α-SiO$_2$ and kaolinite. To accomplish this, 0.1m Ca(NO$_3$)$_2$ solution was added to the suspensions at an ionic strength of 0.01m NaNO$_3$. Figures 50 and 51 show that Ca(II) is more strongly adsorbed to α-SiO$_2$ than to kaolinite below pH 5. For α-SiO$_2$, Ca(II) adsorption increases abruptly at pH 7 and above, while adsorption on kaolinite is essentially constant at pHs less than 9. Figures 48-51 show that calcium has a strong competitive effect on radium
Figure 48. Effect of calcium on the adsorption of radium (II) by α-SiO₂ at 25°C in NaNO₃ electrolyte solution (I = 0.01 m).

α-SiO₂
5 g/l (20.75 m²/l)
Σ Ra = 1000 pCi/l
I = 0.01 m
Figure 49. Effect of calcium on the adsorption of radium (II) by kaolinite at 25°C in NaNO₃ solutions (I = 0.01 m).
$\alpha$-$\text{SiO}_2$-$\text{NaNO}_3$

5 g/l (20.75 m$^2$/l)
$\Sigma \text{Ca} = 0.0001$ m
$I = 0.01$ m

Figure 50. Adsorption of calcium (II) vs pH onto $\alpha$-$\text{SiO}_2$ at 25°C in NaNO$_3$ electrolyte solution ($I = 0.01$m).
Kaolinite—NaNO₃

2.5 g/l (30.75 m²/l)
I = 0.01 m

Figure 51. Adsorption of calcium (II) vs pH onto kaolinite at 25°C in NaNO₃ electrolyte solution (I = 0.01m). Data are for \( \Sigma \text{Ca} = 10^{-4} \) and \( 10^{-3} \) m.
adsorption, and that this competition is greatest at neutral and alkaline pHs.

Based on the data shown in Figures 48 and 49, Kd values for Ra(II) adsorption were calculated and are plotted in Figures 52 and 53. These plots show that Kd values vary by several orders of magnitude and depend upon the concentration of calcium in solution, the pH, and the nature of the adsorbent material. This suggests that attempts to model the transport of radium in waters based on a single Kd value may be unrealistic. Again, a comprehensive geochemical model is needed to simultaneously account for solution and sorbent properties, so as to accurately predict and model trace metal transport.
Figure 52. Effect of pH and calcium competition on the distribution coefficient (Kd) for radium (II) adsorption by α-SiO₂.
Figure 53. Effect of pH and calcium competition on the distribution coefficient (Kd) for radium (II) adsorption by kaolinite.
APPLICATION AND RESULTS OF ADSORPTION MODELING

To explain the adsorption of a trace metal species at the solid-liquid interface, a number of theoretical models have been proposed ranging in sophistication from simple, nonspecific binding of the metal ion, to complex models which require several energies to define adsorbate-adsorbent interactions. The most complex models also include specified structures for the electrical double layer. To some degree, all of these models have been effective in simulating adsorption reactions. In cases where the chemical system is well defined and contains only a few components or independent variables, the simple theoretical models often suffice. However, to describe the adsorption of a trace species from various electrolyte solutions on complex mineral surfaces, a comprehensive adsorption model is needed.

In this study, the data for thorium (IV) and radium (II) adsorption on α-SiO₂ and kaolinite were examined using (1) the thermodynamic adsorption model (James and Healy, 1972c), (2) the surface complexation site binding model (Davis et al., 1978), and (3) the power exchange function model (Langmuir, 1981). Previous studies have shown that these three models are the most successful in modeling experimental adsorption data for systems approaching natural
solution conditions. Each of the models is capable of modeling adsorption reactions as a function of pH, ionic strength, competing ions and complexes, adsorbate concentration, and surface charge.

The Thermodynamic Adsorption Model

The equilibrium computations for the adsorption of thorium (IV) and radium (II) on α-SiO₂ and kaolinite using the thermodynamic adsorption model were performed with the SORSE computer program described in a previous section. The method of calculation incorporated in the program has been described in detail by James and Healy (1972c). Modifications to the calculations including the speciation and adsorption of metal-ligand complexes have been described under "The Adsorption Isotherm". The equilibrium concentrations of all the metal ion species were calculated using the hydrolysis and complex stability constants of the particular metal ion and the pH and ligand concentration of the solutions. The thermodynamic data used in these calculations are described under "The Geochemistry of Thorium and Radium".

In the following sections, the theoretical calculations from the thermodynamic adsorption model are compared with the experimental adsorption data for: (1) 10⁻⁵.₈₅ and 10⁻⁵₅m
Th(IV) on α-SiO$_2$ in 10$^{-2}$m NaNO$_3$ solution, (2) 10$^{-5}$m Th(IV) on α-SiO$_2$ in Na$_2$SO$_4$ solutions having an ionic strength of 10$^{-3}$, 10$^{-2}$, and 10$^{-1}$m, (3) 1000 pCi/l Ra(II) on α-SiO$_2$ in 10$^{-2}$m NaCl solution, and (4) 1000 pCi/l Ra(II) on kaolinite in 10$^{-2}$m NaNO$_3$ solution. The theoretical calculations were made with ΔG°chem as the sole fitting parameter and tacitly assume that the free energy of adsorption is independent of the fractional surface coverage, θ. This assumption is valid if sorbate ions or molecules occupy a relatively large area per adsorption site, as compared with the area that would be covered by the free metal ion itself (cf. James and Healy, 1972c). The fixed parameters used in the calculations are summarized in Table 9. The radius of the water molecule (r$_w$) was taken as 1.38 Å and the dielectric constant of water (ε$_{bulk}$) is 78.5.

At equilibrium, the amount of adsorbed metal ion, with fixed pH and ionic strength, is a function of the total concentration of the metal and the available surface area. The available surface area is a function of the maximum surface coverage which can be calculated through the equation

$$
\Gamma_{\text{max}} = \frac{1}{\pi(r_{\text{ion}} + 2r_w)^2N} \text{ mol/m}^2
$$

(66)
Table 9. Some fixed parameters for the computation of adsorption isotherms. The $pH_{pzc}$ and $\epsilon_{solid}$ values used for $\alpha$-SiO$_2$ and kaolinite were 3.0 and 4.3, and 4.0 and 4.6, respectively. The radii of the adsorbed ions were 0.99Å for Th$^{4+}$ and 1.43Å for Ra$^{2+}$.

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<th>Metal</th>
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<th>Electrolyte and Ionic Strength (m)</th>
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<th>$p^*\beta_2$</th>
<th>$p^*\beta_3$</th>
<th>$p^*\beta_4$</th>
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</table>
In this study, a surface coverage of 40 $A^2$ was assumed for each sorbate species. This value thus sets the surface site density for the adsorbents and the monolayer coverage for the adsorbed species.

Adsorption of Thorium Species on Quartz

For an aqueous solution containing $10^{-5}$m Th(IV), the equilibrium speciation diagram in Figure 1 shows that the hydrolysis of Th(IV) begins at pH 2 and continues through pH 6. At pHs above 4, essentially all of the free metal ion is hydrolyzed. According to the Figure, the predominant solution complexes include ThOH$_3^+$, Th(OH)$_2^{2+}$, Th(OH)$_3^+$, and Th(OH)$_4^0$. The precipitation of Th(OH)$_4$(am) should theoretically occur at pHs less than 2 at the concentration of thorium shown, but was not observed in this study. Blank adsorption experiments indicated that Th precipitation occurs at pHs slightly above the appearance of significant Th(OH)$_4^0$(aq). Presumably, the precipitation of thorium hydroxide is kinetically hindered over the relatively short time frame of the adsorption experiments, or occurs as a hydrated solid hydroxide having a greater solubility than that reported for Th(OH)$_4$(am) (Langmuir and Herman, 1980).

From the adsorption data presented in the previous sections, it is apparent that Th(IV) exhibits the same general adsorption properties as other hydrolyzable metals
described by James and Healy (1972c), in that adsorption is followed by the appearance of hydrolyzed metal species. The experimental adsorption data shown in Figure 28 for $10^{-5.85}$ and $10^{-5}$m Th(IV) show an abrupt increase in adsorption on $\alpha$-SiO$_2$ at pHs between 2.5 and 4.0. For $10^{-5.85}$m thorium, the initial increase in adsorption corresponds to the predominance of the ThOH$_3^{3+}$ and Th(OH)$_2^{2+}$ complexes. For the $10^{-5}$m thorium data, adsorption follows the development of ThOH$_3^{3+}$, Th(OH)$_2^{2+}$, and Th(OH)$_3^{+}$ hydroxy complexes. Both adsorption curves appear to be controlled by the Th(OH)$_4^0$ complex at high pH.

To quantitatively describe the adsorption of thorium (IV) on $\alpha$-SiO$_2$, the adsorption data were modeled by arbitrarily selecting values for $\Delta$$G^0$chem. Results of the model calculations are shown as the solid curves in Figures 54 and 55 along with the experimental data. In both Figures, the overall features of the experimental data at adsorption densities higher than 40 percent are reproduced. The $10^{-5}$m thorium adsorption data are accurately described above pH 3.5 by assuming $\Delta$$G^0$chem = -9.0 kcal/mol, while the $10^{-5.85}$m adsorption data are described reasonably well above pH 3.5 with $\Delta$$G^0$chem = -11.0 kcal/mol. At both thorium concentrations, the model calculated results indicate that the abrupt increase in adsorption follows the formation and
Figure 54. Comparison of the experimental data for thorium (IV) adsorption on $\alpha$-SiO$_2$ vs pH with the model calculated adsorption curve: $\Sigma$Th = 10$^{-5}$ m and I = 0.01 m (NaNO$_3$).
Figure 55. Comparison of the experimental data for thorium (IV) adsorption on α-SiO₂ vs pH with the model calculated adsorption curve: $\Sigma Th = 10^{-5.85}$ m and $I = 0.01$ m (NaNO₃).
predominance of the aqueous thorium hydroxy complexes, and that the free metal ion, Th$^{4+}$, is not strongly adsorbed. This reflects the greater solvation energy of highly charged versus lower charged species, which opposes the coulombic and chemical free energy contributions to adsorption. Adsorption increases when the solvation energy is lowered, primarily by increasing the concentrations of the lower valence hydrolysis products. Also, as the solution pH increases, the coulombic attraction of a given ion is increased as a result of increased surface charge and potential of the sorbent. For both thorium concentrations, the Th(OH)$_2^{2+}$, Th(OH)$_3^+$, and Th(OH)$_4^0$ complexes are apparently the most strongly adsorbed.

Unfortunately, the same $\Delta G^0_{\text{chem}}$ correction term could not be used to model the adsorption of thorium from both the $10^{-5}$ and $10^{-5.85}$ m (Th(IV)) solutions. At these low metal concentrations, the model calculations predict a rapid increase in adsorption as soon as the surface acquires a negative charge as the pH is increased above the pH$_{pzc}$. With $\Delta G^0_{\text{chem}} = -9.0$ kcal/mol, the calculated adsorption curve is shifted only slightly to more acid pH with decreased total thorium (IV) concentration. However, the experimental adsorption data shown in Figure 55 indicate that 70% of the total thorium is adsorbed at pHs less than
the p.z.c. This specific adsorption of thorium is postulated to occur as a result of residual negative surface sites present below the p.z.c. Unlike the surface complexation site binding model discussed in a subsequent section, the thermodynamic adsorption model cannot explain metal adsorption or the development of negative surface sites below the pH_pzc of the adsorbent. In order to successfully model the adsorption of thorium from the 10^{-5.85} \text{m} \text{Th(IV)} solutions, it was necessary to decrease the $\Delta G^\text{chem}$ correction term to -11.0 kcal/mole. James and Healy (1972c) reported similar difficulties in modeling the adsorption of 10^{-6}\text{m} \text{Co(II)} solutions with $\alpha$-\text{SiO}_2 but offered no explanation for the discrepancy. The overall agreement between the experimental data and the model calculations could have been improved using unique $\Delta G^\text{chem}$ terms for each thorium species but would also increase the number of model-adjustable parameters.

Effect of Ionic Strength and Sulfate Complexing on Thorium Adsorption

According to James and Healy (1972c) and Vuceta (1976), the ionic strength of the supporting electrolyte affects the adsorption of dissolved metal ions in several ways. First, the ionic strength controls the charge density in the diffuse layer of a suspended colloid. As the ionic strength
is increased at constant pH, the electrical double layer is compressed. Consequently, at a given point, the electrical field, \(d\psi/dx\), is increased and the electrostatic potential at the same point is decreased. Increased field strength results in higher solvation energy contributions to the free energy of adsorption and a decrease in the coulombic energy. The overall effect then, is reduced adsorption of a given metal ion. Secondly, the supporting electrolyte can influence adsorption by complex formation with the dissolved metal ion. Resulting solution complexes may increase or decrease adsorption depending on their chemical affinity for the surface.

Figures 2-4 showed the effect of increasing ionic strength and sulfate complexing on the aqueous speciation of thorium (IV). As the ionic strength is increased by addition of Na\(_2\)SO\(_4\), the overall effect is to increase the importance of the thorium sulfate complexes and to extend their predominance to higher pH values. Results of the adsorption experiments indicated that the presence of sulfate strongly inhibits thorium adsorption and favors its desorption, particularly at pHs below 4. Figure 56 summarizes the results of the thorium (IV) adsorption experiments conducted in Na\(_2\)SO\(_4\) solutions at ionic strengths of 10\(^{-3}\), 10\(^{-2}\), and 10\(^{-1}\)m. The plot clearly shows
Figure 56. Effect of sulfate complexing on the adsorption of thorium (IV) by α-SiO₂ at 25°C in Na₂SO₄ electrolyte solutions (I = 0.001, 0.01, and 0.1m).
displacement of the adsorption edge to higher pHs with increasing ionic strength.

Using $\Delta G^\circ_{\text{chem}} = -9.0$ kcal/mole, the thorium (IV) adsorption data were compared with computed adsorption based on the modified James-Healy thermodynamic adsorption model. Results of the calculations are shown in Figures 57 to 59 as the solid curves along with the corresponding experimental data. The model calculated adsorption curves show good agreement with the adsorption data particularly above pH 4-4.5. At both low and high pH values, changes in the ionic strength do not have a large influence on the adsorption of Th(IV) on α-SiO₂. However, pronounced changes do occur in the pH region characterized by the sharp increase in adsorption. An increase in the ionic strength from $10^{-3}$ to $10^{-2}$m results in a shift of the model calculated adsorption curve of 0.5 pH units. At the same time, the model calculated curve accurately predicts that the amount of thorium adsorbed is reduced by almost 50 percent at pH 4. Further increase in the ionic strength to $10^{-1}$m results in a similar but less drastic change.

The model calculated adsorption curves shown in Figures 57 to 59 were obtained by allowing only the hydrolyzed thorium species ThOH$^{3+}$, Th(OH)$^{2+}$, Th(OH)$^{3+}$, and Th(OH)$^{4+}$ to adsorb. The calculations indicate that the Th(OH)$^{3+}$ and
Figure 57. Comparison of the experimental data for thorium (IV) adsorption on α-SiO₂ vs pH with the model calculated adsorption curve: ΣTh = 10⁻⁵ m, and I = 0.001 (Na₂SO₄).
Figure 58. Comparison of the experimental data for thorium (IV) adsorption on $\alpha$-SiO$_2$ vs pH with the model calculated adsorption curve: $\Sigma$Th = $10^{-5}$ m, and I = 0.01 m (Na$_2$SO$_4$).
Figure 59. Comparison of the experimental data for thorium (IV) adsorption on $\alpha$-SiO$_2$ vs pH with the model calculated adsorption curve: $\Sigma$Th = $10^{-5}$ m, and I = 0.1 m (Na$_2$SO$_4$).
Th(OH)$_4^-$ complexes control the position of the Th(IV) adsorption isotherm and are the major solution species adsorbed from the Na$_2$SO$_4$ solutions by α-SiO$_2$. Adsorption of these species is preferred assuming the thermodynamic adsorption model because of their low charge and low solvation energies. Incorporating the thorium sulfate complexes in the adsorption reactions did not improve model fits of the empirical adsorption data. Despite the low charge and predominance of the ThSO$_2^{2+}$ and Th(SO$_4$)$_2^-$ complexes at acid pHs, these species are apparently not important in the adsorption process. Model calculations indicate that ThSO$_4^{2+}$ was only slightly adsorbed at pHs less than 4.5. Adsorption of Th(SO$_4$)$_3^{2-}$ was neglected in the calculations because of its negative charge.

Adsorption of Radium on Quartz and Kaolinite

The experimental adsorption data for radium (II) on α-SiO$_2$ and kaolinite were also used to test the applicability of the thermodynamic adsorption model for predicting trace metal adsorption, in this case, at extremely low concentrations (I Ra = 1000 pCi/l). Results of the model calculations along with the experimental data are shown in Figures 60 and 61. The model calculations describe the adsorption of Ra(II) on α-SiO$_2$ with reasonable accuracy only over the pH range 5 to 9.5. Over this range, the
Figure 60. Comparison of the experimental data for radium (II) adsorption on α-SiO₂ vs pH with the model calculated adsorption curve; $I = 0.01 \text{m (NaCl)}$. 

\[ \Delta G_{\text{chem}}^0 = -9.1 \text{ kcal/mol} \]
Figure 61. Comparison of the experimental data for radium (II) adsorption on kaolinite vs pH with the model calculated adsorption curve: $I = 0.01 \text{m (NaNO}_3)$. 
theoretical calculations are within 0.75 pH units of the experimental data points. At pHs of 7 to 9, the model calculations reproduce the apparent tailing off of radium (II) adsorption. For radium adsorption on kaolinite, the thermodynamic model calculations do not describe the adsorption nearly as well and, in fact, predict a much steeper adsorption increase than was observed. In addition, approximately 25% of ERa(II) adsorbed below pH 4 is not predicted by the calculations. Again, this discrepancy is attributed to residual negative surface charge or the persistence of constant negative surface charge below the pH_{pzc} of the kaolinite. Clearly, a more sophisticated adsorption model is required to accurately fit the experimental data.

In Figure 60, the model calculations describe the adsorption of radium on α-SiO$_2$ with ΔG°_chem = -9.1 kcal/mole. To model the adsorption of radium on kaolinite, the ΔG°_chem correction term was lowered to -11.2 kcal/mole assuming a dielectric constant for the solid of 4.6. It should be noted that the same ΔG°_chem for α-SiO$_2$ could also be used to model the adsorption on kaolinite, if the solid's dielectric constant is raised to 6.5. This demonstrates the strong dependence of model calculations on the dielectric constant of the solid. Grim (1968) reports dielectric constants for kaolinite ranging from 5.24 to 6.45 at 75°C.
The Surface Complexation Site-Binding Model

The surface complexation site-binding model as discussed in a previous section is the product of several earlier double layer approaches including the thermodynamic adsorption model of James and Healy. It is a reasonably complete model which considers both the physical double layer structure and the chemical site-binding interactions of solutes with oxide surfaces. The model can simultaneously predict the adsorption of dissolved ions and the development of surface charge and potential at the oxide-water interface. The set of equations which make up the model can be solved at any pH with known values for the sorbent properties $N_s$, $pK_{al}$, $pK_{a2}$, $pK_{cation}$, $pK_{anion}$, $C_1$, $C_2$, and electrolyte concentrations. This is done by using $[\exp(-e\psi_o/kT)]$, $[\exp(-e\psi_b/kT)]$, and [SOH] as independent variables in the solution equilibria program MINEQL devised by Westall et al. (1976). From an operational standpoint, the simultaneous solution of all the available data for a given sorbent and sorbate is accomplished in two consecutive steps. First, the potentiometric titration data for the sorbent are simulated using equations for the acid-base surface species and surface complexes of major electrolyte ions. Following this, the adsorption isotherm data are simulated as a
function of sorbate concentration and pH by incorporating reactions for the surface-sorbate complexes.

Determination of Intrinsic Equilibrium Constants

In order to solve the equations given previously for the surface complexation site-binding model, it is necessary to determine values for the intrinsic ionization and complexation constants. These constants $(K_{a1}, K_{a2}, K_{C}^*, K_{A}^*)$, where A and C indicate any anion and cation are not measureable directly since the surface activities of the potential determining ions and electrolyte ions (e.g., $[H^+]_S$, $[Na^+]_S$) are not directly measureable. However, the intrinsic constants can be estimated from experimental acid-base titration data measured over a wide pH range at various electrolyte concentrations.

During the course of the potentiometric titrations, formation of surface complexes alters the acid-base equilibrium measured in the bulk solution and affects the mineral-oxide surface charge. This surface charge, determined from the proton balance in the suspensions, represents the net number of protons released or consumed by all surface reactions. From the surface charge data,
apparent stability quotients \((Q_{a1}, Q_{a2}, Q_{c}, Q_{A})\) can be computed which are related to the intrinsic equilibrium constants through an electrostatic correction term (Schindler and Gamsjäger, 1972; Hohl and Stumm, 1976). The intrinsic constants can be determined by extrapolating the apparent stability quotients to conditions of zero surface charge and potential.

Recently, James et al. (1977) and Davis and Leckie (1978) developed a graphical double extrapolation technique to obtain the intrinsic equilibrium constants. According to these authors, at low electrolyte concentrations, the mineral oxide surface charge measured by titration can be approximated by assuming simple ionization of the surface. For pH values greater than \(pH_{pzc}\), negative surface sites predominate such that

\[
[SO^-] = \sigma_o/B \tag{67}
\]

and

\[
[SOH] = (N_s - |\sigma_o|)/B \tag{68}
\]

where \(B = 10^6F/A\), and \(N_s\) is expressed in terms of charge/cm². From equation (45)

\[
K_{a2}^{\text{int}} = \frac{[SO^-](H^+)}{[SOH]} \exp(-e\psi_e/\kappa T) \tag{69}
\]
and

\[ K_{a2}^{\text{int}} = Q_{a2} \exp(-e \psi_o / kT) \]  \hfill (70)

where \( Q_{a2} \) is an apparent stability quotient evaluated from bulk solution concentrations. Substituting in the above approximations gives

\[ K_{a2}^{\text{int}} = \frac{-\sigma_o (H^+)}{N_s - [\sigma_o]} \exp(-e \psi_o / kT) \]  \hfill (71)

If the fraction of charged sites at the negative surface is defined by \( \alpha_- = -\sigma_o / N_s \) (Davis et al., 1978), then

\[ K_{a2}^{\text{int}} = (\frac{\alpha_-}{1 - \alpha_-}) (H^+) \exp(-e \psi_o / kT) \]  \hfill (72)

and in negative logarithmic form

\[ pK_{a2}^{\text{int}} = pH - \log(\frac{\alpha_-}{1 - \alpha_-}) + e \psi_o / 2.3kT \]  \hfill (73)

and

\[ pK_{a2}^{\text{int}} = pQ_{a2} + e \psi_o / 2.3kT \]  \hfill (74)

Thus, by plotting \( pQ_a \) versus \( \alpha \) and extrapolating to zero surface charge and potential (i.e., \( \alpha = 0 \)) at low electrolyte concentrations (i.e., \( I = 0 \)), values for the intrinsic constants \( pK_{a1}^{\text{int}} \) and \( pK_{a2}^{\text{int}} \) may be obtained. Similar considerations for the region less than the \( pH_{pzc} \) where
\[
[\text{SOH}_2^+] = \frac{\sigma_0}{B}, \quad [\text{SOH}] = \frac{N_s - \sigma_0}{B}
\]  
(75)

and

\[
\alpha_+ = \frac{\sigma_0}{N_s}
\]  
(76)

gives

\[
p_{\text{Kal}}^{\text{int}} = \text{pH} + \log\left(\frac{\alpha_+}{1 - \alpha_+}\right) + e\psi_0/2.3kT
\]  
(77)

At high background electrolyte concentrations, surface complexes (e.g., \text{SOH}^+\text{NO}_3^-, \text{SO}^-\text{Na}^+) dominate the surface charge development. For regions greater than the \(p\text{H}_{\text{pzc}}\) in NaNO\(_3\) electrolyte, for example, the contribution of \text{SO}^-\text{Na}^+ is greatest so that

\[
\text{SO}^-\text{Na}^+ = \frac{\sigma_0}{B}, \quad \text{SOH} = \frac{(N_s - |\sigma_0|)}{B}
\]  
(78)

and

\[
\alpha = \frac{[\sigma_0]}{N_s}
\]  
(79)

Substitution of these assumptions into

\[
\frac{K_{\text{int}}}{\text{Na}^+} = \frac{[\text{SO}^-\text{Na}^+] (H^+)}{[\text{SOH}] [\text{Na}^+]} \frac{\exp(-e\psi_0/kT)}{\exp(-e\psi_\beta/kT)}
\]  
(80)

gives

\[
\frac{K_{\text{int}}}{\text{Na}^+} = \frac{\alpha_-(H^+)}{(1 - \alpha_-)(\text{Na}^+)} \frac{\exp[(e\psi_\beta - e\psi_0)/kT]}{}
\]  
(81)
which in negative logarithmic form gives

\[ p^*_{K_{int}} = pH - \log \frac{a_-}{1 - a_-} + \log(\text{Na}^+) + e(\psi_\beta - \psi_\sigma)/2.3kT \]  

(82)

and

\[ p^*_{K_{int}} = p^*Q_{\text{Na}^+} + e(\psi_\beta - \psi_\sigma)/2.3kT \]  

(83)

Similarly, for pHs less than the pH_{pzc} in NaNO_3 electrolyte, assuming

\[ [\text{SOH}_{2}\text{NO}_3^-] = \sigma_\sigma/B, \quad [\text{SOH}] = (\sigma_\sigma - \sigma_\sigma)/B \]  

(84)

and

\[ a_+ = \sigma_\sigma/\sigma_\sigma \]

(85)

we obtain

\[ p^*_{K_{int}} = pH + \log \frac{a_+}{1 - a_+} - \log(\text{NO}_3^-) + e(\psi_\beta - \psi_\sigma)/2.3kT \]

(86)

and

\[ p^*_{K_{int}} = p^*Q_{\text{NO}_3^-} + e(\psi_\beta - \psi_\sigma)/2.3kT \]  

(87)

Plots of pQ versus \( \alpha \) can be extrapolated to zero surface charge (\( \alpha = 0 \)) and to 1m electrolyte concentration to obtain these intrinsic complexation constants. From this discussion, then, it is obvious that by selection of the
proper pH range and background electrolyte concentration, the experimentally determined surface charge provides an estimate of the surface concentration of each of the four possible surface species.

In this study, intrinsic ionization constants (pK_{a_2}) and complexation constants (pK_{cation}^{*}) were determined for α-SiO_2 and kaolinite by the double extrapolation method using the potentiometric titration data described earlier. Both minerals have relatively low points of zero charge; consequently, the lack of titration data at pHs below the p.z.c. precluded extrapolation of the constants pK_{al}^{int} and pK_{anion}^{*}. Having defined the point of zero charge for both substrates by electrophoresis, values for pK_{al}^{int} were estimated from the fact that intrinsic ionization constants are symmetrical about the pH_{PZC} (Davis et al., 1978).

Figures 62 to 69 present the graphical extrapolations of intrinsic constants for α-SiO_2 in NaNO_3, NaCl, Na_2SO_4, and CaCl_2 electrolytes. To spread out the data more evenly and increase the accuracy of the extrapolations, pQ is plotted versus α_+ + (I)^{1/2} for ionization constants and α - log I for complexation constants. The intrinsic equilibrium constants obtained for α-SiO_2 in NaNO_3 and NaCl are identical and compare favorably with those determined by Davis et al. (1978) for SiO_2 in KCl using data from
\( \alpha - \text{SiO}_2 - \text{NaNO}_3 \)

\[
pQ_{a2} = \text{pH} - \log \left( \frac{\alpha}{1 - \alpha} \right)
\]

\[
pK_{a2}^{\text{int}} = 6.95
\]

Figure 62. Double extrapolation plot for determination of \( pK_{a2}^{\text{int}} \) of \( \alpha - \text{SiO}_2 \) in \( \text{NaNO}_3 \) electrolyte solutions at 25ºC.
Figure 63. Double extrapolation plot for determination of $p^*K_{Na^+}^{int}$ of $\alpha$-SiO$_2$ in NaNO$_3$ electrolyte solutions at 25°C.
Figure 64. Double extrapolation plot for determination of $pK_{a_2}^{\text{int}}$ of $\alpha$-$\text{SiO}_2$ in NaCl electrolyte solutions at 25°C.
Figure 65. Double extrapolation plot for determination of \( p^{\text{INT}}_{\text{Na}^+} \) of \( \alpha\text{-SiO}_2 \) in \( \text{Na}_2\text{SO}_4 \) electrolyte solutions at 25°C.
Figure 66. Double extrapolation plot for determination of $pK_{a2}^{int}$ of $\alpha$-SiO$_2$ in Na$_2$SO$_4$ electrolyte solutions at 25°C.
Figure 67. Double extrapolation plot for determination of $p^*K^\text{int}_{\text{Na}^+}$ of $\alpha$-$\text{SiO}_2$ in Na$_2$SO$_4$ electrolyte solutions at 25°C.
Figure 68. Double extrapolation plot for determination of $pK_{a2}^{\text{int}}$ of $\alpha$-SiO$_2$ in CaCl$_2$ electrolyte solutions at 25°C.
Figure 69. Double extrapolation plot for determination of $p^*k_{Ca^{2+}}^{\text{int}}$ of $\alpha$-SiO$_2$ in CaCl$_2$ electrolyte solutions at 25°C.
Abendroth (1970). Surface ionization constants obtained in Na₂SO₄ and CaCl₂ are also similar; however, the intrinsic cation complexation constants determined in these electrolytes are slightly stronger. This may result from some slight surface charge asymmetry which develops in potentiometric titrations with 1:2 or 2:1 electrolytes (Davis et al., 1978).

Graphical extrapolations of the intrinsic equilibrium constants for kaolinite in NaNO₃, Na₂SO₄, and CaCl₂ electrolytes are presented in Figures 70 to 75, respectively. These extrapolations were made above pH 6 in order to minimize the effects of aluminum dissolution and precipitation discussed previously. To accomplish this, the surface charge curves were normalized to the pHₚζc measured for the kaolinite by electrophoresis. Fortunately, this normalization is not critical since near the p.z.c. the surface charge curves reach a minimum slope. Double extrapolations for the intrinsic ionization constants in all three electrolytes give pKₐ² int equal to 6.25 ± 0.1, similar to that obtained for α-SiO₂. Presumably, these ionization constants are representative of strong acid silanol-type (SiOH) surface sites. Surface complexation constants obtained by this technique vary from 3.5 to 4.5 for pKₐ Na⁺ int Na⁺ to 5.9 for pKₐ Ca⁺₂ int Ca⁺₂⁺. Westall (1981) determined pKₐ Na⁺ int Na⁺ = 3.5
Figure 70. Double extrapolation plot for determination of $pK_{a2}^{\text{int}}$ of kaolinite in NaNO$_3$ electrolyte solutions at 25°C.
Figure 71. Double extrapolation plot for determination of $p^*k^\text{int}_{\text{Na}^+}$ of kaolinite in NaNO$_3$ electrolyte solutions at 25°C.
Figure 72. Double extrapolation plot for determination of $pK^\text{int}_{a_2}$ of kaolinite in $\text{Na}_2\text{SO}_4$ electrolyte solutions at 25°C.
Figure 73. Double extrapolation plot for determination of $p^*K^\text{int}_\text{Na}^+$ of kaolinite in $\text{Na}_2\text{SO}_4$ electrolyte solutions at 25°C.
Figure 74. Double extrapolation plot for determination of $pK_{a2}^{int}$ of kaolinite in CaCl$_2$ electrolyte solutions at 25°C.
Figure 75. Double extrapolation plot for determination of $p^*K_{Ca^{2+}}^{int}$ of kaolinite in CaCl$_2$ electrolyte solutions at 25°C.
for the same kaolinite in NaCl by fitting surface charge
data with the model FIDEQL. Unfortunately, no published
data are available for intrinsic calcium complexation with
kaolinite. Additional intrinsic equilibrium constants
representative of weakly acid A1OH sites could not be
estimated by the double extrapolation technique but were
obtained by modeling the kaolinite potentiometric titrations
as described in the following section.

The intrinsic equilibrium constants determined in this
study, together with those available from previous
investigators, are summarized in Table 10 for \( \alpha-\text{SiO}_2 \) and
kaolinite.

Computation of Electrical Double-Layer Properties

Having determined numerical values for the SOH surface
equilibrium constants, the surface complexation site-binding
model was used to compute the surface properties of the
\( \alpha-\text{SiO}_2 \) and kaolinite in simple electrolyte solutions. This
was done by employing a modified version of the computer
program MINEQL originally developed by Westall et al. (1976)
and modified by James et al. (1978).

For a single site amphoteric surface such as \( \alpha-\text{SiO}_2 \),
the surface complexation site-binding model potentially has
at least eight adjustable parameters (Westall and Hohl, 1980). These are the surface area, the number of surface
Table 10. Surface parameters for $\alpha$-SiO$_2$ and kaolinite applicable to electrical double layer modeling. All data are from this study except for that for subsystem SiO$_2$/KCl reported by Abendroth (1970), as recomputed by Davis, et al., (1978). For both minerals, $C_2 = 20 \mu F/cm^2$. Data for the system beidelellite/NaOH from James and Parks (1981) are provided for comparison.

<table>
<thead>
<tr>
<th>System</th>
<th>Surface Area (m$^2$/g)</th>
<th>Surface Site Density (sites/nm$^2$)</th>
<th>pK$_{int}$al</th>
<th>pK$_{int}$a2</th>
<th>p*K$_{int}$cation</th>
<th>$C_1$ (µF/cm$^2$)</th>
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<tr>
<td>$\alpha$-SiO$_2$/NaNO$_3$</td>
<td>4.15</td>
<td>4.5</td>
<td>-0.95</td>
<td>6.95</td>
<td>6.6</td>
<td>130</td>
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<tr>
<td>$\alpha$-SiO$_2$/NaCl</td>
<td>4.15</td>
<td>4.5</td>
<td>-0.95</td>
<td>6.95</td>
<td>6.6</td>
<td>130</td>
</tr>
<tr>
<td>$\alpha$-SiO$_2$/Na$_2$SO$_4$</td>
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<td>4.5</td>
<td>-0.90</td>
<td>6.9</td>
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<tr>
<td>$\alpha$-SiO$_2$/CaCl$_2$</td>
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<td>4.5</td>
<td>-0.80</td>
<td>6.8</td>
<td>6.25</td>
<td>130</td>
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<tr>
<td>SiO$_2$/KCl</td>
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<td>NA</td>
<td>7.2</td>
<td>6.7</td>
<td>125</td>
</tr>
<tr>
<td>Kaolinite/NaNO$_3$</td>
<td>12.3</td>
<td>6.0</td>
<td>1.75*</td>
<td>6.25</td>
<td>3.5*</td>
<td>240</td>
</tr>
<tr>
<td>Kaolinite/Na$_2$SO$_4$</td>
<td>12.3</td>
<td>6.0</td>
<td>1.75*</td>
<td>6.2</td>
<td>4.25*</td>
<td>240</td>
</tr>
<tr>
<td>Kaolinite/CaCl$_2$</td>
<td>12.3</td>
<td>6.0</td>
<td>1.80*</td>
<td>6.25</td>
<td>5.9*</td>
<td>240</td>
</tr>
<tr>
<td>Beidelellite/NaOH</td>
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<td>?</td>
<td>NA$^+$</td>
<td>6.0</td>
<td>3.0$^+$</td>
<td>250</td>
</tr>
</tbody>
</table>
Table 10 (continued)

*Other intrinsic constants determined for TOH sites: \( p^{\text{int}}_{k_{a2},\text{TOH}} = 7.4; \)
\( p^{\text{int}}_{k_{\text{cation}}} = 7.4 \)

\( p^{\text{int}}_{k_{a2},\text{TOH}} = 7.4; \ \ p^{\text{int}}_{k_{\text{Na}^+,\text{TOH}}} = 7.4 \)
sites (Nₙ), the inner and outer layer capacitances (C₁ and C₂), the surface hydrolysis constants (K⁺₁ and K⁺₂), and the surface complexation constants (*K⁺⁺ and *K⁻⁻). However, as noted by Davis et al. (1978), the intrinsic equilibrium constants, surface area, and surface site density are all fixed parameters derived from measurable surface properties. The only two adjustable parameters, therefore, are the inner and outer layer capacitances which may be determined by properly fitting the potentiometric titration data or surface charge data with the revised MINEQL program. This approach was used to determine the surface properties of α-SiO₂.

For a mixed two-site surface such as kaolinite, the number of adjustable model parameters increases with the number of intrinsic constants required to describe additional surface functional groups. In this study, the intrinsic constants for the weakly acidic TOH sites representing ALOH surface sites were used along with C₁ and C₂ as adjustable parameters to determine the surface properties of kaolinite.

α-SiO₂: a single site surface

Stumm et al. (1970) and Lyklema and Overbeek (1961) found that an outer layer capacitance of 20 μF/cm² provided reasonable agreement for electrokinetic data with AgI and
Hg. This value for $C_2$ is the generally accepted value for most oxide surfaces as well (cf. Hsi, 1981; Balistrieri and Murray, 1981), and was adopted for use in this study for both $\alpha$-SiO$_2$ and kaolinite. James and Parks (1981) and Davis et al. (1978) found that an inner layer capacitance of 125 $\mu$F/cm$^2$ and an outer layer capacitance of 20 $\mu$F/cm$^2$ gave good agreement between the site-binding model and the surface charge data measured by Abendroth (1970) on pyrogenic silica. In this study, a value for $C_1 = 130$ $\mu$F/cm$^2$ provided the best agreement between the model calculations and the experimental surface charge data on $\alpha$-SiO$_2$. In Figures 76 to 79, the model calculations are compared with the experimental surface charge data in NaNO$_3$, NaCl, Na$_2$SO$_4$, and CaCl$_2$ electrolytes. The solid curves in these figures depict the surface complexation site-binding model calculations and the symbols represent the experimental data. Generally, good to excellent agreement was obtained between the experimentally determined surface charge data and model calculations for all four electrolytes. Some discrepancy ($<5$ $\mu$C/cm$^2$) is apparent between the model calculations and the experimental data for the NaNO$_3$ electrolyte, but this can be attributed to titrator error in the addition of titrant.
Figure 76. Experimental and computed surface charge density of $\alpha$-SiO$_2$ dispersions in NaNO$_3$ electrolyte solutions at 25°C as a function of pH and ionic strength.
Figure 77. Experimental and computed surface charge density of α-SiO₂ dispersions in NaCl electrolyte solutions at 25°C as a function of pH and ionic strength.
Figure 78. Experimental and computed surface charge density of $\alpha$-SiO$_2$ dispersions in Na$_2$SO$_4$ electrolyte solutions at 25$^\circ$C as a function of pH and ionic strength.
Figure 79. Experimental and computed surface charge density of α-SiO₂ dispersions in CaCl₂ electrolyte solutions at 25°C as a function of pH and ionic strength.
Kaolinite: a mixed site surface

In order to describe the double layer properties of kaolinite and simultaneously determine the necessary intrinsic ionization and complexation constants for weakly acidic surface functional groups, several assumptions were necessary regarding charge development at the mineral surface. In this study, it was assumed that the kaolinite surface could be represented by a mixture of two distinct functional groups corresponding to SiOH and ALOH sites. These surface sites were incorporated in the model calculations assuming they represented hypothetical SOH (strong acid) and TOH (weak acid) sites, respectively, as described previously. Intrinsic equilibrium constants for the SOH (SiOH) sites were determined by the double extrapolation technique. Intrinsic equilibrium constants for the TOH (AlOH) sites were derived by adjusting model calculations of the potentiometric titrations to the experimental data at pHs above 8.5. It was further assumed that the surface charge development of the kaolinite is due primarily to surface ionization and complexation reactions. Surface charge due to isomorphous substitution in the clay lattice was neglected since measured cation exchange capacities were minimal at moderately acid pHs. Currently, it is not possible to determine the absolute
number of SiOH and ALOH surface functional groups. Based on
the chemical composition of kaolinite \((Al_2Si_2O_5(OH)_4)\), the
total number of SiOH surface sites was set equal to the
total number of ALOH surface sites, such that

\[
N_s^{SOH} = N_s^{TOH} \tag{88}
\]

and

\[
N_s^{TOTAL} = N_s^{SOH} + N_s^{TOH} \tag{89}
\]

Using assumptions similar to those above, Garrels and
Christ (1956) and Blackmon (1958) described the ion exchange
behavior of a beidellite, illite, and montmorillonite clay
based on the acid-base titration data of Marshall and others
(Marshall and Bergman, 1942a, 1942b; Marshall and Krinbill,
1942). These authors assumed that ion exchange occurred
through the reactions

\[
HC + K^+ \leftrightarrow KC + H^+ \tag{90}
\]

and

\[
HE + K^+ \leftrightarrow KE + H^+ \tag{91}
\]

and were able to evaluate values for \(K_{KC-HC}\) and \(K_{KE-HE}\) by
adjusting the total concentrations of the two clay acid
sites, HC and HE. In this study, it was assumed that the
surface sites HC and HE are equivalent to the strong acid SOH (SiOH) and weak acid TOH (AlOH) sites, respectively. Recently, James and Parks (1981) have improved on the work of Garrels and Christ (1956), and Blackmon (1958) by adding electrical double-layer constraints to the calculations and allowing for ionization of the surface described by the reactions

\[ \text{SOH} \leftrightarrow \text{SO}^- + \text{H}^+ \quad (92) \]

and

\[ \text{TOH} \leftrightarrow \text{TO}^- + \text{H}^+ \quad (93) \]

With these modifications, James and Parks (1981) modeled potentiometric titration curves for a Putnam clay (beidellite) and derived values for $K_{\text{int}, \text{SOH}, \text{Na}^+}$, $K_{\text{int}, \text{SOH}, \text{Na}^+}$, $K_{\text{int}, \text{TOH}, \text{Na}^+}$, and $K_{\text{int}, \text{TOH}, \text{Na}^+}$. The surface equilibrium constants determined by these authors for the Putnam clay are summarized in Table 10.

In this study, the potentiometric titrations for kaolinite were reproduced using the SOH intrinsic equilibrium constants estimated in the previous section. The inner and outer layer capacitances ($C_1$ and $C_2$) and the TOH surface equilibrium constants ($K_{\text{int}, \text{TOH}}$ and $K_{\text{int}, \text{cation}, \text{TOH}}$) were used as model adjustable parameters.
Results of the model calculations for systems with NaNO$_3$, Na$_2$SO$_4$, and CaCl$_2$ as background electrolytes are presented in Figures 80 to 82 along with the experimentally determined potentiometric titration data.

In modeling each of the titrations, the best agreement with the experimental data was obtained with $C_1 = 240 \ \mu$F/cm$^2$, $C_2 = 20 \ \mu$F/cm$^2$, $pK_{\text{int}}^{\text{a}_2,\text{TOH}} = 7.4$, and $pK_{\text{int}}^{\text{cation},\text{TOH}} = 7.4$, identical to the constants used for the Putnam clay previously described by James and Parks (1981). Aside from these constants, it was also found that the potentiometric titrations could be successfully modeled with $pK_{\text{int}}^{\text{a}_2,\text{TOH}} = 9.1$ and $pK_{\text{int}}^{\text{cation}} = 7.5$, representative of a gibbsite-type AlOH surface site having a pH$_{\text{pzc}}$ of 8.5 (Huang and Stumm, 1973). These findings together suggest (1) that the surface charge development of kaolinite is similar to that for the Putnam clay, and (2) that the intrinsic constants determined for a given clay mineral may be applicable to describing the surface properties of another. Additionally, it may be hypothesized that the surface behavior of complex mineral oxides can be described by intrinsic equilibrium constants consistent with each of the mineral oxide components. This is to say that the surface properties of kaolinite may possibly be modeled using a combination of intrinsic equilibrium constants for
Figure 80. Experimental and computed potentiometric titration curves for kaolinite in NaNO₃ electrolyte solutions at 25°C assuming initial $\sum \text{Al(aq)} = 10^{-3.0}$ m at pH = 3.
Figure 81. Experimental and computed potentiometric titration curves for kaolinite in Na$_2$SO$_4$ electrolyte solutions at 25°C assuming initial $\Sigma$Al(aq) = 10$^{-3.0}$ m pH = 3.
Figure 82. Experimental and computed potentiometric titration curves for kaolinite in CaCl₂ electrolyte solutions at 25°C assuming $P_{CO_2} = 10^{-4.5}$ atm and initial $\Sigma Al(aq) = 10^{-3.55}$ m at pH = 3.
the separate octahedral gibbsite layer and the tetrahedral silica layer. Unfortunately, it was not possible to fully test this hypothesis because of the limited ionization of TOH sites at pHs greater than 8.0 and the resulting insensitivity of TOH surface intrinsic constants to the potentiometric titrations.

More importantly, it was discovered that the kaolinite titrations could be described with reasonable success employing solely the intrinsic equilibrium constants for the SOH sites and neglecting the ionization or complexation of TOH sites. This indicates that the silanol (SiOH) surface sites are the principal functional group responsible for the pH dependent surface charge of kaolinite. Moreover, it is conceivable that the SOH sites are representative of the silica sites at the edges of the clay particles and that their slightly stronger tendency for ionization than those on α-SiO₂ results from some slight charge imbalance within the clay lattice.

During the kaolinite acid-base titrations described in a previous section, it was noted that excessive hydroxide was required to raise the suspension pH from 3.0 to 4.5. This titrant consumption was presumed due to (1) the hydrolysis of dissolved aluminum, and (2) the precipitation of amorphous aluminum hydroxide. It was also noted that the
effects of these aluminum reactions were most pronounced at high ionic strengths. For this reason, modeling of the kaolinite titrations was limited to those suspensions having the shortest exposure to acid pHs. Nevertheless, in order to accurately model the kaolinite titrations at pHs less than 4.5, it was necessary to assume the presence of dissolved aluminum during the titrations. The presence of dissolved aluminum was confirmed by atomic adsorption analysis of solutions, which were removed from separate kaolinite suspensions equilibrated for the same time as the titrated suspensions. For the titrations in NaNO₃ and Na₂SO₄ electrolytes, 25 ppm Al (III) was assumed present in the initial solutions at pH = 3. For the CaCl₂ suspensions which were only equilibrated for a few hours, the titration results were adjusted assuming an initial Al (III) concentration of 7.5 ppm and P_{CO₂} = 10^{-4.5} \text{ atm at pH} = 3. At pHs above 3, the dissolved aluminum concentration was controlled by speciation reactions and precipitation of Al(OH)_3(\text{am})(K_{sp} = 10^{-32.3}).

After having successfully modeled the kaolinite acid-base titrations, the estimated intrinsic equilibrium constants for both the SOH and TOH sites were used to calculate hypothetical surface charge curves for the kaolinite as a function of pH and ionic strength. These
curves, presented in Figures 83 to 85, are very similar to those determined for α-SiO₂ and further emphasize the importance of SiOH sites to the surface charge development of the clay.

To further test the applicability of the surface complexation site-binding model in describing the surface properties of kaolinite, the variation of the diffuse layer potential, \( \psi_d \), with pH was calculated. The calculated potential is plotted in Figure 86 along with the electrophoretic mobility data for the clay. The agreement between the experimental data and theory is far from perfect; however, there is at least qualitative agreement in the position and shapes of the calculated potential curves, particularly at low ionic strengths. Accurate representation of the experimental data is most likely hindered by the nonspherical geometry of the clay particles.

Adsorption Modeling of Thorium and Radium on Quartz and Kaolinite

The experimental data for Th(IV) and Ra(II) adsorption on α-SiO₂ and kaolinite were used to assess the utility of the surface complexation site-binding model in predicting the adsorption of trace metal ions from dilute solutions. In the following sections, this model is tested in systems
Figure 83. Computed surface charge density for kaolinite dispersions in NaNO$_3$ electrolyte solutions at 25°C as a function of pH and ionic strength.
Figure 84. Computed surface charge density for kaolinite dispersions in Na₂SO₄ electrolyte solutions at 25°C as a function of pH and ionic strength.
Figure 85. Computed surface charge density for kaolinite dispersions in CaCl$_2$ electrolyte solutions at 25°C as a function of pH and ionic strength.
Figure 86. Experimental and computed variation of the diffuse layer potential for kaolinite as a function of pH and ionic strength.
containing metal complexing ligands and competing ions at various ionic strengths and as a function of pH.

Adsorption of thorium species from pure water

According to the surface complexation site-binding model, metal ion adsorption reactions may be written in a manner analogous to the surface complexation reactions involving supporting electrolyte ions. For thorium (IV) adsorption onto α-SiO₂ as depicted in Figure 28, one may assume, for example, that Th⁴⁺ is the only thorium species adsorbed at the quartz-water interface. This adsorption may be described by the reaction:

\[ \text{SOH} + \text{Th}_s^{4+} + \text{SO}^- \rightarrow \text{Th}_s^{4+} + \text{H}_s^+ \]  

(94)

where the subscripts s denote the surface concentrations of the dissolved species, and SOH and SO⁻ represent the quartz surface. As with the supporting electrolyte ions, this reaction can be rewritten in terms of the bulk concentrations of the ions and the electrostatic potentials corresponding to the adsorption planes of mean charge, \( \sigma_\alpha \) and \( \sigma_\beta \), as follows:

\[ [\text{SO}^- - \text{Th}^{4+}] = K_{\text{int}} \frac{[\text{SOH}][\text{Th}^{4+}]}{[\text{H}^+] \exp[e(\psi_\alpha - 4\psi_\beta)/kT]} \]  

(95)
This reaction was incorporated in the input data to the program MINEQL to model the adsorption of thorium (IV) on α-SiO₂. In addition to this reaction, the surface ionization and complexation reactions for α-SiO₂ described by the parameters \( K_{a1}^{\text{int}} \), \( K_{a2}^{\text{int}} \), \( K_{\text{cation}}^{\text{int}} \), \( C_1 \), \( C_2 \), and \( N_S \) were also incorporated as input to the computer program.

Assuming this single reaction to describe thorium (IV) adsorption, the model calculated adsorption isotherm versus pH (the lower curve in Figure 87) is in very poor agreement with the experimental data. Adjustment of the value for \( K_{\text{int}}^{\text{Th}^{4+}} \) does not improve the model fit, but only raises or lowers the calculated adsorption density without changing its pH dependence. The slope of the experimental percent adsorption data suggests that more than one proton is released per Th(IV) ion adsorbed. However, there are two additional surface reactions which may account for the release of additional protons. The first involves adsorption of thorium hydroxy complexes, while the second possibility requires formation of multidentate surface complexes as proposed by Schindler et al. (1976). In this study, it was found that consideration of multidentate surface complexes did not significantly improve model calculated adsorption. In fact, formation of these surface complexes by reactions, such as
Figure 87. Adsorption of thorium (IV) on α-SiO₂ at 25°C in 0.01m NaNO₃. Circles denote the experimental data. Solid curves are model calculated and consider different surface reactions of Th(IV).
\[
\text{Th}_s^{4+} + 2\text{SOH} + (\text{SO}^-)_2 - \text{Th}_s^{4+} + 2\text{H}_s^+
\]

(96)

was relatively insensitive to pH. This is because of the increased dependence of adsorption on \(\psi_o\) which is evident if we rewrite the adsorption reaction consistent with electrical double layer theory, as

\[
[(\text{SO}^-)_2 - \text{Th}^{4+}] = \beta_{\text{int}} \frac{[(\text{SOH})_2][\text{Th}^{4+}]}{[\text{H}^+]^2} x 
\exp[(2e\psi_o - 4e\psi_B)/kT]
\]

(97)

where \(\beta_{\text{int}}\) represents the intrinsic constant for a multidentate surface complex. In this equation, the quadratic dependence on pH is counterbalanced by increased dependence on \(\psi_o\) reducing the coulombic repulsion of \(\text{H}^+\) at the \(\sigma_o\) plane. This dependence has been discussed in detail by Davis and Leckie (1978) with respect to lead complexes on the surface of amorphous iron oxyhydroxides. In this study, therefore, the formation of multidentate complexes was considered insignificant.

Because the experimental thorium (IV) adsorption data could not be satisfactorily modeled, assuming \(\text{Th}^{4+}\) was the principal species adsorbed, it was apparent that thorium hydroxy complexes must also be adsorbed. Examination of the percentage distribution diagram for thorium (IV) in pure water (Figure 1) indicates that the hydroxy complexes,
ThOH\textsuperscript{3+}, Th(OH)\textsubscript{2}\textsuperscript{2+}, Th(OH)\textsuperscript{3+}, and Th(OH)\textsubscript{4}\textsuperscript{0} predominate over much of the pH range for which thorium is most strongly adsorbed (i.e., pH > 2.5). Further, adsorption of the hydroxy complexes is consistent with the additional proton release upon adsorption, since during complex formation protons are released by hydrolysis of the metal ion. According to MacNaughton and James (1974), the adsorption of a free metal ion followed by hydrolysis at the solid-water interface is thermodynamically equivalent to adsorption of the hydrolyzed complex. It was, therefore, assumed that thorium hydroxy complexes were also adsorbed by α-SiO\textsubscript{2} according to the reactions:

\begin{align*}
\text{SOH} + \text{Th}^{4+} + \text{H}_2\text{O} & \rightleftharpoons \text{SO}^- + \text{ThOH}^{3+} + 2\text{H}^+ \quad (98) \\
\text{SOH} + \text{Th}^{4+} + 2\text{H}_2\text{O} & \rightleftharpoons 2\text{SO}^- + \text{Th(OH)}^{2+} + 3\text{H}_2\text{O} \quad (99) \\
\text{SOH} + \text{Th}^{4+} + 3\text{H}_2\text{O} & \rightleftharpoons 3\text{SO}^- + \text{Th(OH)}^{3+} + 4\text{H}_2\text{O} \quad (100) \\
\end{align*}

and

\begin{align*}
\text{SOH} + \text{Th}^{4+} + 4\text{H}_2\text{O} & \rightleftharpoons 4\text{SO}^- + \text{Th(OH)}^{4+} + 5\text{H}_2\text{O} \quad (101) \\
\end{align*}

In order to investigate the contribution of each of these complexes to the adsorption of thorium (IV), the mass action
equations were rewritten in accordance with the electrical double layer requirements of the site-binding model as follows:

\[
[\text{SO}^- - \text{ThOH}^{3+}] = \frac{K_{\text{ThOH}}^{\text{int}}}{[\text{H}^+]} \frac{[\text{SOH}][\text{Th}^{4+}]}{[\text{H}^+]^2} \times \exp \left[ \frac{(e\psi_0 - 3e\psi_\beta)}{kT} \right] \tag{102}
\]

\[
[\text{SO}^- - \text{Th(OH)}_{2}^{2+}] = \frac{K_{\text{Th(OH)}}^{\text{int}}}{[\text{H}^+]} \frac{[\text{SOH}][\text{Th}^{4+}]}{[\text{H}^+]^3} \times \exp \left[ \frac{(e\psi_0 - 2e\psi_\beta)}{kT} \right] \tag{103}
\]

\[
[\text{SO}^- - \text{Th(OH)}_{3}^{+}] = \frac{K_{\text{Th(OH)}}^{\text{int}}}{[\text{H}^+]} \frac{[\text{SOH}][\text{Th}^{4+}]}{[\text{H}^+]^4} \times \exp \left[ \frac{(e\psi_0 - e\psi_\beta)}{kT} \right] \tag{104}
\]

and

\[
[\text{SO}^- - \text{Th(OH)}_{4}^{0}] = \frac{K_{\text{Th(OH)}}^{\text{int}}}{[\text{H}^+]} \frac{[\text{SOH}][\text{Th}^{4+}]}{[\text{H}^+]^5} \times \exp \left( \frac{e\psi_0}{kT} \right) \tag{105}
\]

Each adsorption reaction was added to the computer program and tested to determine which hydroxy complex best fit the experimental data (see Figure 87). Significantly better agreement was obtained between the model calculated adsorption curve and the experimental data by assuming that Th(OH)_{2}^{2+} was the principal species responsible for Th(IV)
adsorption. This agreement was improved upon by allowing simultaneous adsorption of the ThOH$^{3+}$, Th(OH)$_3^+$, and Th(OH)$_4^0$ complexes along with Th(OH)$_2^{2+}$. In fact, according to the model calculations, the contribution of equation 97 to surface adsorption was so small that it could be neglected, indicating that only the thorium hydroxy complexes are significantly adsorbed by α-SiO$_2$. It was found that a combination of $pK^{\text{int}}_{\text{ThOH}}^{3+} = -0.6$, $pK^{\text{int}}_{\text{Th(OH)}}^{2+} = 3.7$, $pK^{\text{int}}_{\text{Th(OH)}}^+ = 9.8$, and $pK^{\text{int}}_{\text{Th(OH)}}^0 = 15.5$ gave the best agreement between the model calculations and experimental results for adsorption from solutions containing $10^{-5}$ and $10^{-5.85}$m Th(IV) (Figure 88).

Although the model calculated adsorption curves fit the experimental data extremely well when plotted as percent thorium (IV) adsorbed versus pH, the same agreement was not always found when results were plotted in terms of total dissolved thorium (IV) versus pH. Figures 89 and 90 show the model calculated curves for $10^{-2}$m NaNO$_3$ solutions containing $10^{-5}$ and $10^{-5.85}$m thorium (IV), respectively. Figure 89 shows that the model calculated curve fits the experimental data very well over the full pH range from 2.5 to 6.0. However, Figure 90 shows that the theoretical adsorption curve deviates from the experimental data at dissolved thorium (IV) concentrations less than 15 ppb. In
Figure 88. Adsorption of thorium (IV) vs pH onto α-SiO$_2$ at 25°C with I = 0.01m (NaNO$_3$). Circles and triangles are experimental data for ΣTh = 10^{-5.85} m and 10^{-5} m. Solid curves are model calculated assuming the surface equilibria shown in the Figure.
Figure 89. Adsorption of thorium (IV) onto α-SiO₂ at 25°C with ΣTh = 10⁻⁵ m and I = 0.01 m (NaNO₃). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
Figure 90. Adsorption of thorium (IV) onto α-SiO₂ at 25°C with ΣTh = 10⁻⁵.₈₅ m and I = 0.01 m (NaNO₃). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
these and subsequent figures, the analytical error of the experimental data is represented by the vertical bars through the data points. In comparing the two figures, it is apparent that the adsorption model correctly predicts that more thorium should be removed from the solution originally containing $10^{-5.85}$ m thorium; however, the experimental data in both figures level off at 10 to 15 ppb dissolved thorium. This discrepancy is attributed to trace amounts of adsorbent in the supernatant which were not completely removed during centrifugation. If 0.8 mg of quartz remained in the supernatant, its adsorbed thorium would be sufficient to account for the apparent leveling of dissolved thorium at 10 ppb.

Adsorption of thorium from Na$_2$SO$_4$ solutions

As discussed in a previous section, sulfate complexing strongly inhibits the adsorption of thorium (IV) and favors desorption, particularly at pHs below 5.0. The percent distribution diagrams in Figures 2 to 4 for total Th(IV) = $10^{-5}$ m in Na$_2$SO$_4$ electrolyte solutions indicate that ThSO$_4^{2+}$, Th(SO$_4$)$_2^0$, and Th(SO$_4$)$_3^{2-}$ complexes are the predominant dissolved thorium species at pHs less than 4.5 to 5.0. Comparison of these figures with the adsorption data for $\alpha$-SiO$_2$ and kaolinite (Figures 40 to 42, and 46) indicate that the thorium sulfate complexes are probably not
adsorbed on \(\alpha\text{-SiO}_2\) and only partially adsorbed on kaolinite. In \(\alpha\text{-SiO}_2\) suspensions, the thorium (IV) adsorption edge shifts to higher pH with increasing sulfate concentration, and its position coincides closely with the formation of thorium hydroxy complexes. In kaolinite suspensions, the presence of sulfate also shifts the adsorption edge to higher pH, but thorium adsorption still occurs in the pH range where thorium sulfate complexes predominate.

With the intrinsic complexation constants given in Figure 89 and the other surface parameters listed in Table 10, the surface complexation site-binding model was used to calculate Th(IV) adsorption curves for \(\alpha\text{-SiO}_2\) in the presence of \(\text{Na}_2\text{SO}_4\) electrolyte. Figures 91 to 93 show that the model calculated curves agree extremely well with the experimental data neglecting adsorption of thorium sulfate complexes. The dashed lines in these figures again represent the precipitation of amorphous thorium hydroxide determined from "blank" adsorption experiments which were adsorbent-free. Efforts to incorporate thorium sulfate adsorption reactions in the model calculated adsorption curves only detracted from the accuracy of the model fits to the experimental data.
Figure 91. Adsorption of thorium (IV) onto α-SiO$_2$ at 25°C with ΣTh = 10$^{-5}$m and I = 0.001m (Na$_2$SO$_4$). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
Figure 92. Adsorption of thorium (IV) onto α-SiO₂ at 25°C with ΣTh = 10⁻⁵ m and I = 0.01 m (Na₂SO₄). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
Figure 93. Adsorption of thorium (IV) onto α-SiO₂ at 25°C with ΣTh = 10⁻⁵ m and I = 0.1 m (Na₂SO₄). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
Adsorption modeling of thorium (IV) on kaolinite was accomplished by arbitrarily selecting intrinsic adsorption constants for the reaction

$$\int K_{\text{ThSO}_4^{2+}} \quad \text{Th}_s^{4+} + \text{SOH} + \text{SO}_4^{2-} + 4 \text{SO}^- = \text{ThSO}_4^{2+} + \text{H}_s^+$$ (106)

in combination with surface complexation reactions for the hydrolyzed thorium complexes \(\text{ThOH}^{3+}, \text{Th(OH)}_2^{2+}, \text{and Th(OH)}_3^+\) as follows:

$$\int K_{\text{ThOH}^{3+}} \quad \text{Th}_s^{4+} + \text{SOH} + \text{H}_2\text{O} \quad \text{SO}^- = \text{ThOH}^{3+} + 2\text{H}_s^+$$ (107)

$$\int K_{\text{Th(OH)}_2^{2+}} \quad \text{Th}_s^{4+} + \text{SOH} + 2\text{H}_2\text{O} \quad 2\text{SO}^- = \text{Th(OH)}_2^{2+} + 3\text{H}_s^+$$ (108)

and

$$\int K_{\text{Th(OH)}^+} \quad \text{Th}_s^{4+} + \text{SOH} + 3\text{H}_2\text{O} \quad 3\text{SO}^- = \text{Th(OH)}^+ + 4\text{H}_s^+$$ (109)

In addition to these reactions, the surface parameters \(K_{\text{al},\text{SOH}, K_{\text{a}_2\text{SOH}}}, K_{\text{Na}_+\text{SOH}, K_{\text{Na}_2\text{SOH}}}, K_{\text{Na}_+\text{TOH}, K_{\text{Na}_2\text{TOH}}}, C_1, C_2, N_{\text{SOH}}, \text{and } N_{\text{TOH}}\) determined in previous sections were incorporated in the computer program to define the adsorptive properties of the clay. The best agreement between the experimental data and the model calculations was obtained with \(pK_{\text{ThSO}_4^{2+}} = -8.0, pK_{\text{ThOH}^{3+}} = -0.2,\)
$pK_{\text{int}}^{\text{Th(OH)}}_{2} = 4.6$, and $pK_{\text{int}}^{\text{Th(OH)}}_{3} = 10.1$. Incorporation of reactions for adsorption of the complexes $\text{Th(SO}_4)^{2-}_2$ and $\text{Th(SO}_3)^{2-}_3$ did not improve model fits of the experimental data. Results of the model calculations are shown in Figure 94 along with the experimental data for $\text{Na}_2\text{SO}_4$ solutions having an ionic strength of $10^{-3}$, $10^{-2}$, and $10^{-1}$ m.

Agreement between the theoretically calculated adsorption curves and the adsorption data is not perfect, but there is at least qualitative agreement in the shape and position of the curves. The plot shows that at high sulfate concentrations more thorium is adsorbed than is predicted by the model calculations. This discrepancy may be due to coupled adsorption in which thorium sulfate complexes are adsorbed to the mineral oxide surface through the sulfate ligand. Alternatively, there may be a sufficient number of positive sites on the kaolinite surface to allow for adsorption of the $\text{Th(SO}_4)^{2-}_3$ complex which becomes more important (15% of $\Sigma\text{Th(IV)}$) at high sulfate concentrations.

Accurate determination of these effects requires the extrapolation of intrinsic surface complexation constants for $\text{HSO}_4^-$ and $\text{SO}_4^{2-}$. In this study, determination of these constants was not possible due to the inaccuracy of potentiometric titration data below the p.z.c. of the kaolinite and the instability of the clay in strong acid solutions.
Figure 94. Adsorption of thorium (IV) onto kaolinite at 25°C with ΣTh = 10⁻⁵m and I = 0.001, 0.01, and 0.1m (Na₂SO₄). Solid curves are model calculated assuming the surface equilibria shown in the Figure.
Adsorption of radium from pure water

The surface complexation constants that describe the adsorption of radium (II) on α-SiO₂ and kaolinite were determined in a manner similar to that discussed for thorium (IV) adsorption in the previous sections. Values for the constants were arbitrarily selected and tested with the revised MINEQL program until the adsorption data as a function of pH could be reproduced. The calculations also required consideration of the intrinsic constants for the electrolyte ions, the surface hydrolysis constants, the inner and outer layer capacitances, and the surface site densities listed in Table 10 for each of the sorbents.

Two reactions were used to describe the adsorption of radium (II) on α-SiO₂ and kaolinite. These reactions describe the adsorption of the free metal ion, Ra²⁺, and the first hydrolysis product, RaOH⁺, as follows:

\[
K_{\text{Ra}^{2+}}^{\text{int}} \quad \text{SOH} + \text{Ra}^{2+}_S \quad \leftrightarrow \quad \text{SO}^- + \text{Ra}^{2+} + H^+_S \quad (110)
\]

and

\[
K_{\text{RaOH}^+}^{\text{int}} \quad \text{SOH} + \text{Ra}^{2+}_S + H_2O \quad \leftrightarrow \quad \text{SO}^- + \text{RaOH}^+ + 2H^+_S \quad (111)
\]

where SOH represents a hypothetical surface site on either mineral oxide. The reactions were incorporated in the model
calculations by rewriting the mass action expressions to include the necessary double layer corrections to the surface concentrations of Ra\(^{2+}\) and H\(^+\), so that:

\[
[SO^- - Ra^{2+}] = \frac{K_{Ra_2^+}^{int} [SOH][Ra^{2+}]}{[H^+]^n} \exp[e(\psi_o - 2\psi_b)/kT]
\]  

(112)

and

\[
[SO^- - RaOH^+] = \frac{K_{RaOH}^{int} [SOH][Ra^{2+}]}{[H^+]^2} \exp[e(\psi_o - \psi_b)/kT]
\]  

(113)

For radium (II) adsorption on α-SiO\(_2\), the best agreement between the experimental data and the model calculated adsorption curve was obtained with \(pK_{Ra_2^+}^{int} = -2.2\), and \(pK_{RaOH}^{int} = 7.5\) (see Figure 95). Close agreement was found between the experimental data and the theoretically calculated adsorption curve. Since the adsorption data were obtained at pHs for which Ra\(^{2+}\) is the predominant aqueous species, it is apparent that the contribution of equation (110) to the total radium adsorbed is minimal. Nevertheless, the adsorption of RaOH\(^+\) is included in the calculations since it improves the model fit at high pH and is likely to be important because of the
Figure 95. Adsorption of radium (II) onto α-SiO$_2$ at 25°C with I = 0.01 m (NaCl). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
large positive entropy change caused by the neutralization of charge within the double layer (Davis and Leckie, 1979; 1980).

For radium (II) adsorption on kaolinite, it was found that significant corrections to the model calculations were required in order to successfully fit the experimental data. Results of the model calculations are shown in Figure 96, adjusted by 20% to account for the specific adsorption of radium below pHs of 4.5 (see below). The model calculated adsorption curve was obtained with $p^{*}K_{Ra}^{int^+} = 1.1$, and $p^{*}K_{RaOH^+} = 10.1$.

At pH values less than the p.z.c., where kaolinite has a net positive surface charge, approximately 20% of the total radium has already been adsorbed. In the same pH range, the surface complexation site-binding model predicts that only a few percent of the total radium should be adsorbed. This adsorption, as discussed previously, most likely occurs because of a slight charge imbalance in the kaolinite lattice which produces limited ionization of the SiOH or AlOH surface sites. Formation of these surface sites may be the result of incongruent dissolution of the clay at acid pH, or be caused by lattice substitutions of trace constituents. According to the work of Schofield and Samson (1953), replacement of only one silicon atom in 400
Figure 96. Adsorption of radium (II) onto kaolinite at 25°C with I = 0.01 m (NaNO₃). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
by aluminum is sufficient to obtain a cation exchange capacity of 2 meq/100g for kaolinite. Similar calculation in this study indicates that replacement of only one silicon atom in $10^{11}$ is necessary to produce an exchange capacity sufficient to remove all the radium from solution. Under these circumstances, it is unrealistic to expect that the model can accurately predict the adsorption of only picograms of Ra(II).

Effect of calcium competition on radium adsorption

As discussed in a previous section, the presence of calcium in radium-bearing solutions strongly inhibits the adsorption of Ra(II) and favors desorption, particularly at alkaline pHs. In this study, an effort was made to model the competitive effects of dissolved calcium on radium adsorption onto both $\alpha$-SiO$_2$ and kaolinite. To accomplish this, it was first necessary to determine the intrinsic complexation constants for calcium adsorption alone. Two reactions were used to model the formation of calcium surface complexes. These reactions describe the adsorption of the free ion, Ca$^{2+}$, and the first hydrolysis product, CaOH$^+$, as follows:

$$SOH + Ca^{2+}_S \leftrightarrow SO^- + Ca^{2+} + H^+_S \quad (114)$$
and

$$\begin{align*}
\text{SOH} + \text{Ca}^{2+} + \text{H}_2\text{O} & \quad \Rightarrow \quad \text{SO}^- - \text{CaOH}^+ + 2\text{H}_s^+ \\
\end{align*}$$

(115)

where SOH represents a hypothetical surface site on the adsorbents. With the intrinsic equilibrium constants and other surface parameters listed in Table 10, the model was used to calculate Ca(II) percent adsorption curves for $\alpha$-SiO$_2$ and kaolinite in the presence of $10^{-2}$m NaNO$_3$.

Results of the model calculations for $10^{-4}$m Ca with $\alpha$-SiO$_2$ and $10^{-3}$ and $10^{-4}$m Ca with kaolinite are shown in Figures 97 and 98, respectively. The figures show that the model calculated adsorption curves agree reasonably well with the experimental data, particularly for $\alpha$-SiO$_2$. The best fit of the adsorption data for $\alpha$-SiO$_2$ was obtained with $pK_{\text{Ca}^{2+}}^{\text{int}} = -2.0$ and $pK_{\text{CaOH}^+}^{\text{int}} = 8.5$. For kaolinite, the model calculations accurately reproduce the $10^{-3}$m adsorption data, but predict significantly less adsorption from the $10^{-4}$m calcium solution at pHs less than 7. The model curves shown in Figure 98 were obtained with $pK_{\text{Ca}^{2+}}^{\text{int}} = 1.7$ and $pK_{\text{CaOH}^+}^{\text{int}} = 11.45$. The discrepancy between the model calculations and the experimental adsorption data is attributed to the specific adsorption of Ca$^{2+}$ on kaolinite below the pH$_{pzc}$. Here, again, the discrepancy becomes more apparent and increasingly more important in the model calculations as the total metal concentration decreases.
\[ \alpha-\text{SiO}_2 \rightarrow \text{NaNO}_3 \]

5 g/l (20.75 m\(^2\)/l)  
\( \Sigma Ca = 0.0001 \text{ m} \)  
I = 0.01 m

\[ \text{SO}^- - \text{Ca}^{2+} \quad p^*K_{\text{mt}} \]

\[ \text{SO}^- - \text{CaOH}^+ \quad 8.5 \]

Figure 97. Adsorption of calcium (II) onto \( \alpha-\text{SiO}_2 \) at 25\(^\circ\)C with \( \Sigma Ca = 10^{-4}\text{m} \) and I = 0.01m (NaNO\(_3\)). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
Figure 98. Adsorption of calcium (II) onto kaolinite at 25°C with $\Sigma Ca = 10^{-4}$ and $10^{-3}$m, and $I = 0.01$ m (NaNO$_3$). Circles are experimental data. Solid curves are model calculated assuming the surface equilibria shown in the Figure.
To model the adsorption of radium (II) in the presence of competing calcium, the surface complexation reactions described by the intrinsic constants $K_{\text{int}}^{\text{Ca}^{2+}}$, $K_{\text{int}}^{\text{CaOH}^+}$, $K_{\text{int}}^{\text{Ra}^{2+}}$, and $K_{\text{int}}^{\text{RaOH}^+}$ were added as input data to the MINEQL program. These reactions were then solved simultaneously with the appropriate sorbent ionization and electrolyte binding reactions. Results of the model calculations for Ra(II) adsorption in the presence of $10^{-4}$ m total calcium are presented in Figures 99 and 100 for $\alpha$-SiO$_2$ and kaolinite. The figures show good agreement between the model calculated adsorption curves and the experimental data for both adsorbent minerals, but particularly for $\alpha$-SiO$_2$. The model calculations for kaolinite, as described previously, were adjusted by 20% at pHs less than 4.5 to account for specific adsorption of radium. For both $\alpha$-SiO$_2$ and kaolinite, the surface complexation site-binding model accurately models the competitive effects of dissolved calcium on radium adsorption. More importantly, the model correctly predicts that the competitive effect of calcium adsorption is slight at pHs less than 5 where Ca$_2^+$ is not strongly adsorbed, but increases with pH and total surface coverage.

Effect of sorbent to solution ratio

To further test the predictive capability of the surface complexation site-binding model, adsorption data
Figure 99. Adsorption of radium (II) onto α-SiO₂ at 25°C with $\Sigma$Ca = 10⁻⁴ m and I = 0.01 m (NaNO₃). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
Figure 100. Adsorption of radium (II) onto kaolinite at 25°C with \( \Sigma \text{Ca} = 10^{-4} \text{m} \) and \( I = 0.01 \text{m} \) (NaNO₃). Circles are experimental data. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
from experiments conducted at different sorbent to solution ratios were subjected to the same modeling procedures described in the previous sections. An example of the model calculations for thorium (IV) adsorption on α-SiO₂ is given in Figure 101. The calculated adsorption isotherm was obtained by using the intrinsic stability constants for thorium (IV) adsorption shown in Figure 89, and the same surface parameters for α-SiO₂ estimated in the previous sections. The surface area of α-SiO₂ used in the experiments described in Figure 101 was three times greater than that used for the experiments depicted in Figure 89. The plot shows excellent agreement between the model calculated curve and the experimental results. This suggests that the surface complexation site-binding model calculations are independent of the system solid to solution ratio.

The Power Exchange Function Model

As described in a previous section, the power exchange function is a two-parameter equation which can accurately model the exchange behavior of major and minor cations on sorbent surfaces. In this section, the thorium (IV) and radium (II) adsorption data on α-SiO₂ and kaolinite will be tested with the model.
\( \alpha - \text{SiO}_2 - \text{NaNO}_3 \)

15 g/l (62.25 m²/l)
\( \Sigma \text{Th} = 10^{-5} \text{ m} \)
\( I = 0.01 \text{ m} \)

\[ \begin{align*}
\text{SO}^- - \text{ThOH}^{3+} & : p^* \text{K}_{\text{int}} = 0.6 \\
\text{SO}^- - \text{Th(OH)}^2^+ & : 3.7 \\
\text{SO}^- - \text{Th(OH)}^3^+ & : 9.8 \\
\text{SO}^- - \text{Th(OH)}^4^+ & : 15.5
\end{align*} \]

Figure 101. Adsorption of thorium (IV) onto \( \alpha - \text{SiO}_2 \) at 25°C with \( I = 0.01 \text{ m (NaNO}_3) \). Circles are experimental data measured at different solid to solution ratio. Solid curve is model calculated assuming the surface equilibria shown in the Figure.
In order to successfully apply the power exchange function model to the metal ion adsorption data, a knowledge of the cation exchange capacity (CEC) and/or base exchange capacity (BEC) of the sorbents was required. In this study, the cation exchange capacity is defined as the sum of all the readily exchangeable cations including protons on the surface. The cation exchange capacity equals the sum of the base exchange capacity plus the proton exchange capacity (PEC), which is defined as the sum of all the readily exchangeable protons on the surface, so that

\[ \text{CEC} = \text{BEC} + \text{PEC} \]

The CEC, BEC, and PEC are each functions of the pH of the solution in which they are determined, particularly for sorbents whose surface charge is strongly pH-dependent. At pHs above roughly 6-7 in typical natural waters, PEC becomes negligible so that CEC = BEC.

Determination of Cation Exchange Capacity for Clays and Amphoteric Mineral Oxide Surfaces

Ozsvath (1979) suggested a titration method to determine the BEC of calcium-montmorillonite for different pH conditions. The BEC versus pH curve thus determined was used as the basis for modeling Cd\(^{2+}\) - Ca\(^{2+}\) and Pb\(^{2+}\) - Ca\(^{2+}\)
exchange reactions occurring on the surface of calcium-
montmorillonite (Ozsvath, 1979). Hsi (1981), in describing
the adsorption of uranium (VI) on iron oxyhydroxide
minerals, indicated that the same technique could not be
applied directly to determine the CEC of an amphoteric
mineral oxide surface because of the presence of several
amphoteric ionization reactions of the surface functional
groups. In this study, it was assumed that the base
exchange capacity measured by the titration procedure of
Ozsvath is equivalent to the total cation exchange capacity
of the sorbent regardless of whether it is a clay mineral or
mineral oxide. During the course of the calcium titrations
discussed in a previous section, it was apparent that the
amount of dissolved calcium adsorbed or exchanged with the
sorbent surface increased as a function of pH. For the
\( \alpha\)-SiO\(_2\) oxide-water system, which was essentially devoid of
metal cations other than calcium, the increase in exchange
capacity with pH can only be attributed to readily
exchangeable surface protons, and thus to the PEC. For a
clay mineral suspension as previously described, the
exchangeable calcium measured during the titration procedure
is equivalent to the sum of the exchangeable metal counter-
ions in the double layer and the readily exchangeable
surface protons at a given pH. The calcium titration
exchange capacity measurements were, therefore, taken as a measure of the total cation exchange capacity.

Since the calcium titrations were conducted in approximately \(10^{-3}\) m total calcium solutions, however, the measured cation exchange capacities for both the \(\alpha\)-SiO\(_2\) and kaolinite are probably most accurate at pHs above 5 to 6. At these pHs, the dissolved calcium concentration is in 100 to 1000 fold excess of the proton concentration. Over this pH range and higher, the competition of the proton for available surface exchange sites is minimized, thereby ensuring complete occupancy of available surface sites by calcium.

**Thorium and Radium Adsorption at Variable pH**

The data for thorium and radium adsorption onto \(\alpha\)-SiO\(_2\) (Figures 32 and 34) and kaolinite (figures 33 and 35) were tested with the power exchange function model. Thorium adsorption data over the pH range 2.5 to 6 and radium adsorption data from pH 3 to 9 were used in the calculations. In these experiments, \(\Sigma\text{Th(IV)} = 10^{-5}\) m and \(\Sigma\text{Ra} = 1000\) pCi/l. Because the metal adsorption data were collected as a function of pH, and the sorbent cation exchange capacities are also dependent on pH, the model was tested with both the variable CEC data determined by titration, and assuming constant CEC values. Constant CEC
values of 1.6 meq/100g and 2.5 meq/100g were selected for 
$\alpha$-SiO$_2$ and kaolinite, respectively, based on the calcium 
titration measurements at pH 7, and the surface site density 
data determined by tritium exchange.

Computer calculations of the dissolved thorium 
speciation showed that the predominance of the Th(OH)$_2^{2+}$ 
complex corresponded most closely with the abrupt increase 
in adsorption, particularly onto $\alpha$-SiO$_2$. ThOH$^{3+}$ and 
Th(OH)$_2^{2+}$ are probably the predominant species adsorbed on 
kaolinite. The thermodynamic model and the surface 
complexation site-binding model also confirmed the fact that 
Th(OH)$_2^{2+}$ is one of the principal species adsorbed on 
$\alpha$-SiO$_2$. It was therefore assumed that the thorium hydroxy 
complex, Th(OH)$_2^{2+}$, is the principal adsorbed species and 
that the following exchange reaction occurs:

$$K_{ex} \left[\text{Th(OH)}_2^{2+}\right] + \left(\text{HX}\right) \leftrightarrow \left(X^-\text{Th(OH)}_2^{2+}\right) + \left[\text{H}^+\right]$$ (116)

where $[\text{Th(OH)}_2^{2+}]$ and $[\text{H}^+]$ are activities of the aqueous 
species and $(\text{HX})$ and $(X^-\text{Th(OH)}_2^{2+})$ are mole fractions of the 
adsorbed species on the exchange sites. The same data cast 
in power exchange form according to equation (61) are 
plotted in Figures 102 and 103 for the $\alpha$-SiO$_2$ and kaolinite, 
respectively. As shown in the plots, a single function fits 
each set of data regardless of the adsorption mechanism or
Figure 102. Power exchange function plot of Th(OH)$_2$$^+$-H$^+$ exchange onto $\alpha$-SiO$_2$ assuming a constant cation exchange capacity (CEC) of 1.6 meq/100 g. "r" is the correlation coefficient for the line through the data points.
Figure 103. Power exchange function plot of Th(OH)$_2^{2+}$-H$^+$ exchange onto kaolinite assuming a constant cation exchange capacity (CEC) of 2.5 meq/100 g. "r" is the correlation coefficient for the line through the data points.
mechanisms. It is evident from the figures that adsorption of \( \text{Th(OH)}^2+ \) is increasingly favored over that of protons for thorium concentrations down to \( 10^{-6.1} \text{m} \) at pH 4.2 for \( \alpha - \text{SiO}_2 \) and \( 10^{-7.1} \text{m} \) at pH 3.75 for kaolinite. The model calculations depicted in Figures 102 and 103 were obtained assuming constant CEC values for both the \( \alpha - \text{SiO}_2 \) and kaolinite, primarily because of the low reliability of CEC measurements below pH 6. Similar calculations incorporating an increasing cation exchange capacity with pH, however, did not significantly improve the model fits. This is because of the small change in CEC for \( \alpha - \text{SiO}_2 \) between pH 3 and 6 and the high fractional surface coverage of the kaolinite for the full pH range of the adsorption experiments (fractional coverage > 0.12).

In order to examine the effect of additional surface reactions on the model calculations, other exchange reactions incorporating the adsorption of \( \text{ThOH}^3+ \) and \( \text{Th(OH)}_3^+ \) were tested. The surface exchange of these species was represented by the following equations

\[
[\text{ThOH}^3+] + (\text{HX}) \leftrightarrow (X^-\text{ThOH}^3+) + [H^+] \tag{117}
\]

and

\[
[\text{Th(OH)}_3^+] + (\text{HX}) \leftrightarrow (X^-\text{Th(OH)}_3^+) + [H^+] \tag{118}
\]
The results of the model calculations with these thorium complexes indicate that as the valence of the adsorbed species increases, $K_{ex}$ decreases and the slope of the best fit line decreases. Using $\text{ThOH}^3^+$ as the principal adsorbed species yields $\log K_{ex} = -1.84$ and $n = 2.78$, whereas with $\text{Th(OH)}^+_3$, $\log K_{ex} = -5.81$ and $n = 6.75$. From this information, it is apparent that the power exchange function accurately fits the thorium adsorption data regardless of the exchange reaction which is selected. Unfortunately, the model calculations themselves do not provide an insight as to the specific solution species which are adsorbed.

The radium (II) adsorption data on $\alpha$-$\text{SiO}_2$ and kaolinite were also tested using the power exchange function model. Since the aqueous species $\text{Ra}^{2^+}$ predominates over the full pH range of the adsorption experiments, only a single exchange reaction needed to be considered in the model calculations. This reaction is given by:

$$[\text{Ra}^{2^+}] + (\text{HX}) = (X^-\text{Ra}^{2^+}) + [\text{H}^+]$$

(119)

where $[\text{Ra}^{2^+}]$ and $[\text{H}^+]$ are activities of the aqueous species and $(\text{HX})$ and $(X^-\text{Ra}^{2^+})$ are the mole fractions of the adsorbed species on the exchange sites. The radium adsorption data for $\alpha$-$\text{SiO}_2$ and kaolinite are plotted in Figures 104 and 105 along with the power exchange function model fits. As shown
Figure 104. Power exchange function plot of $\text{Ra}^{2+}-\text{H}^+$ exchange onto $\alpha$-SiO$_2$ assuming a constant cation exchange capacity (CEC) of 1.6 meq/100 g. "r" values are correlation coefficients for the lines through the data points.
Figure 105. Power exchange function plot of $\text{Ra}^{2+} - \text{H}^+$ exchange onto kaolinite assuming a constant cation exchange capacity (CEC) of 2.5 meq/100 g. "r" is the correlation coefficient for the line through the data points.
in Figure 104, the plot exhibits two linear segments indicating that two separate exchange expressions are required in order to fit the adsorption data. The reason for the two linear segments is not clear, but may be attributed to a large change in the $\alpha$-SiO$_2$ exchange capacity from pH 3 to 9. The usual interpretation would be that each line segment corresponds to a different adsorption mechanism. Such an explanation, however, seems inconsistent with the simplicity of the Ra$^{2+}$ - $\alpha$-SiO$_2$ system. Figure 105 shows that only a single function was required to fit the radium adsorption data on kaolinite. The experimental data points plot in a sigmoidal-shaped curve but are fitted with a single line having a correlation coefficient of 0.98. Hsi (1978) suggested that incorrect estimation of the CEC could be one cause for the poorness of fit between the experimental data and the model calculations.

Because the radium adsorption experiments were conducted over a wide pH range, the experimental data were also examined by incorporating the effects of variable cation exchange capacity in the model calculations. The cation exchange capacities for $\alpha$-SiO$_2$ and kaolinite shown in Figures 26 and 27 as a function of pH were used in the calculations. Under these circumstances, the model again predicts that two separate power exchange functions are
required to successfully fit the adsorption data. Figure 106 shows the results for radium (II) adsorption on kaolinite. As shown in the figure below pH 4.5, \( \log \left( \frac{[\text{Ra}^{2+}]}{[H^+]} \right) < -5.7 \), radium is strongly preferred by the surface exchange positions. However, at pHs above 4.5 \( \log \left( \frac{[\text{Ra}^{2+}]}{[H^+]} \right) > -5.7 \), the model calculated adsorption curve shows a negative slope. These calculations indicate that as the radium-to-proton ratio in solution increases, the surface coverage of the sorbent by radium decreases. This effect results from the dramatic increase in exchange capacity of the kaolinite with increasing pH. Apparently, as the solution pH increases, the exchange capacity of the kaolinite increases faster than the fractional surface coverage of the sorbent by radium. Corresponding calculations for radium adsorption on \( \alpha\text{-SiO}_2 \) yielded similar results.

Predictive Capability of the Power Exchange Function Model

The power exchange function model is a simple two-parameter semi-empirical expression which can simulate the adsorptive or exchange behavior of many major and minor cations on adsorbent surfaces. The simplicity of the function makes it particularly attractive for use in describing a variety of natural or laboratory aqueous systems in which exchange reactions dominate the equilibrium
Figure 106. Power exchange function plot of Ra$^{2+}$ -H$^+$ exchange onto kaolinite assuming a pH dependent cation exchange capacity (CEC). "r" values are correlation coefficients for the lines through the data points.
chemistry. The results of the model calculations in this study indicate that the power exchange function accurately describes the adsorption of thorium (IV) on both $\alpha$-SiO$_2$ and kaolinite, particularly at low pH. However, the same agreement between the model calculations and the experimental data was not observed for radium adsorption on either $\alpha$-SiO$_2$ or kaolinite, especially when the variation in CEC with pH was accounted for. These results suggest that the applicability of the model to extremely low trace metal concentrations (i.e., less than $10^{-11}$m) is limited.
CONCLUSIONS

Important conclusions based on the results of this study can be summarized as follows:

1. Dissolved thorium hydroxy complexes are strongly adsorbed at pHs above about 3 to 4 for α-SiO₂ and about 2 to 3 for kaolinite.

2. Thorium adsorption reactions equilibrate rapidly and reach reversible equilibrium conditions within a few days to one week.

3. Thorium adsorption density is directly proportional to the specific surface areas of the sorbents and to the aqueous solid/solution ratio.

4. Thorium sulfate complexing inhibits thorium adsorption onto both α-SiO₂ and kaolinite and favors desorption, especially at pHs below 4. The amount of desorption is directly proportional to the total dissolved sulfate.

5. Thorium sulfate complexes are not significantly adsorbed on α-SiO₂ and are only weakly adsorbed on kaolinite. ThSO₄²⁺ is the predominant sulfate complex adsorbed on kaolinite.

6. Adsorption of radium increases with increasing pH above about pH 3 onto quartz and pH 2 for kaolinite. At a total initial Ra(II) concentration of 1000 pCi/l in the
absence of competing ions, approximately ten percent of the initial radium remains in solution at pH 8 to 9 for both sorbents.

7. The presence of competing divalent cations such as Ca$^{2+}$ at concentrations of $10^{-4}$ to $10^{-3}$M strongly inhibits the adsorption of Ra$^{2+}$ by competing for surface adsorption sites.

8. Important adsorption of positively charged thorium and radium species occurs at pHs below the pH$_{pzc}$ of the sorbent minerals. For kaolinite, this may reflect minor isomorphous substitution in the clay lattice, while for α-SiO$_2$ the adsorption may be the result of residual negative surface charge below the pH$_{pzc}$.

9. The modified thermodynamic adsorption model of James and Healy successfully modeled the adsorption data for thorium and radium in simple electrolyte solutions above pHs of 4-5.

10. The surface complexation model of Davis, James, and Leckie successfully modeled thorium and radium adsorption data on α-SiO$_2$ and kaolinite in electrolyte solutions containing complex-forming ligands (e.g., OH$^-$, SO$_4^{2-}$, NO$_3^-$, and Cl$^-$) and competing ions (e.g., Ca$^{2+}$, Na$^+$, and H$^+$). However, when quantitative adsorption occurred below
the $pH_{pzc}$ of the sorbent, modeling of the data became less accurate.

11. The power exchange function model successfully modeled the thorium and radium adsorption data for both $\alpha$-SiO$_2$ and kaolinite under variable pH conditions, assuming a constant cation exchange capacity for the adsorbents. The function was less successful in fitting the adsorption data for radium when the increase in CEC of the sorbents with pH was accounted for. This fact may be the result of the extremely low concentration of dissolved radium (II) and the inaccuracies in measuring the CEC.

12. Adsorption behavior of thorium and radium cannot be predicted using simple distribution coefficients (Kds). The value of Kd varied by orders of magnitude as a function of pH, metal complexing ligands, the concentration of competing ions, and the character of the mineral sorbent.
RECOMMENDATIONS FOR FUTURE RESEARCH

Experimental Studies

Experimental studies of Th(IV) and Ra(II) adsorption similar to those described in this work should be performed on other important sorbent minerals including manganese and iron oxides, aluminum hydroxides, and various clay minerals. Future work should be focused on mineral phases having low p.z.c.'s and should include studies on mixtures of adsorbents, as well as common clay minerals which can be characterized by measurements of their surface areas, and charge and types and number of surface sites. The metal adsorption data and surface parameters determined from these studies would be of great value in understanding the relative importance of specific minerals as controls on the natural transport of thorium and radium in groundwater systems, and for the development of more comprehensive adsorption models.

The results of this study indicate that nonhydroxyl complexation of thorium can strongly inhibit thorium adsorption and that the presence of competing ions strongly limits the adsorption of radium. However, the adsorption of thorium hydroxy complexes and thorium sulfate complexes cannot be predicted solely from their relative
concentrations in solution. Adsorption studies are needed involving other common complex-forming ligands in natural groundwaters, particularly phosphate, fluoride, and simple organic molecules to further evaluate the role of complexation in thorium adsorption. These studies should incorporate surface measurements by Raman spectroscopy, electron spin resonance spectroscopy (ESR), and nuclear magnetic resonance (NMR), which give direct information about surface binding of adsorbates and may provide additional information on the formation of ternary surface complexes. For metals present in sufficient concentrations, electrochemical measurements by ion-selective electrodes can be used to monitor their sorption and desorption behavior, and when coupled with precise potentiometric acid-base titration data, may yield semi-quantitative information about surface reaction stoichiometries and binding energies.

Additional adsorption studies are needed to evaluate the competitive influence of monovalent and divalent ions, such as Na\(^+\), K\(^+\), and Mg\(^{2+}\) on Ra(II) adsorption. Improved experimental design, including the use of radioactive tracers, can increase the precision of adsorption measurements at trace metal concentration levels.

No studies of the effect of temperature on adsorption performed in sufficient detail to allow application of the
surface complexation site-binding model have been performed. Such research is critically needed before results of studies such as this can be applied with confidence to natural systems.

Field-oriented studies of natural groundwaters and host rocks around uranium mill-tailing waste disposal sites and high level nuclear waste repositories are also needed. These should include the collection of data on the relative and absolute amounts of adsorbed metals on natural geologic materials, and the measurement of parameters which define their adsorptive capacity. This work would greatly improve our ability to accurately model the role of adsorption reactions in attenuating the transport of dissolved metals and radionuclides in these environments.

Adsorption Models

The Thermodynamic Adsorption Model

In this study, the thermodynamic adsorption model of James and Healy was modified to account for the speciation and adsorption on individual sorbent surfaces of metal ligand complexes, as well as metal hydroxy complexes. This model could be expanded further to describe the adsorption of competing metal ions in the presence of various minerals or single minerals having several types of surface sites.
This would be accomplished by expanding the mass balance expressions and adding additional chemical free energy correction terms for each adsorbate. Additionally, the theoretical basis of the model could be improved by computing surface potentials from ionization constants and double layer capacitances rather than by the Nernstian equation, which effectively corresponds to a constant activity of the potential determining ions at the surface. Also, more research is needed in calculating variable dielectric constants at the mineral-water interface.

However, it should be noted that such improvements may simply lead to the surface complexation site-binding model of Davis and others. Nevertheless, in spite of these suggested improvements, the relative simplicity and few adjustable parameters of the thermodynamic model make it potentially attractive for incorporation in hydrologic models which would then allow for the consideration of adsorption reactions in flowing groundwater systems.

The Surface Complexation Site-Binding Model

The surface complexation site-binding model of Davis, James, and Leckie is the most sophisticated adsorption model currently available and was found to be the most successful in modeling the metal adsorption data in this study. Several important problems, however, remain to be solved in
order to extend the applicability of this model to natural systems.

First, application of the model to more complex electrolytes and heterogeneous solutions is needed. The model has, so far, been tested only in relatively simple electrolyte solutions. More experimental studies are required to test the predictive capability of this model to complex rock-water systems containing a mixture of complexing ligands and competing ions.

Second, application of the model to more complex sorbent surfaces, such as montmorillonite-type or chlorite clay minerals, is needed. Surface charge development and adsorption characteristics of these surfaces could possibly be verified with model systems containing known ratios of individual component phases, such as $\alpha$-SiO$_2$ and Al(OH)$_3$, for example, in the case of kaolinite. Results of this study indicated that the electrical properties of kaolinite may be described assuming a mixture of aluminum hydroxide and hydroxylated silica surface sites. Similar studies are recommended for synthetic chlorites and for sepiolite, for example.

Finally, more research is needed regarding the determination of the stoichiometry of surface reactions so that only the appropriate adsorption reactions and intrinsic
constants for the system of interest are included in the model calculations. The lack of any prior information on the stoichiometry of surface complexes is one of the few major limitations which remain among the most recently proposed adsorption models.

The Power Exchange Function Model

As described in a previous section, the power exchange function model currently lacks a sound theoretical basis for the full range of solute concentrations to which it has been applied. Research is recommended which will lend a greater theoretical significance to the model function and its remarkable success in fitting experimental data. Some effort should be made to incorporate surface ionization reaction constants within the function which would then extend its applicability to adsorption processes occurring in solutions with changing pH on sorbent minerals having variable exchange capacities. More empirical adsorption data is also needed in order to better evaluate and predict exchange constants and n values for a wide variety of metal ions and sorbent minerals for later application to natural systems.


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