SORPTION OF URANIUM (VI)

BY

IRON OXIDES

by

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ABSTRACT

Previous work has shown that dissolved uranyl species are strongly adsorbed onto different ferric oxides and oxyhydroxides. The presence of carbonate complexing inhibits this adsorption and favors desorption, especially in alkaline solutions. In this study, these effects as well as the competitive adsorption of $\text{H}^+$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$ and phosphate complexing effects were examined more quantitatively. Synthetic goethite, amorphous ferric oxyhydroxide, hematite and natural specular hematite were used in the study. The composition, crystallinity, particle size and morphology, surface area and charge, and P.Z.C. of these solid phases were characterized by x-ray diffraction, SEM, BET nitrogen adsorption, potentiometric titration, and electrophoretic mobility measurements. Uranyl adsorption was measured for $\text{IU}=10^{-6}$ to $10^{-8}$M, and pH 4-10. All the phases strongly adsorbed uranyl from pure water at pHs above 5 to 6, with adsorption greatest onto the amorphous phase, and least onto hematite. The presence of $\text{Ca}^{2+}$, or $\text{Mg}^{2+}$ at $10^{-3}$M did not affect uranyl adsorption. However, uranyl carbonate complexing severely inhibited adsorption. As total carbonate ($C_T$) was increased from zero to $10^{-2}$M, the pH of maximum adsorption and extent of adsorption decreased.
Thus, $C_T = 10^{-2}$ M reduced uranyl adsorption onto goethite as measured in pure water by from 2 to 3 orders of magnitude. The same desorption effects were not observed in the presence of uranyl phosphate complexing. In fact, phosphate complexing slightly enhanced uranyl adsorption, especially for acidic pHs. The adsorption data were modeled using the surface ionization and complexation treatment of Davis, et al. (1978) and the power exchange function of Langmuir (1981). The surface ionization and complexation model was able to successfully model the uranyl adsorption data in simple electrolyte systems. However, in more complex solutions, modeling procedures became more difficult and uncertain. The power exchange function successfully modeled uranyl adsorption data for constant pH conditions. For variable pH conditions, its application was less successful. The lack of a good estimate of cation exchange capacities at different pHs may have been the main cause for this failure. Study results have potential applicability to the genesis of sedimentary uranium deposits, in-situ leaching and restoration of ground water quality in such deposits, and to the management of radioactive wastes in underground burial sites.
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Adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃ solutions. Circles are experimental data. Solid curve is model calculated considering UO₂OH⁺ surface monodentate complex and (UO₂)₃(OH)⁵⁻ surface tridentate complex equilibria.

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INTRODUCTION

The release, disposal, and partitioning of uranium in natural hydrological environments are largely controlled by precipitation-dissolution and sorption-desorption reactions (Muto et al., 1968; Langmuir, 1978; and Chatham et al., 1981). Currently, sufficient thermodynamic data are available for many common uranium minerals and complexes (Hostetler and Garrels, 1962; Langmuir, 1978; Dongarra and Langmuir, 1980) to permit equilibrium modeling of the simplest precipitation-dissolution processes. In recent studies, Lueck (1978), Langmuir and Chatham (1980) and Chatham et al. (1981) were able to predict and explain many of the observed changes in ground-water chemistry near known uranium deposits using only precipitation-dissolution equilibria models. However, the equilibrium models would be more applicable if sorption-desorption effects were also considered. In fact, sorption-desorption reactions may have been chiefly responsible for the partitioning of uranium between aqueous and solid phases, preliminary to the formation of many or most sedimentary uranium ore deposits. This is because, in general, sorption-desorption reactions equilibrate fast (in order of seconds to days), whereas ground-water mineral precipitation-dissolution reactions usually require months to years to attain equilibrium. Also, uranium adsorption isotherm plots (van der
Weijden et al., 1976; and Langmuir, 1978) also indicate that the lower the dissolved uranium concentration, the greater the percentage of total uranium sorbed in a given water-sediment system. Thus, when dissolved uranium concentrations are in the parts per billion range (as they usually are in average ground-water), typically in excess of 99% of the total uranium is sorbed.

In spite of its importance, not enough is known about the detailed mechanisms of uranium sorption onto individual sorbents. Also, there is no comprehensive sorption model that can accurately predict the role of sorption-desorption reactions in natural environments. The purpose of this study was to examine uranium sorption-desorption reactions in a quantitative fashion and to develop sorption models to explain the empirical adsorption data.

Based on a review of the literature, uranium adsorption studies have been carried out on a variety of sorbents (e.g., hematite, limonite, amorphous silica, aluminum oxide, ferric oxyhydroxide, etc.). Unfortunately, most previous studies did not determine such surface properties as the surface area, cation exchange capacity, and surface charge as a function of pH. These data are critically needed for the develop-
ment of predictive sorption models. In this study, uranium sorption experiments were performed using well characterized synthetic amorphous ferric oxyhydroxide, goethite, hematite, and natural specular hematite. The reasons for selecting these materials as uranium sorbents were that: (1) These materials have a strong sorptive capacity for dissolved uranyl species, particular in the pH range of 5-9 (Muto et al., 1968; van der Weijden et al., 1976; and Hsi and Langmuir, 1980). This is in spite of the fact that both the uranyl species and sorbents are sometimes positively charged at the lower pHs; (2) Ferric oxide and oxyhydroxide minerals (chief­ly hematite and goethite) are common accessory minerals associated with sandstone-type uranium deposits. Previous studies suggest that these minerals may scavenge uranium from surface and sub-surface waters. Such scavenging by sorption may preconcentrate uranium, which is subsequently released to form nearby roll-front-type uranium deposits (Barton, 1956; Muto et al., 1968; van der Weijden et al., 1976); (3) The sorption behavior of these materials is probably similar to that of other common oxide or oxyhydroxide sorbents (e.g., titanium oxide, aluminum oxide and silica) in natural environments (Langmuir, 1980; personal communication).

Previous studies also indicate that the presence of carbonate complexing in alkaline solutions inhibits adsorption
and favors desorption of uranyl from these materials (van der Weijden et al., 1976; Hsi and Langmuir, 1980). Crystallization (aging) of the ferric oxyhydroxides also leads to desorption of uranyl (Barton, 1956; van der Weijden et al., 1976). In this study, these effects as well as the competitive adsorption of H^+, Ca^{2+}, and Mg^{2+} were all carefully examined. The experimental data were subsequently used to develop general models for uranium sorption reactions.

Results of this study have potential application to the genesis of sedimentary uranium deposits, in-situ leaching and restoration of ground-water quality of such deposits, and to the management of radioactive wastes in underground burial sites.
EXPERIMENTAL METHODS AND MATERIALS

A. Reagents

All reagents used in this study were of analytical reagent (AR) grade or better and all water used was double deionized water with a conductivity of less than 1.0 µmho/cm at 25°C. Ionic strength in the sorption studies was adjusted by the addition of 1.0M NaNO₃. The pH was adjusted with 0.1M HNO₃ or 0.1M NaOH.

B. Preparation of Starting Materials

Four different ferric oxyhydroxide sols of relatively uniform shape and narrow particle size distribution were used in the sorption studies. They were prepared as follows:

(A) Goethite (α-FeOOH): A colloidal dispersion of goethite was prepared according to the method of Atkinson et al. (1967). 160 ml of 2.5M KOH was slowly added to a vigorously stirred ferric nitrate solution (40 g of Fe(NO₃)₃·9H₂O dissolved in 660 ml of double deionized water) to give a final pH near 12. The solution was subsequently aged in an oven for 24 hours at 60°C. After aging, the solution was cooled to room temperature. Colloidal particles were washed repeatedly with double deionized...
water until the $\text{NO}_3^-$ concentration was lower than $10^{-5}$M. The particles were resuspended in double deionized water and kept in a polyethylene bottle under a pure $\text{O}_2$-atmosphere. Electron microscopy showed no detectable change in particle size or shape in sols stored for several months.

(B) **Amorphous ferric oxyhydroxide:** Due to the unstable nature of the amorphous ferric oxyhydroxide, samples were prepared in batches immediately before each titration or adsorption experiment, using the method of Davis and Leckie (1978). Double deionized water was kept under a circulating purified oxygen atmosphere. $\text{NaNO}_3$ salt was added to achieve an ionic strength of 0.1M after the addition of all reagents. Acidified stock ferric nitrate solution was then added and amorphous ferric oxyhydroxide was precipitated by the drop-wise addition of $\text{CO}_2^-$ free 1.0N NaOH solution until a pH of 7.0 was obtained. The precipitate was aged at pH 7 for 4 hours before beginning the titration or adsorption experiments.
(C) Hematite ($\alpha$-Fe$_2$O$_3$): A colloidal dispersion of hematite was prepared according to the method of Matijevic and Scheiner (1978). Solutions containing 0.0315M FeCl$_3$ and 0.005M HCl were heated in tightly stoppered glass bottles at 100°C for one week in the oven. After aging, the solutions were cooled to room temperature. Colloidal particles were washed with CO$_2$-free deionized water by repeated centrifugation and decantation until the Cl$^-$ concentration was less than 10$^{-6}$M. The colloidal particles were then resuspended in double deionized water and kept in a glass bottle under a pure O$_2$-atmosphere for later electron microscopy, surface charge, x-ray, and sorption studies. Electron microscopy showed no detectable changes in particle size or shape in sols stored for several months. Ultrasonication, which was used to repeptize settled sols, has been reported to have no effect on the morphology of the dispersed particles (Matijevic and Scheiner, 1978).

(D) Natural specular hematite ($\alpha$-Fe$_2$O$_3$): A natural specular hematite sample was obtained from Ishpering, Michigan. The sample was crushed and ground in a mechanical mill for 30 minutes and passed through a 45 µm stainless steel sieve.
The sample was stored as a dry powder in a desiccator.

C. Characterization of Starting Materials

Properties such as particle size and shape, composition, crystallinity, surface area, electrophoretic mobilities, and types and numbers of functional groups on the particle surface are of great value in interpreting experimental adsorption data, and also in the development of adsorption models. The various experimental techniques used to characterize these properties are discussed separately as follows.

Electron Microscopy

Electron microscopy was used to determine the size and morphology of the colloidal materials. According to Yates (1975) and James and Parks (1981) the evacuation or heating by the electron beam during the analyses may cause dehydration and shrinkage of the samples. Nevertheless, the particle size and crystal face dimensions obtained by this technique are still very useful in interpreting the results of surface area measurements and in estimating surface site densities.

The freeze-dried samples were mounted on a stainless steel sample plate and coated with a thin film of evaporated Au/Pd alloy. The samples were then examined under the electron microscope. The results of electron microscopy studies
showed that starting material A (goethite, $\alpha$-FeOOH) formed by aging at 60°C for 24 hours, consisted of rod-like particles with an average length of 1 $\mu$m and cross sectional radius of 0.2 $\mu$m. Starting material B (amorphous ferric oxyhydroxide) was comprised of agglomerates of very small spherical particles. Based on electron microscopy and density gradient ultracentrifugation studies, Murphy et al. (1976) and Davis (1977) have concluded that the size of individual particles is approximately 20 Å in diameter at the end of four hours aging.

Starting material C (hematite, $\alpha$-Fe$_2$O$_3$), formed by aging at 100°C for one week, consisted of spherical particles with a reasonably uniform radius of 0.3 $\mu$m. Starting material D (natural specular hematite) was irregular in shape and had a modal particle radius of around 1.0 $\mu$m.

**X-Ray Diffraction**

X-ray diffraction was used to check the surface composition and crystallinity of the starting materials. The line broadening effect observed from the x-ray diffraction pattern provided information about particle thickness, supplementing the planar particle size information obtained from electron microscopy.

The x-ray diffraction pattern of freeze-dried material A showed it to be pure goethite ($\alpha$-FeOOH) with an average
grain size of 0.1 μm. X-ray diffraction of freeze-dried material B (amorphous ferric oxyhydroxide) showed no evidence of crystalline structure after 2 days of aging. It was clearly x-ray amorphous. Of course, microcrystalline structure undetectable by x-ray diffraction techniques still exists. Some signs of crystallinity became evident after one week of aging. The goethite pattern was clearly identified after aging for two weeks or longer. The pattern of freeze-dried material C showed it was pure hematite (α-Fe₂O₃). The average particle size after one week of aging was about 0.3 μm. The x-ray analysis of freeze-dried material D showed it to be pure hematite (α-Fe₂O₃) with an average particle size of 1 μm.

Surface Area Measurement

Specific surface areas of the colloidal particles are important to estimate the surface charge densities as well as the ionizable surface site densities. The surface areas of the freeze-dried starting materials were measured by the BET nitrogen adsorption method in a Cahn Gravimetric Adsorption Balance. Samples were outgassed at room temperature for 24 hours before each analysis. The BET surface area of material A (goethite) was measured as 45 m²/g. Yates (1975) reported a surface area of 48 m²/g for goethite prepared in a similar manner. The BET surface area of material B (amorphous ferric
oxyhydroxide) was measured as 306 m$^2$/g. Other reported values for BET surface area of ferric oxyhydroxide prepared in a similar manner are 257 m$^2$/g (Gast et al., 1974), 320 m$^2$/g (Yates, 1975), and 182 m$^2$/g (Davis et al., 1978). The BET surface area of material C (hematite) was 3.1 m$^2$/g, that of material D (natural specular hematite) 1.8 m$^2$/g.

The BET nitrogen surface area measurement, especially for amorphous ferric oxyhydroxide (material B), must be used with some caution. Yates (1975) presented evidence that outgassing of amorphous ferric oxyhydroxide even at room temperature caused some surface decomposition. The result is probably an underestimate of the true specific surface area.

Specific surface areas of suspended charged particles can also be derived from the measurement of the negative adsorption of co-ions. This method, which involves the mathematics of diffuse double layer theory, was introduced by Schofield (1947, 1948), and modified by van den Hul and Lyklema (1967). The principal advantages of the method are that no drying of the sample is necessary, and that the molecular cross-section and orientation of the adsorbing molecule or ion need not be known. However, the accuracy and sensitivity of this method are strongly limited by the precision of the analytical method employed, since the changes in bulk concentrations due to negative adsorption are generally very small. In this study, K$^+$ ions were used for surface area
measurement (at pH = 4), and were analyzed by atomic absorption spectrophotometry. The surface area determined for amorphous ferric oxyhydroxide was 250 m²/g. The surface area of other amorphous ion oxyhydroxide materials prepared in a similar manner has been estimated in the range of 270-335 m²/g by negative adsorption of Na⁺ at pH 4 (Davis, 1977) and ~700 m²/g by negative adsorption of Mg²⁺ at pH 5 (Avotins, 1975). Surface areas for the other oxyhydroxides could not be determined by negative adsorption due to the poor precision of the analytical method. Besides, this method is based on the measurement of adsorption densities in the diffuse layer. Surface areas are measured, in a sense, with double layer "thickness" of Debye length as a yardstick. Pores and other non-planar microstructural surface features with dimensions smaller than or close to the Debye length are not detected (James and Parks, 1981). Therefore, negative adsorption and BET measurement techniques may provide low surface area estimates for materials such as amorphous ferric oxyhydroxides because of porosity and surface decomposition effects, respectively. By assuming spherical particles of 20 Å diameter and a density of 3.57 g/cm³, Davis (1977) estimated a specific surface area of 840 m²/g for amorphous ferric oxyhydroxide. The true specific surface area is probably less than 840 m²/g, but more than that determined by negative adsorption or BET methods.
P.Z.C. and Surface Charge Density Determination by Potentiometric Titration

Potentiometric acid/base titration of a sol can provide a direct measure of surface charge density (\( \sigma_0 \)), and point of zero charge (P.Z.C.; the pH of the solution at which there is no net surface charge) if the supporting electrolyte ions have no specific affinity for the surface or if the positive and negative ions of the supporting electrolyte have equal specific affinity for the surface (James and Parks, 1981). Bolt (1957) and Parks and de Bruyn (1962) were among the first to apply potentiometric titration to the study of oxide-surface equilibria and confirmed the importance of H\(^+\) and OH\(^-\) as the potential determining ions (P.D.I.) for hydrous oxides at the oxide/water interface.

The surface charge density on the hydrous oxide surface is a function of pH and can be defined by the net uptake or release of the P.D.I. (i.e., H\(^+\) and OH\(^-\)) at the oxide/solution interface.

\[
\sigma_0 = F \left( \Gamma_{H^+} - \Gamma_{OH^-} \right)
\]

\[
\sigma_0 = F \left( C_A - C_B + [OH^-] - [H^+] \right)/A
\]

where

- \( \sigma_0 \) : surface charge density (coulombs/cm\(^2\))
- \( F \) : Faraday constant
- \( \Gamma_{H^+}, \Gamma_{OH^-} \) : adsorption density of H\(^+\) and OH\(^-\) on the surface (mole/cm\(^2\))
\[ C_A, C_B: \] concentrations of acid and base added to reach a point on the titration curve

\[ [H^+], [OH^-]: \] equilibrium concentrations (not activities) of \( H^+ \) and \( OH^- \) at that point

\[ A: \] total surface area of the sol (cm\(^2\)/liter)

The potentiometric titrations are usually performed in an indifferent electrolyte at various concentrations, and, when appropriately matched, the point where the \( \sigma \_O \) versus pH curves cross each other gives the p.z.c. of the interface (Arnold, 1978).

In this study, the titration procedure of Parks and de Bruyn (1962) and Yates and Healy (1975) was followed. An appropriate amount of previously prepared ferric oxide or oxyhydroxide sol was withdrawn from the storage bottle and transferred into a Metrohm water-jacketed titration vessel to give a total surface area of around 20 m\(^2\). Enough CO\(_2\) -free deionized water was added to the suspension to bring the total volume to 500 ml, and NaNO\(_3\) salt was added to bring the total ionic strength to 10\(^{-3}\) M. The titration procedure consisted of first bubbling purified and H\(_2\)O-saturated O\(_2\) gas through the suspension for 24 hours to remove the dissolved CO\(_2\). The suspension was then titrated with 0.1N HNO\(_3\) and 0.1N NaOH using a microsyringe. The pH was measured using a Beckman model 4500 digital pH meter. In most experiments, a Beckman glass electrode and a Corning Ag/AgCl double-junction reference
electrode, with the external reservoir containing 1M NaNO₃, were used to avoid chloride contamination of the solution. Following each addition of titrant, the suspension was stirred until pH drift was negligible. The pH was then measured with the magnetic stirrer turned off. A very slow rate of equilibration was observed near the p.z.c. It was necessary to arbitrarily select as the equilibrium pH, a point when the pH drift was less than 0.005 units/min.

The suspension in 10⁻³M electrolyte was titrated to pH 5 and 10 with acid and base. Then solid NaNO₃ salt was added to bring the total NaNO₃ concentration to 10⁻²M and the titration repeated. The same procedure was followed at 10⁻¹M electrolyte concentration. The amount of H⁺ or OH⁻ adsorbed was calculated from the difference in the total volume of acid or base needed to titrate a blank solution and the suspension to the same pH. The adsorption curves were reversible within ± 0.2 pH units. Figures 1 and 2 show titration curves of aged goethite and freshly prepared amorphous ferric oxyhydroxide. In each plot, the P.Z.C. of the sample is located at the intersection of all the titration curves. A P.Z.C. of pH 8.5 ± 0.3 is indicated in Fig. 1. Yates and Healy (1975) reported a value of pH 7.5 ± 0.1 for goethite in KNO₃ solutions. Balistrieri and Murray (1979) reported a P.Z.C. of pH 7.5 for goethite in NaCl and KCl solutions. The P.Z.C.
Figure 1. Variation of the surface charge of goethite as a function of pH in aqueous solutions of NaNO₃.
Figure 2. Variation of the surface charge of amorphous ferric oxyhydroxide as a function of pH in aqueous solutions of NaNO$_3$. 

According to the graph, the surface charge $\sigma_0$ (in $\mu$C/cm$^2$) changes with pH for different concentrations of NaNO$_3$: 0.001 M (circles), 0.01 M (triangles), and 0.1 M (squares). The data points show a decrease in surface charge with increasing pH, indicating a change in surface charge due to the reaction with NaNO$_3$.
of amorphous ferric oxyhydroxide was determined to be pH 7.9 ± 0.2, which is in good agreement with values reported by Yates (1975) (pH_{PZC} = 8.0) and Davis (1977) (pH_{PZC} = 7.9). Unfortunately, experimental difficulties were encountered in acid-base titration of synthetic hematite and natural hematite. A very slow rate of equilibration was observed in the pH region of 6-9. The pH could drift continuously for several days. Hysteresis problems were also serious. From pH 6-9, an acid titration curve was sometimes separated by as much as 0.6 pH units from a base titration curve. As a result, no consistent and reproducible value of pH_{PZC} could be derived from either the fast or slow potentiometric titrations. Similar problems have also been reported by other investigators (e.g., Onoda and de Bryun, 1966; Berube et al., 1967; Yates, 1975). A salt titration method of Yates (1975) and Davis and Leckie (1978) was used to estimate the pH_{PZC} for these two materials. This method was performed by observing the change in pH (ΔpH) upon the addition of dry NaNO_3 salt to the iron oxide suspensions. The added salt shifts pH toward pH_{PZC} by increasing |σ_0|. At pH_{PZC}, there should be no change in pH upon the addition of salt to the suspension. In this manner, a pH_{PZC} of 7.5 ± 0.5 was estimated for the synthetic hematite (material C) and a pH_{PZC} of 7.8 ± 0.5 was estimated for natural hematite (material D).
The slow reaction rate during acid/base titration of hematite samples together with other evidence from electron microscopy and differential thermal analysis (Parks, 1960) and hysteresis in gas adsorption isotherms (Yates, 1975) all suggest that the hematite surface may be hydrous, perhaps coated with a hydrous oxide precipitate. The surface may have some porosity, so that protons can penetrate into and/or diffuse out of the bulk solid as well as from the surface (James and Parks, 1981).

**Electrophoretic Mobility Studies**

A Rank Brothers Mark II Microelectrophoresis Apparatus (Rank Bros., Cambridge, U.K.) in conjunction with a van Gils type thin-walled cylindrical glass cell were used for electrophoretic mobility studies. The glass cell is connected to a peristaltic pump and a 500 ml Metrohm glass equilibration vessel. Except during actual measurements, the dispersion under investigation can be continuously pumped around a circuit consisting of the thermostatted cell and the equilibration vessel. A constant temperature of 25°C and a circulating purified oxygen atmosphere were always maintained in the equilibration vessel. pH measurement and the adjustment of pH and ionic strength were carried out in the equilibration vessel. At least 10 particles were observed at each stationary level with the polarity of the platinum black
electrode reversed between successive observations to minimize polarization effects. The average error of a single mobility determination was less than $\pm 10\%$ for mobilities greater than $1 \, \mu\text{m/sec/v/cm}$. Errors were larger for low mobilities, becoming as great as $\pm 0.2 \, \mu\text{m/sec/v/cm}$ for mobilities close to zero. Figures 3 to 5 show the electrophoretic mobilities of goethite, synthetic hematite and natural hematite. The particles of amorphous ferric oxyhydroxide were too small to be observed with the optical microscope and the conventional quartz-iodine illuminator equipped in the standard instrument. For goethite, the iso-electric point (IEP; the pH at which the net electrophoretic mobility is zero) was between 8.8-9.1. The IEP of synthetic hematite was between 6.5-7.7 and that of natural hematite between 6.5-7.4. It is also evident that reversibilities of the mobility curves were very poor for the hematite samples. This non-reversible behavior may reflect the slowness of the surface reactions and/or the diffusion of ions into the surface.

**Tritium Exchange Method**

The tritium exchange method of Berube et al., (1967) and Yates (1975) was used to determine the surface site densities ($N_s$) of the four starting materials. The ferric oxide or oxyhydroxide samples were labeled with tritium. Enough sample was dispersed in tritiated water of known activity
Figure 3. Electrophoretic mobility of goethite. Open circles represent increasing pH between successive measurements; solid circles represent decreasing pH.
Figure 4. Electrophoretic mobility of synthetic hematite. Open circles represent increasing pH between successive measurements; solid circles represent decreasing pH.
Figure 5. Electrophoretic mobility of natural specular hematite. Open circles represent increasing pH between successive measurements; solid circles represent decreasing pH.
(2.2 \times 10^7 \text{ cpm cm}^{-3}) to give a total surface area of about 20 \text{ m}^2. The suspension was sealed in a polycarbonate centrifuge tube and shaken continuously at room temperature for 3 days.

Following the labeling, the suspension was centrifuged and the excess water was removed by decanting. The centrifuge tube containing the wet oxide was then outgassed in a vacuum for 2 days. After the outgassing step, dry nitrogen gas was let into the vacuum line, the tube containing the sample removed, 20.0 \text{ cm}^3 of distilled water was added immediately, and the tube was again sealed. The solids were redispersed by ultrasonication and continuous shaking. After the desired equilibration time, the suspension was centrifuged and 0.5 \text{ cm}^3 samples were removed from the clear supernatant. The radioactivity of these samples was determined by the conventional liquid scintillation counting method. For goethite, an equilibration time of four hours was used. For synthetic and natural hematites, an equilibration time of 7 days was allowed.

The total number of exchangeable sites or site density ($N_s$) on the ferric oxide or oxyhydroxide surfaces was calculated according to the following equation (Yates and Healy, 1975):

\[ N_s = \frac{A_t}{A_L S_{\text{BET}} M} \text{ moles m}^{-2} \]
where \( A_t \) is the total activity (in cpm) removed from the surface, \( A_L \) is the activity per mole \( H \) (cpm mole\(^{-1}\)) of the labeling solution, \( S_{\text{BET}} \) is the BET surface area (m\(^2\)/g\(^{-1}\)), and \( M \) is the mass (g) of the solid sample present. The site density determined for goethite was 18 sites/nm\(^2\), which is in good agreement with the value of 16.8 sites/nm\(^2\) reported by Yates (1975) for his goethite sample. The site density (\( N_s \)) of amorphous ferric oxyhydroxide was 20 sites/nm\(^2\). Yates (1975) reported a value of 11.4 sites/nm\(^2\). Because the reported site density depends on the specific surface area measured, and a large range of specific surface areas for amorphous ferric oxyhydroxide have been estimated by different techniques, Davis (1977) has suggested that a site density based on mass may be more appropriate for amorphous materials. Accordingly, a site density of 1.05 x 10\(^{-2}\) moles per gram of amorphous ferric oxyhydroxide was computed. This is in good agreement with a value of 9.85 x 10\(^{-3}\) moles/g recalculated from the raw data of Yates (1975). The site density of synthetic hematite and natural hematite was 19 sites/nm\(^2\) and 15 sites/nm\(^2\), respectively.

**Water Content**

Water content was determined by weight loss after heating in an oven at 650\(^\circ\)C for 15 minutes. The water content of material A (goethite) was 11.5%, of material B (amorphous
ferric oxyhydroxide) 13%, material C (synthetic hematite) 2%, and material D (natural hematite) 1%.

The physical and surface properties of these four starting materials are summarized in Table 1.
Table 1. Physical and Surface Properties of the Four Starting Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Particle Shape</th>
<th>Particle Size (length)</th>
<th>Surface Area (m$^2$/g)</th>
<th>Site Density</th>
<th>PZC</th>
<th>IEP</th>
<th>Water Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Goethite (α-FeOOH)</td>
<td>Rod like</td>
<td>1 µm</td>
<td>45 (BET)</td>
<td>18 sites/nm$^2$ (1.35×10$^{-3}$ mol/g)</td>
<td>8.5±0.3</td>
<td>8.8-9.1</td>
<td>11.5</td>
</tr>
<tr>
<td>B</td>
<td>Amorphous Ferric Oxyhydroxide</td>
<td>Spherical</td>
<td>20 Å</td>
<td>306 (BET)</td>
<td>20 sites/nm$^2$ (1.05×10$^{-2}$ mol/g)</td>
<td>7.9±0.2</td>
<td>---</td>
<td>13</td>
</tr>
<tr>
<td>C</td>
<td>Synthetic Hematite</td>
<td>Spherical</td>
<td>0.3 µm</td>
<td>3.1 (BET)</td>
<td>19 sites/nm$^2$</td>
<td>7.5±0.5</td>
<td>6.7-7.7</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>Natural Hematite</td>
<td>Irregular</td>
<td>1 µm</td>
<td>1.8 (BET)</td>
<td>15 sites/nm$^2$</td>
<td>7.8±0.5</td>
<td>6.5-7.4</td>
<td>1</td>
</tr>
</tbody>
</table>
SORPTION OF URANIUM (VI) BY IRON OXIDES:  
METHODS AND EMPIRICAL RESULTS

A. Experimental Procedures

Preparation and characterization of ferric oxide and oxyhydroxide sols for uranium sorption studies were discussed in the previous section. Sorption experiments were conducted in batches as follows. A measured amount of iron oxide sol previously prepared was transferred from the storing bottle into a 125 ml polyethylene bottle. The same volume of sol was transferred into a pre-weighed crucible. The weight was taken as the weight of the solid particles after drying in an oven at 110°C for 15 minutes. The ionic strength was adjusted by the addition of 1.0M NaNO₃ solution. The pH was adjusted when necessary by addition of 0.1N HNO₃ or 0.1N NaOH solution. Enough CO₂-free deionized water was then added to bring the total volume of the suspension to 100 ml; the desired amount of uranium was added to the suspension from a stock 0.01M uranyl nitrate solution. After bubbling with purified and H₂O-saturated O₂ gas to purge dissolved CO₂, the bottle was tightly sealed. The bottle was shaken continuously in a constant temperature shaker bath. The oxygen atmosphere and a constant temperature of 25°C were maintained throughout the experiment. No pH adjustments were made during the
adsorption reaction. After the desired reaction period, 40 ml aliquots of suspension were delivered to screw-capped polycarbonate centrifuge bottles. Final pH measurements were made on the remaining suspension at the time of sampling. The 40 ml aliquots were centrifuged at 3,000 rpm for 15 minutes to separate the colloidal particles. The clear supernatant after centrifugation was analyzed for its uranium content using a SINTREX UA-3 uranium analyzer. The manufacturer reported measurement accuracy for this instrument is ±15% at and above the 1 ppb level.

**B. Adsorption Kinetics**

In order to determine the optimum reaction time period for uranium (VI) sorption reactions, a series kinetic studies were first conducted. Other procedures being the same as previously described, samples were taken for analysis at different times. Figures 6 to 9 show the results of the kinetic studies carried out using goethite, amorphous ferric oxyhydroxide, synthetic hematite, and natural hematite respectively. The results revealed a two-step kinetic reaction. The first step is rapid, being complete within a few minutes. The second step is much slower, often continuing for days. The same two-step kinetics have also been reported for trace metal sorption onto manganese dioxide (Loganathan and Burau,
Figure 6. Kinetics of uranium (VI) adsorption onto goethite at 25°C in 0.1M NaNO₃.
Figure 7. Kinetics of uranium (VI) adsorption onto amorphous ferric oxyhydroxide at 25°C in 0.1M NaNO₃.
Figure 8. Kinetics of uranium (VI) adsorption onto synthetic hematite at 25°C in 0.1M NaNO₃.
Figure 9. Kinetics of uranium (VI) adsorption onto natural hematite at 25°C in 0.1M NaNO₃.
1973), amorphous iron hydroxide (Davis, 1977), α-SiO₂ (Benjamin, 1978), and titanium dioxide (Berube and de Bruyn, 1968a,b). Diffusion of adsorbate into the solid matrix and slow alteration of the bulk solid characteristics have been postulated as main causes for the slower step reactions (Yates, 1975; Benjamin, 1978). Since the goal of this work was to study surface adsorption under equilibrium or at least pseudo-equilibrium conditions, reaction times were chosen to assure completion of the rapid adsorption step and to minimize the effect of the diffusion step. Based on the results of this study and those reported in the literature, an equilibration time of four hours after addition of adsorbate was chosen for experiments using goethite or amorphous ferric oxyhydroxide as sorbents. For experiments using synthetic hematite or natural hematite as sorbents, a seven-day equilibration period was used.

C. Effect of pH on Adsorption

In order to examine the effect of pH on the adsorption of dissolved uranyl species, 0.1N HNO₃ or NaOH solution was used to adjust the pH of the suspensions, and then enough uranium was added to each suspension from the stock 0.01M uranyl nitrate solution to give an initial total uranium concentration of 10⁻⁵M (2.38 ppm). Figures 10 to 13 show
Figure 10. Adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃ without CO₂.
Figure 11. Adsorption of uranium (VI) onto amorphous ferric oxyhydroxide at 25°C in 0.1M NaNO₃ without CO₂.
Figure 12. Adsorption of uranium (VI) onto synthetic hematite at 25°C in 0.1M NaNO₃ without CO₂.
Figure 13. Adsorption of uranium (VI) onto natural specular hematite at 25°C in 0.1M NaNO₃ without CO₂.
the percentage of uranium (VI) adsorbed at different pHs for goethite, amorphous ferric oxyhydroxide, synthetic hematite, and natural hematite, respectively. The results suggest that uranium (VI) is strongly adsorbed onto all four materials, especially at pH 5 and above. This is in spite of the fact that both the uranyl species and the sorbing oxides or oxyhydroxides have net positive charges at some of these pHs. It is also evident that dissolved uranyl species are most strongly adsorbed onto amorphous ferric oxyhydroxide and least onto natural hematite. Because a geochemist is most interested in the data at the uppermost part of the plots (more than 90% of the uranium (VI) adsorbed), and because total dissolved uranyl concentrations (ΣU (VI)) of average ground-water are usually in the parts per billion range, we have also presented the data to emphasize these conditions. In Figs. 14-17, (ΣU (VI)) in the solution phase after centrifugation was plotted against the pH. The plots again show that uranium (VI) is most strongly adsorbed by amorphous ferric oxyhydroxide, followed in decreasing order by goethite, synthetic hematite, and natural hematite. The dotted line shown in Figs. 14-17 represents the computed schoepite precipitation curve. Because most of the data points are several orders of magnitude lower than the precipitation curve, it is clear that they are controlled by
Figure 14. Adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. The dotted line represents the computed solubility of schoepite.
Figure 15. Adsorption of uranium (VI) onto amorphous ferric oxyhydroxide at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. The dotted line represents the computed solubility of schoepite.
Figure 16. Adsorption of uranium (VI) onto synthetic hematite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. The dotted line represents the computed solubility of schoepite.
Figure 17. Adsorption of uranium (VI) onto natural hematite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. The dotted line represents the computed solubility of schoepite.
U (VI) adsorption reactions rather than by the precipitation of schoepite. It is also evident in Figs. 16 and 17 that several data points exceed the computed solubility of schoepite. Dissolved uranyl concentrations for these data points are probably controlled by the precipitation and dissolution of schoepite in addition to sorption and desorption. The same uranium (VI) adsorption experiments were repeated at a lower initial $\Sigma U$ (VI) of $10^{-6}$ M (238 ppb) for synthetic hematite and natural hematite. These data are plotted in Figs. 18 - 21. The plots show similar trends, although only two data points in Fig. 21 exceed the computed solubility of schoepite.

D. Reversibility of the Uranium (VI) Adsorption Reactions

Barton (1956) reported that the adsorption of uranyl onto synthetic limonite was generally reversible. In this study, the reversibility of $U$ (VI) adsorption onto goethite, amorphous ferric oxyhydroxide, and natural hematite was studied between pH 4 and 9. The open circles in Figs. 22 - 24 represent data points for uranium (VI) adsorption experiments carried out in exactly the same fashion as described in the previous section. After a small amount of the suspension was withdrawn for uranium analysis, the pH of the remaining suspension was readjusted with 0.1N HNO$_3$ or 0.1N NaOH to a
Figure 18. Adsorption of uranium (VI) onto synthetic hematite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution.
Figure 19. Adsorption of uranium (VI) onto synthetic hematite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. The dotted line represents the computed solubility of schoepite.
Figure 20. Adsorption of uranium (VI) onto natural hematite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution.
Figure 21. Adsorption of uranium (VI) onto natural hematite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. The dotted line represents the computed solubility of schoepite.
new pH value (represented by broken circles in Figs. 22-24). Allowing sufficient time for re-equilibration, the final uranium concentrations and pH values were determined and plotted as double circles on the same figures. In the goethite and amorphous ferric oxyhydroxide experiments, four hours elapsed between the readjustment of pH and the final analysis. For natural hematite, three days were allowed between pH readjustment and final analysis. As shown in Figs. 22-24, the new data points after pH readjustment all return to the initial adsorption curve, indicating that the adsorption reaction is reversible.

E. Effect of Surface Area on Adsorption

The uranyl adsorption curves for the four starting materials are plotted together in Fig. 25 for comparison. The plot shows that U (VI) is most strongly adsorbed by ferric oxyhydroxide and least strongly by natural specular hematite. Because specific surface areas for these four materials ranged widely (e.g., 306 - 1.8 m²/g), it was decided to check if the observed differences in adsorption were caused solely by the differences in surface areas. The adsorption experiments were repeated for these four materials using suspensions which all contained a specific surface area of 45 m²/l. The experimental results are
Figure 22. Reversibility of uranium (VI) adsorption onto goethite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. See text.
Figure 23. Reversibility of uranium (VI) adsorption onto amorphous ferric oxyhydroxide at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. See text.
Figure 24. Reversibility of uranium (VI) adsorption onto natural hematite at 25°C in 0.1M NaNO₃ and in a CO₂-free (oxygenated) solution. See text.
Figure 25. Adsorption of uranium (VI) onto 1g/l of amorphous ferric oxyhydroxide, goethite, synthetic hematite, and natural hematite at 25°C in 0.1M NaNO₃ and in CO₂-free systems.
plotted in Fig. 26. The four adsorption isotherms are much closer together, showing that surface area is an important factor but not the only factor determining the position and shape of the isotherms.

F. The Effect of Carbonate Complexing on Adsorption

To examine the effect of carbonate complexing on U (VI) adsorption, enough NaHCO$_3$ salt was added to the suspensions to bring the total carbonate concentration (C$_T$) in the suspensions to 0.001 or 0.01M. Other conditions were the same as described in previous experiments. Figures 27-32 compare adsorption from 0.001 and 0.01M total carbonate solutions to adsorption from a carbonate-free (oxygenated) solution. The plots indicate that carbonate complexing inhibits adsorption and favors desorption of uranyl onto all of the four materials. It is also clear that adsorption inhibition is proportional to C$_T$. The percentage distribution diagrams of uranyl-hydroxy-carbonate complexes vs. pH in 0.1M NaNO$_3$ electrolyte solutions have been calculated and are plotted in Figs. 33 and 34. The calculations were carried out using an expanded version of the computer program WATEQF (Plummer et al., 1976), with thermochemical data for uranium species from Langmuir (1978) and Dongarra and Langmuir (1980). The percentage distribution diagrams indicate that the uranyl
Figure 26. Adsorption of uranium (VI) onto 45 m²/l of amorphous ferric oxyhydroxide, goethite, synthetic hematite, and natural hematite at 25°C in 0.1M NaNO₃ and in CO₂-free systems.
Figure 27. Effect of carbonate complexing on the adsorption of uranium (VI) by goethite.
Figure 28. Effect of carbonate complexing on the adsorption of uranium (VI) by amorphous ferric oxyhydroxide.
Figure 29. Effect of carbonate complexing on the adsorption of uranium (VI) by synthetic hematite. The dotted line represents the computed solubility of schoepite.
Figure 30. Effect of carbonate complexing on the adsorption of uranium (VI) by natural hematite. The dotted line represents the computed solubility of schoepite.
Figure 31. Effect of carbonate complexing on the adsorption of uranium (VI) by synthetic hematite.
Figure 32. Effect of carbonate complexing on the adsorption of uranium (VI) by natural hematite.
Figure 23. Distribution of uranyl-hydroxy and carbonate complexes vs pH for \( \Sigma U(\text{VI}) = 10^{-5} \text{M} \) and \( C_T = 10^{-3} \text{M} \) at 25°C in 0.1 M NaNO₃ solutions.
Figure 34. Distribution of uranyl-hydroxy and carbonate complexes vs pH for EU (VI) = 10^{-5}M, and C_t = 10^{-2}M at 25°C in 0.1 M NaNO_3 solutions.
di- and tri- carbonate complexes are weakly adsorbed if at all, relative to strong adsorption of the hydroxyl complexes, $UO_2\text{OH}^+$, $(UO_2)_2(\text{OH})_2^+$, and $(UO_2)_3(\text{OH})_5^+$. In Figs. 27 and 28, the uranium (VI) adsorption curves for carbonate-free (oxygenated) solutions tend to rise slightly at pH above 9. This suggests that U(VI) is either slightly desorbed at very alkaline pHs, or the effect is caused by contamination with trace amounts of atmospheric CO$_2$ during sample transfer and/or centrifugation. These and other possible explanations for the rising adsorption curves above pH 9 are discussed in more detail on p.103.

The enrichment factor (EF) and distribution coefficient ($K_d$) concepts are two approaches used by geochemists and environmental scientists to define the sorption behavior of geological materials. For uranium, EF is defined as the weight of sorbed U per weight of sorbent plus U, divided by the weight of dissolved U per weight of solution. $K_d$ is defined as the weight of sorbed U per weight of sorbent divided by the gram mass of U dissolved in one milliliter of solution. Thus, EF is dimensionless and can be converted to $K_d$ (in milliliters per gram) by division by the solution density. Using the data shown in Fig. 27, $K_d$ values for adsorption by goethite were calculated and are listed in Table 2. It is evident that these values depend on both pH and $C_T$ and vary by
Table 2. Effect of pH andCarbonate Complexing on the Distribution Coefficient ($K_d$) for Uranyl Adsorption by Goethite at $C_T = 0$, $10^{-2}$ and $10^{-1}$M.

<table>
<thead>
<tr>
<th>pH</th>
<th>$C_T = 0$</th>
<th>$C_T = 10^{-2}$M</th>
<th>$C_T = 10^{-1}$M</th>
</tr>
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<tr>
<td>4</td>
<td>$7.1 \times 10^2$</td>
<td>$7.1 \times 10^2$</td>
<td>$7.1 \times 10^2$</td>
</tr>
<tr>
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<td>$9.9 \times 10^3$</td>
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<tr>
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<td>$2.6 \times 10^5$</td>
<td>$2.9 \times 10^4$</td>
</tr>
<tr>
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<tr>
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<td>$2.7 \times 10^6$</td>
<td>$2.0 \times 10^5$</td>
<td>$9.9 \times 10^2$</td>
</tr>
<tr>
<td>9</td>
<td>$2.2 \times 10^6$</td>
<td>$5.9 \times 10^4$</td>
<td>$1.9 \times 10^2$</td>
</tr>
</tbody>
</table>
several orders of magnitude. This suggests that any attempt to predict and model uranium transport in natural hydrologic environments based on a single measured EF or $K_d$ value is dangerous. A comprehensive model is needed to simultaneously take into account pH, complexation, and other effects.

G. The Effect of Calcium and Magnesium on Adsorption

Because natural waters contain calcium and magnesium concentrations typically around $10^{-3}$ M, it was decided to examine their competitive effect on uranyl adsorption. For this purpose, 0.1M calcium or magnesium nitrate solution was added to the ferric oxyhydroxides in suspension to give a total Ca or Mg concentration of 0.001M. Figures 35-37 compare the effects of Ca and Mg on uranyl adsorption by the oxyhydroxides relative to the adsorption from Ca and Mg-free solutions. The plots show that uranyl adsorption is independent of Ca or Mg concentrations within the uncertainty of the measurements at all pHs considered. If the same behavior applies to Na$^+$ and K$^+$ which is very likely, then the important conclusion is that uranyl adsorption is independent of major cation concentrations. This suggests that our adsorption results have general applicability to natural systems.
Figure 35. Effect of Mg and Ca on the adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃ without CO₂.
Figure 36. Effect of Mg and Ca on the adsorption of uranium (VI) onto amorphous ferric oxyhydroxide at 25°C in 0.1M NaNO₃ without CO₂. The solid line is the adsorption curve in the absence of dissolved Mg and Ca (see Fig. 15)
Figure 37. Effect of Mg and Ca on the adsorption of uranium (VI) onto natural hematite at 25°C in 0.1M NaNO₃ without CO₂. The solid line is the adsorption curve in the absence of dissolved Mg and Ca (see Fig. 21).
Dissolved phosphate species, although minor constituents in average ground-water (usually less than $10^{-5}$M), form very stable complexes with uranyl ions (Langmuir, 1978; Dongarra and Langmuir, 1980). Therefore, it is of interest to learn the effect of phosphate complexing on uranyl adsorption. For this purpose, weighed amounts of Na$_2$HPO$_4$ salt were added to the oxyhydroxide suspensions to give initial total phosphate concentrations of $10^{-5}$M or $10^{-3}$M. Other conditions were the same as described in previous experiments. Figures 38-40 show the results. The solid lines depict the adsorption of $\overset{V}{\overset{I}{U}}$ (VI) by amorphous ferric oxyhydroxide, synthetic hematite, and natural hematite in the absence of phosphate species. The symbols represent the experimental data for uranyl adsorption in the presence of $10^{-5}$M or $10^{-3}$M total phosphate concentrations. As shown in Figs. 38-40, the presence of total phosphate at $10^{-5}$M or $10^{-3}$M enhances the adsorption, particularly at low pHs. The symbols shown in Figs. 38-40 are all below the calculated solubility limits of Na-autunite and H-autunite (Langmuir, 1978), suggesting that U (VI) concentrations are not controlled by the precipitation or dissolution of these phases. The percentage distribution diagrams of uranyl-hydroxy and phosphate complexes vs. pH in 0.1M NaNO$_3$ electrolyte solutions were calculated and are
Figure 38. Effect of phosphate complexing on the adsorption of uranium (VI) by amorphous ferric oxyhydroxide. The solid line is the uranyl adsorption curve in the absence of dissolved phosphate species (see Fig. 15).
Figure 39. Effect of phosphate complexing on the adsorption of uranium (VI) by synthetic hematite. The solid line is the uranyl adsorption curve in the absence of dissolved phosphate species (see Fig. 19).
Figure 40. Effect of phosphate complexing on the adsorption of uranium (VI) by natural hematite. The solid line is the uranyl adsorption curve in the absence of dissolved phosphate species (see Fig. 21).
plotted in Figs. 41 and 42. The figures indicate that $\text{UO}_2(\text{HPO}_4)_2^{2-}$ is the predominant dissolved uranyl species in the pH range of 4 to 9. This suggests that in contrast to the behavior of the uranyl carbonate complexes, the $\text{UO}_2(\text{HPO}_4)_2^{2-}$ complex is strongly adsorbed. Hinston et al. (1972, 1974) have shown that dissolved phosphate species are strongly adsorbed to the surface of goethite and hematite, especially at acidic pHs. It is likely that when the dissolved phosphate species greatly exceeds $\Sigma\text{UO}_2^{(VI)}$ (as in the case of $10^{-3}$ M $\Sigma\text{PO}_4$), the excess phosphate is adsorbed and covers many of the positive sites on the iron oxide surface. This then enhances the adsorption of $\text{UO}_2^{(VI)}$.

The experimental data shown in Figs. 38 - 40 show more scatter than the data in previous figures. The UA-3 Uranium Analyzer analytical procedure involves the addition of a buffered phosphate complexing reagent, FLURAN, during analysis. It therefore seems likely that the presence of additional phosphate in the sample solution interferes with the analysis and causes the observed scatter in the analytical results.
Figure 41. Distribution of uranyl-hydroxy and phosphate complexes vs. pH for $\Sigma U$ (VI) = $10^{-7}$ M, and $\Sigma PO_4 = 10^{-5}$ M at 25°C in 0.1M NaNO$_3$ solutions.
Figure 42. Distribution of uranyl-hydroxy and phosphate complexes vs pH for $\Sigma U$ (VI) = $10^{-5}$ M, and $\sum PO_4 = 10^{-3}$ M at 25°C in 0.1 M NaNO$_3$ solutions.
A comprehensive sorption model is critically needed to explain and predict the adsorption behavior of uranium in natural systems. A variety of empirical and theoretical models have been used to explain and/or fit laboratory heavy metal adsorption data. These include: (1) simple isotherm equations, such as the Freudlich and Langmuir equations (Soldatini et al., 1976; Garcia-Miragaya and Page, 1976; Harmsen, 1977); (2) mass action type equations, including Donnan exchange (Krishnamoorthy and Overstreet, 1949, 1950) and more general expressions (Garrels and Christ, 1956, 1965; Maes et al., 1975; and Langmuir, 1981); (3) composite models which combine isotherms and/or mass-action-type sorption concepts with double or triple layer mathematical treatments (c.f. Yates, 1975; James and Parks, 1981; James, 1981). However, the applicability of these models to complicated natural systems has usually been seriously limited, or not yet been tested.

In this study, the uranium sorption data were examined using (1) a composite model, the surface ionization and complexation model (Davis et al., 1978), and (2) a mass-action-type model, the power exchange function model
Previous studies have shown that these two models have a relatively high tolerance for changing solution conditions, such as pH, ionic strength, competing ions and adsorbate concentrations, etc., and that they are capable of modeling multiple simultaneous adsorption reactions.

B. The Surface Ionization and Complexation Model

The surface ionization and complexation model, proposed by Davis and others (Davis et al., 1978; Davis and Leckie, 1978, 1980) is a direct outgrowth of several earlier electrical double layer approaches (James and Healy, 1972; Yates et al., 1974; and Stumm et al., 1976). It is a reasonably complete model in which both physical and chemical interactions are considered in its formulation. The model has the advantage of being conceptually simple. It can ideally predict the simultaneous adsorption behavior of ions and the development of surface charge and potential at the hydrous oxide/water interface. The model has also been applied with reasonable success to the adsorption of different cations and anions in dilute to moderately concentrated solutions (c.f. Davis and Leckie, 1978, 1980; Balistrieri and Murray, 1979).
Model Background

According to Davis et al. (1978), the development of surface charge at the ferric oxyhydroxide/water interface is due to amphoteric ionization reactions of surface functional groups (Fe-OH) through the uptake or release of potential determining ions (i.e., H⁺ and OH⁻). Thus,

\[
\begin{align*}
\text{Fe-OH}_2^+ & \overset{K_{a1}}{\underset{\text{int}}{\rightleftharpoons}} \text{Fe-OH} + H_s^+ \\
\text{Fe-OH} & \overset{K_{a2}}{\underset{\text{int}}{\rightleftharpoons}} \text{Fe-O}^- + H_s^+
\end{align*}
\]

where \( \text{Fe-OH}_2^+ \), \( \text{Fe-O}^- \) are ionized surface species, \( H_s^+ \) denotes activities of protons on the surface, and \( K_{a1}, K_{a2} \) are intrinsic acidity constants determined at zero surface charge and zero potential conditions.

In addition to these reactions, the interaction of supporting electrolyte ions with the ferric oxyhydroxide/water interface can provide further surface charge effects through surface complexation reactions.

\[
\begin{align*}
\text{Fe-OH} + \text{cation}_s & \overset{K_{\text{cation}}}{\underset{\text{int}}{\rightleftharpoons}} \text{FeO}^- + \text{cation} + H_s^+ \\
\text{Fe-OH} + H_s^+ + \text{anion}_s & \overset{1/K_{\text{anion}}}{\underset{\text{int}}{\rightleftharpoons}} \text{FeOH}_2^+ + \text{anion}
\end{align*}
\]

Here, the subscript \( s \) denotes activities of individual ions on the surface, and the symbols \( *_{\text{int}}, K_{\text{cation}}, K_{\text{anion}} \) denote intrinsic complexation constants determined at zero surface charge and zero potential conditions.
The model further assumes that the ionized surface sites are confined to a mean surface plane and the specifically adsorbed ions to a second mean plane at a distance of $\beta$ from the mean surface plane (Fig. 43).

For a ferric oxyhydroxide dispersion in a simple NaNO$_3$ electrolyte system, the surface charge ($\sigma_o$) and the charge in the mean plane of specifically adsorbed counter-ions ($\sigma_\beta$) can be defined as:

\[ \sigma_o = 10^6 \frac{F}{A} \left( [\text{SOH}_2^+] + [\text{SOH}_2^+ \text{NO}_3^-] - [\text{SO}^-] \right) \]

\[ \sigma_\beta = 10^6 \frac{F}{A} \left( [\text{SO}^- \text{Na}^+] - [\text{SOH}_2^+ \text{Cl}^-] \right) \]

where $A$ is the surface area of oxide available in solution in cm$^2$/liter, $F$ is the Faraday constant (96,500 C/mole), and similar bracketed surface species are equivalent concentrations of surface species in moles/liter, and $\sigma_o$ and $\sigma_\beta$ have units of $\mu$C/cm$^2$. Constant capacitances are assumed in the region between the planes (Fig. 44) and the charge potential relationships are as follows:

\[ \psi_o - \psi_\beta = \frac{\sigma_o}{C_1} \]

\[ \psi_\beta - \psi_d = -\frac{\sigma_d}{C_2} \]
$\sigma_0 = [\text{SOH}_2^+] + [\text{SOH}_2^+ - \text{NO}_3^-] - [\text{SO}^-] - [\text{SO}^- - \text{Na}^+]$

$\sigma_\beta = [\text{SO}^- - \text{Na}^+] - [\text{SOH}_2^+ - \text{NO}_3^-]$

$\sigma_0 + \sigma_\beta + \sigma_d = 0$

Figure 43. Schematic representation of an oxide-solution interface showing possible locations of molecules comprising the planes of charge (modified from Davis et al., 1978).
Figure 44. Schematic representation of the charge distribution at an idealized planar surface in aqueous solution and the potential decay away from the surface (Davis et al., 1978).
where $C_1$ and $C_2$ are the integral capacitances of the respective inner and outer regions, $\sigma_d$ is the charge in the diffuse layer and can be derived from Gouy-Chapman diffuse layer theory:

$$\sigma_d (\mu \text{C/cm}^2) = -11.74 \times 10^6 \text{C}^{1/2} \sinh \left( \frac{Z \psi_d}{2KT} \right)$$  (9)

where $C$ and $Z$ are the bulk concentration and charge of the supporting electrolyte counterion in the diffuse layer.

In addition to these equations, electroneutrality and surface mass balance requirements must also be met, hence,

$$\sigma_0 + \sigma_\beta + \sigma_d = 0$$  (10)

$$N_s (\mu \text{C/cm}^2) = 10^6 \frac{F}{A} \left[ \left[ \text{SOH}_2^+ \right] + \left[ \text{SOH}_2^+ - \text{NO}_3^- \right] + \left[ \text{SOH} \right] + \left[ \text{SO}^- \right] + \left[ \text{SO}^- - \text{Na}^+ \right] \right]$$  (11)

where $N_s$ is the total number of sites available on the particle surface.

The entire set of equations (Eqs. (1)-(11)) can be solved numerically at any pH and electrolyte concentration with known values for the parameters $N_s$, $K_{\text{int}}^{a_1}$, $K_{\text{int}}^{a_2}$, $K_{\text{Na}^+}$, $K_{\text{NO}_3^-}$, $C_1$ and $C_2$. The calculations were carried out using a modified version of the computer program MINEQL (Westall, et al, 1976), with thermochemical data for uranium species from Langmuir (1978) and Dongarra and Langmuir (1980).
In order to solve the above equations, it is necessary to determine the intrinsic equilibrium constants. These constants \(K^{\text{int}}\) are thermodynamic constants written for reactions occurring at an hypothetical isolated site on the surface. Since the actual activities of ions on the surface (e.g., \(H^+_s\), \(Na^+_s\)) cannot be determined directly, one can only calculate the apparent stability quotients \((Q)\) based on measureable bulk concentrations. However, according to Davis et al. (1978), the apparent stability quotients \((Q)\) are related to the intrinsic constants \((K^{\text{int}})\) through the electrostatic field correction terms. Therefore, the intrinsic equilibrium constants \((K^{\text{int}})\) can be determined by proper extrapolation of the apparent stability quotients \((Q)\) to zero charge and potential conditions, thereby eliminating electrostatic field effects. Recently, James et al. (1977) and Davis and Leckie (1978) have developed a graphic double extrapolation procedure to obtain intrinsic equilibrium constants. An example of how to use this method to determine intrinsic equilibrium constants for \(K^{\text{int}}_{\text{al}}\) and \(K^{\text{int}}_{\text{NO}_3^-}\) is given in Figs. 45 and 46. The symbols \(\alpha\) and \(C\) denote fractional surface charge and \(\text{NaNO}_3\) electrolyte concentrations, respectively. The potentiometric titration data described in a previous section for goethite (Fig. 1) and amorphous
Figure 45. Double extrapolation plots for the determination of $pK^{int}_{al}$ of goethite in $\text{NaNO}_3$ electrolyte solutions at 25°C.
Figure 46. Double extrapolation plots for the determination of $p_{\text{K}^{\text{int}}_{\text{NO}_3}}$ of goethite in NaNO$_3$ electrolyte solutions at 25°C.
ferric oxyhydroxide (Fig. 2) were used to construct such plots. The double extrapolation method involves extrapolation to zero charge \((\alpha = 0.0)\) and either zero electrolyte concentration \((C = 0.0M)\) for the intrinsic acidity constants \((k_{a1}^{\text{int}} \text{ and } k_{a2}^{\text{int}})\) or 1M electrolyte concentration for intrinsic complexation constants \((k_{\text{cations}}^{\text{int}} \text{ and } k_{\text{anions}}^{\text{int}})\). The intrinsic equilibrium constants determined in this study together with those determined by previous investigators are summarized in Table 3 for different iron oxide or oxyhydroxide surfaces.

**Computation of Electrical Double Layer Properties of Goethite and Amorphous Ferric Oxyhydroxide in Simple Electrolytes**

The surface ionization and complexation model was used first to model the surface properties of goethite and amorphous ferric oxyhydroxide in simple NaNO\(_3\) electrolyte solutions. According to Davis et al. (1978), the intrinsic equilibrium constants \((k_{a1}^{\text{int}}, k_{a2}^{\text{int}}, k_{\text{Na}^+}^{\text{int}}, k_{\text{NO}_3^-}^{\text{int}})\), the surface site density \((N_s)\) and specific surface area are all fixed parameters derived either directly or indirectly from measureable surface properties. The only two adjustable parameters are the inner layer capacitance \((C_1)\) and the outer layer capacitance \((C_2)\). By proper selection of a combination of these two parameters, the model can give a good agreement between calculated and experimentally measured
Table 3. Surface Parameters of Iron Oxides or Oxyhydroxides Used in Surface Ionization and Complexation Model Calculations

<table>
<thead>
<tr>
<th>Systems</th>
<th>Reference</th>
<th>Surface Area (m²/g)</th>
<th>Surface Site Density (sites/nm²)</th>
<th>( \text{pK}_\text{int}^{\alpha} )</th>
<th>( \text{pK}_\text{int}^{\alpha 2} )</th>
<th>( \text{pK}_\text{cation} )</th>
<th>( \text{pK}_\text{anion} )</th>
<th>( C_1 ) (µF/cm²)</th>
<th>( C_2 ) (µF/cm²)</th>
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<td>( \alpha )-FeOOH/NaNO₃</td>
<td>This study</td>
<td>45</td>
<td>18</td>
<td>4.5</td>
<td>12.0</td>
<td>10.1</td>
<td>7.0</td>
<td>140</td>
<td>20</td>
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<tr>
<td>Fe(OH)₃ (am)/NaNO₃</td>
<td>This study</td>
<td>700?</td>
<td>20</td>
<td>4.8</td>
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<td></td>
<td></td>
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<td>( \text{(1.05 \times 10^{-2} \text{ mol/g})} )</td>
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<td>( \alpha )-FeOOH/KNO₃</td>
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<td>48</td>
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<td>20</td>
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<td>Fe(OH)₃ (am)/NaNO₃</td>
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<td>600?</td>
<td>11(a)</td>
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</tr>
<tr>
<td>( \alpha )-FeOOH/NaCl</td>
<td>Hingston, et al (1968)</td>
<td>32</td>
<td>16.8(a)</td>
<td>4.9</td>
<td>( \text{b} )</td>
<td>6.6</td>
<td>( \text{b} )</td>
<td>( \text{b} )</td>
<td>20</td>
</tr>
<tr>
<td>( \alpha )-Fe₂O₃</td>
<td>Breeuwsma (1972)</td>
<td>b</td>
<td>10</td>
<td>6.7</td>
<td>10.3</td>
<td>9.5</td>
<td>7.5</td>
<td>90</td>
<td>20</td>
</tr>
</tbody>
</table>

(a) Data from Yates (1975)

b Not determined

? See discussions in the text
surface charge ($\sigma_o$), and the electrokinetic data. Stumm et al. (1970) and Lyklema and Overbeek (1961) have found that 20 $\mu$F/cm$^2$ is a reasonable value for outer layer capacitance ($C_2$) on Hg and AgI, and provides good agreement with electrokinetic data. This value was also adopted and used in this study for further modeling purposes. Hence, the only adjustable parameter left in the model is the inner layer capacitance ($C_1$). It was found that an arbitrarily selected value of 140 $\mu$F/cm$^2$ for $C_1$ provided the best agreement between the model calculations and the experimentally measured surface charge of goethite (Fig. 47). In Fig. 47 different symbols denote experimental data points, solid curves represent the same properties calculated using the surface ionization and complexation model and intrinsic constants and capacitances given in the figure. The value of 140 $\mu$F/cm$^2$ for $C_1$ is in good agreement with values proposed by others for other iron oxides as shown in Table 3. No attempt was made to correlate model calculated diffuse layer potentials ($\sigma_d$) and the experimentally measured electrokinetic data. This is because the non-spherical geometry (needle shape) of the goethite particles precluded the accurate estimation of the zeta potential from electrophoretic mobility. The same procedures were used to fit the surface charge data of amorphous ferric oxyhydroxide. As shown in Fig. 48, the model
Figure 47. Experimental and computed surface charge density of goethite dispersions in NaNO₃ electrolyte solutions at 25°C as a function of ionic strength and pH.
Figure 48. Experimental and computed surface charge density of amorphous ferric oxyhydroxide dispersions in NaNO₃ electrolyte solutions at 25°C as a function of ionic strength and pH.
calculated curves do not fit the experimental data very well. It is also apparent that the inner layer capacitance \( C_1 \) and surface charge density \( \sigma_0 \) are significantly larger for amorphous ferric oxyhydroxide than for the other iron oxides or oxyhydroxides (Table 3). Davis and Leckie (1978) have suggested that the errors associated with the techniques for surface area measurement may lead to the overestimation of surface charge density. As described in previous sections, different techniques result in a large range of estimated specific surface areas for amorphous ferric oxyhydroxide, e.g., 157-840 m\(^2/g\); hence, neither the specific surface area nor the inner layer capacitance is well known. Nonetheless, Davis and Leckie (1978) have demonstrated that it is possible to select a combination of these two parameters to give good agreement between calculated and experimentally measured surface charges. As shown in Fig. 49, a combination of 130 \( \mu F/cm^2 \) for the inner layer capacitance \( C_1 \) and 700 m\(^2/g\) for the specific surface area provide good agreement between experiment and the model. This value for \( C_1 \) and a surface site density of 20/nm\(^2\) are not significantly larger values than those found for other crystalline iron oxides if the specific surface of 700 m\(^2/g\) is used. Accordingly, these two values were adopted for further modeling purposes. Davis and Leckie (1978) selected a combination of 140 \( \mu F/cm^2 \) \( C_1 \)
Figure 49. Experimental and computed surface charge density of amorphous ferric oxyhydroxide dispersions in NaNO₃ electrolyte solutions at 25°C as a function of ionic strength and pH.

\[
\begin{align*}
C_1 & = 130 \mu F/cm^2 \\
C_2 & = 20 \mu F/cm^2 \\
pK_{a1} & = 4.8 \\
pK_{a2} & = 11.1 \\
p'K_{Na^+} & = 9.3 \\
p'K_{NO_3} & = 7.0
\end{align*}
\]
and 600 m²/g (specific surface area) for their amorphous iron oxyhydroxide sample.

The Adsorption of Uranyl Species

The experimental data of U (VI) adsorption onto goethite in 0.1M NaNO₃ solutions (Fig. 10) were used to further test the applicability of this model to adsorption from dilute solutions. According to the model, the uranyl adsorption-desorption reactions may be written in a manner analogous to those of the swamping electrolyte cations (i.e., Na⁺). The modeling procedure begins by assuming that uranyl ion, UO₂⁻²⁺, is the only dissolved uranyl species that is adsorbed to the goethite surface site (FeOH), and that the simplest surface reaction is followed, i.e.,

\[
\text{FeOH} + \text{UO}_2^{2+} \xrightleftharpoons[\text{FeO}^- \text{UO}_2^{2+} + \text{H}^+]_{\text{s}}^{\text{K}_{\text{UO}_2^{2+}}} \text{FeO}^- \text{UO}_2^{2+} + \text{H}^+_{\text{s}}
\] (12)

where the subscript \(s\) denotes surface concentrations. One can rewrite the mass law equation of the above reaction in terms of bulk concentrations and the mean electrostatic potentials as follows:

\[
\left[\text{FeO}^- \text{UO}_2^{2+}\right] = \frac{\text{K}_{\text{UO}_2^{2+}}}{\text{FeOH}} \left[\text{UO}_2^{2+}\right] \times \exp \left[\left(e\psi^- - 2e\psi^-_B\right)/KT\right]
\] (13)

This single surface reaction is thus incorporated into the computer program MINEQL to model uranium (VI)
adsorption reactions. The same surface parameters, determined or estimated in the previous section for \( K_{\text{al}} \), \( K_{\text{a2}} \), \( K_{\text{Na}^+} \), \( K_{\text{NO}_3^-} \), \( N_s \), \( C_1 \), \( C_2 \), and specific surface area, were used in the model calculations. With this single surface reaction, the model calculated uranyl adsorption curve as a function of pH is in poor agreement with the experimental data (Fig. 50). An increase or decrease in \( K_{\text{UO}_2^{2+}} \) does not improve the agreement, as it simply shifts the calculated adsorption curve to higher or lower positions. One more surface reaction was then proposed. It was assumed that the adsorption of uranyl ions, \( \text{UO}_2^{2+} \), also forms a bidentate surface complex at goethite surface sites, i.e.,

\[
2(\text{FeOH}) + \text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \begin{array}{c} \text{FeO}^- \cr \text{FeO}^- \end{array} \text{UO}_2^{2+} + 2\text{H}^+ \quad (14)
\]

The symbol \( \beta \) is used for the stability constant when a surface reaction involves a bidentate surface site, as in Eq. (14). The inclusion of this additional surface reaction does not significantly improve the agreement between model calculation and the experimental data points. Because the attempt to model uranium (VI) adsorption assuming \( \text{UO}_2^{2+} \) is the only adsorbed species was unsuccessful,
Figure 50. Adsorption of U (VI) by goethite at 25°C in 0.1M NaNO₃ solutions. Circles are experimental data. The solid line is model calculated considering Eq. (12) as the surface reaction involving U(VI).
it was evident (as expected) that uranyl hydroxy complexes must also be adsorbed. Percentage distribution diagrams for the uranyl-hydroxy complexes vs pH in 0.1M NaNO₃ electrolyte solutions have been calculated and are plotted in Figs. 51 and 52 for ΣU = 10⁻⁸ M and ΣU = 10⁻⁵ M, respectively. A careful examination of these plots, together with the U(VI) adsorption curves in Figs. 10 and 11, revealed that in the pH range where uranyl is most strongly adsorbed (i.e., at pH > 5), the predominant dissolved uranyl species are UO₂OH⁺ and (UO₂)₃(OH)⁺. It was therefore assumed that in addition to UO₂⁺, these complexes are also adsorbed by goethite according to the following reactions:

\[
\begin{align*}
\text{FeOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} & \xrightarrow{\text{K}_\text{int}} \left[ \text{FeO}^- \text{UO}_2\text{OH}^+ \right] + 2\text{H}^+ & (15) \\
\text{FeOH} + 3\text{UO}_2^{2+} + 5\text{H}_2\text{O} & \xrightarrow{\text{K}_\text{int}} \left[ \text{FeO}^- \left(\text{UO}_2\right)_3\text{(OH)}^+ \right] + 6\text{H}^+ & (16)
\end{align*}
\]

The mass law equations for the above reactions can be written:

\[
\left[ \text{FeO}^- \text{UO}_2\text{OH}^+ \right] = \text{K}_\text{int} \left[ \text{FeOH} \right] \left[ \text{UO}_2^{2+} \right] \left[ \text{H}^+ \right]^2 \times \exp \left[ (e\psi_0 - e\psi_B)/kT \right] \quad (17)
\]
Figure 51. Distribution of uranyl-hydroxy complexes vs. pH for $\Sigma U$ (VI) = $10^{-8}$ M at 25°C in 0.1M NaNO$_3$ solutions.
Figure 52. Distribution of uranyl-hydroxy complexes vs. pH for $\Sigma_4 = 10^{-5}$M at 25°C in 0.1M NaNO$_3$ solutions.
\[
\frac{[\text{FeO}^-\text{-(UO}_2\text{)}_3\text{(OH)}_5^+]}{\text{FeO}^-\text{-(UO}_2\text{)}_3\text{(OH)}_5^+} = K_{\text{int}}^\text{(UO}_2\text{)}_3\text{(OH)}_5^+ \frac{[\text{FeOH}][\text{UO}_2^{2+}]^3}{[\text{H}^+]^5} \times \\
\exp \left[ \frac{(\psi_0 - \psi_\beta)}{KT} \right]
\]

(18)

Significantly better agreement was achieved by adding these two additional surface reactions to the model calculations. In fact, according to the model calculations, the contribution of Eq. (12) to the total surface reaction is always very small and can be neglected. Therefore, by assuming \text{UO}_2^{2+} and \text{(UO}_2\text{)}_3\text{(OH)}_5^+ are the only uranyl species adsorbed, the model adequately explains the \text{U (VI)} adsorption data onto goethite. It was found that combination of \( p_{\text{int}}^{\text{UO}_2^{2+}} = 8.0 \) and \( p_{\text{int}}^{\text{(UO}_2\text{)}_3\text{(OH)}_5^+} = 15.0 \) gave the best agreement between the model calculations and experimental results (Fig. 53). The same modeling procedures were repeated for the uranyl adsorption data onto amorphous ferric oxyhydroxide (Fig. 54). A combination of \( p_{\text{int}}^{\text{UO}_2^{2+}} = 8.0 \) and \( p_{\text{int}}^{\text{(UO}_2\text{)}_3\text{(OH)}_5^+} = 15.0 \) also gave the best agreement between model calculation and experimental results in this case. However, the model reactions proposed above are not the only ones that can fit the experimental data. For example, the adsorption of uranyl hydroxy complexes could form bidentate or tridentate surface complexes. i.e.,
Figure 53. Adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃ solutions. Circles are experimental data. Solid curve is model calculated considering UO₂OH⁺ and (UO₂)₃(OH)₅⁺ surface equilibria.
Figure 54. Adsorption of uranium (VI) onto amorphous ferric oxyhydroxide at 25°C in 0.1M NaNO₃ solutions. Circles are experimental data. Solid curve is model calculated considering UO₂OH⁺ and (UO₂)₃(OH)₅⁺ surface equilibria.
It was found that by arbitrarily assuming the dissolved uranyl species are adsorbed as $\text{UO}_2\text{OH}^+$ monodentate complexes (Eq.15), and $\text{(UO}_2\text{)}_3\text{(OH)}_5^+$ tridentate surface complexes (Eq.20) and using $p_{\text{int}}^{\text{UO}_2\text{OH}^+} = 8.2$, and $p_{\text{int}}^{\text{(UO}_2\text{)}_3\text{(OH)}_5^+} = 23.6$, the model calculations can fit the experimental data equally well (Fig.55). Therefore, it is not possible to uniquely judge which are the predominant reactions on the surface of goethite based solely on the goodness of the model fit to the data. Although the geometric configuration of the adsorbed $\text{(UO}_2\text{)}_3\text{(OH)}_5^+$ complex and its orientation on the adsorbing iron oxyhydroxide surface are not known, an estimation based on the crystal radii of uranyl ions suggests that the adsorbed $\text{(UO}_2\text{)}_3\text{(OH)}_5^+$ complex may have a minimum cross-section diameter
Figure 55. Adsorption of uranium (VI) onto goethite at 25°C in 0.1 M NaNO₃ solutions. Circles are experimental data. Solid curve is model calculated considering UO₂OH⁺ surface monodentate complex and (UO₂)₃(OH)₅⁺ surface tridentate complex equilibria.
of 6 - 8Å on the surface. However, a calculation based on the measured site density (see Table 2) indicates that each surface (SOH) functional group has a cross-sectional area of only 5Å². It therefore seems likely that each adsorbed $(\text{UO}_2)_3(\text{OH})_5^+$ complex is bounded to more than one surface functional group. This would support the hypothesis that adsorption to form a tridentate surface complex (Eq. 20) is more probable than adsorption as a monodentate complex (Eq. 16). A bidentate surface complex model involving $(\text{UO}_2)_3(\text{OH})_5^+$ was not attempted, but based upon the success of the monodentate and tridentate models, would probably have closely fit the empirical adsorption data. The crystallographic arguments given above would not allow one to decide whether a bi- or tridentate model was the more correct.

It was also found that, although the model calculated curves fit the experimental data very well when plotted on percent uranium (VI) adsorbed vs pH diagrams (see Figs. 53-55), the same goodness of fit was not found when plots were drawn in terms of total dissolved U(VI) vs pH. As shown in Fig. 56, the model calculated curve deviates from the experimental data points at total dissolved U(VI) concentrations \( \leq 1 \) ppb. Model calculations predict a continuous decrease in dissolved U(VI) concentrations as the pH increases, while the actual experimental data indicate the trend levels off
Figure 56. Adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃. Circles are experimental data. Solid curve is model calculated considering UO₂OH⁺ surface monodentate complex and (UO₂)₃(OH)₅⁺ tridentate surface complex equilibria.
at pH $\geq 7$. Unfortunately, the concentration range near 1 ppb is typical of that in average groundwater systems, and therefore is of most interest to geochemists. More discussion is needed to explain this apparent failure of the Davis-Leckie model in dilute U(VI) solutions. Several possible explanations are:

1) The presence of trace amounts of goethite particles in the supernatant, not completely separated during centrifugation: According to a calculation, if 0.05% of the total goethite remained in the supernatant, its adsorbed uranium would suffice to account for the apparent leveling of uranyl adsorption at high pH. This possibility is considered likely in view of the experimental procedures used in this study.

2) Contamination of the adsorption experiments with a trace amount of atmospheric CO$_2$ during sample transfer and centrifugation: As shown in previous sections, carbonate complexing inhibits adsorption and favors desorption especially at alkaline pHs. A comparison of Figs. 27 and 56 suggests that a high total dissolved carbonate concentration ($\approx 10^{-4}$M) is needed to account for the observed discrepancy. This much CO$_2$ contamination is not likely in view of the experimental care taken in this study.

3) The adsorption of dissolved uranyl species reaches a maximum: In the model calculations, it is assumed that each
adsorbed uranyl species is bound to one to three SOH surface functional groups (see Eqs. 15-20). However, due to the relatively larger sizes of uranyl ions and hydroxyl complexes as compared to protons, the uranyl species physically cover more surface functional groups. The pH above which the experimental data starts to deviate from the model calculations, as shown in Fig. 56, may be the pH at which this particular type of site has been used up, so that no further adsorption is possible. Percentage distribution diagrams for all the surface species are plotted in Figs. 57 and 58 based on model calculations. It is evident that adsorbed uranyl species occupy a few percent or less of the total available surface sites. This suggests it is unlikely that all these particular surface sites have been used up at the total uranium (VI) concentrations used in this study.

(4) The presence of anionic uranyl hydroxy complexes: Based on the potentiometric and spectrophotometric studies of Sutton (1949), Lemire and Tremaine (1980) have suggested the presence of an anionic uranyl hydroxy complex (i.e., (UO$_2$)$_3$(OH)$_7$) in basic uranium (VI) solutions. They have also calculated an equilibrium constant (logK = -31 ± 4) for the reaction:

$$3 \text{UO}_2^{2+} + 7 \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_7^- + 7 \text{H}^+ \quad (21)$$

However, the evidence for the formation of this anionic uranyl complex remains uncertain, since most of Sutton's
Figure 57. Distribution of model calculated surface species vs pH on goethite at 25°C in 0.1M NaNO₃ solutions.
Figure 58. Distribution of model calculated surface species vs pH on goethite at 25°C in 0.1M NaNO₃ solutions. (Expansion of the upper 10% from Figure 57).
conclusions were based on potentiometric titration data carried out under metastable conditions. Besides, the thermodynamic data given by Lemire and Tremaine (1980) for different uranyl hydroxy complexes may not be internally consistent, since they have taken values for \((\text{UO}_2)_3(\text{OH})_7^-\) from Sutton (1949) and the values for other uranyl hydroxy complexes directly from Langmuir (1978). Nevertheless, assuming \((\text{UO}_2)_3(\text{OH})_7^-\) does exist in basic solutions, and using constants from Lemire and Tremaine (1980) and Langmuir (1978), the percentage distribution diagram of uranyl hydroxy complexes vs pH for \(\Sigma\text{U}(\text{VI}) = 10^{-8}\text{ M}\) has been calculated and plotted in Fig. 59. It is evident that the anionic complex \((\text{UO}_2)_3(\text{OH})_7^-\) predominates above pH 8. The same modeling procedures, described above for Figs. 55 and 56, were repeated: (a) assuming \((\text{UO}_2)_3(\text{OH})_7^-\) complexes exist in alkaline uranium solutions and are not adsorbed to the surface of goethite; (b) adding Eq. (21) to the model calculations and arbitrarily selecting a log \(K\) value of \(-29.0\) (which is within the uncertainty of the value determined by Sutton (1949) and Lemire and Tremaine (1980) and (c) without changing the other intrinsic constants shown in Figs. 55 and 56. Model calculated values are plotted as a solid curve in Fig. 60. It is evident that significantly better agreement can be
Figure 59. Distribution of uranyl - hydroxy complexes vs pH for $\Sigma$U(VI) = $10^{-8}$ M at 25°C in 0.1M NaNO$_3$ solutions.
Figure 60. Adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃ solutions. Circles are experimental data. Solid curve is model calculated assuming a $\text{UO}_2\text{OH}^+$ surface monodentate complex, a $(\text{UO}_2)_3(\text{OH})_5^+$ tridentate surface complex, and the presence of a dissolved $(\text{UO}_2)_3(\text{OH})_7^-$ complex which is not adsorbed (see text).
achieved by adding this anionic uranyl species in model calculations. Whether this is the correct answer to the observed discrepancy still awaits further confirmation of the presence of $(\text{UO}_2)_3(\text{OH})_7^-$, and better estimation of its formation constant.

**Determination of Proton Release During Adsorption**

The determination of the number of protons released per uranyl ion adsorbed can provide further information on the stoichiometry of the surface reactions. During the uranyl adsorption studies, it was observed that the addition of uranyl nitrate stock solution to the iron oxide or oxyhydroxide suspensions caused a shift of the pH to a lower value. Figure 61 compares such titration curves of goethite in the presence and in the absence of U(VI). The observed shift of the titration curve is caused in part by the hydrolysis of $\text{UO}_2^{2+}$ ions to form uranyl hydroxy complexes and in part by the interaction of uranyl species with iron oxyhydroxide surface. At a given pH, the contribution from the hydrolysis of uranyl species can be carefully calculated and deducted from the total shift of the titration curve. The remaining portion of the observed shift is, then, caused solely
Figure 61. Potentiometric titration curves of goethite suspensions at 25°C in 0.1M NaNO₃ solutions.
by the interaction of U(VI) species with surface functional groups (FeOH). This proton displacement, when divided by the total number of U(VI) species adsorbed, indicates the total number of protons released per U(VI) ion adsorbed. As shown in Fig. 62, the number of protons released per U(VI) ion adsorbed varies between 2 and 3 and averages about 2.3 in the pH range from 4-9. This is in good agreement with model assumptions, in that all the surface reactions proposed (Eq. 15-20) release between 2 and 2.66 protons per U(VI) adsorbed. However, because of the uncertainties associated with the potentiometric titration curves, it is still not possible to decide the relative importance of the reactions proposed above.
Figure 62. Number of proton released per U (VI) adsorbed to the goethite surface. Circles are experimental data. Solid line is the linear, least-square fit of the data points.
Carbonate Complexation Effect on the Uranyl Adsorption

Reactions

As mentioned in a previous section, the presence of carbonate complexing inhibits uranyl adsorption and favors desorption, especially in alkaline conditions. An effort was made to model these carbonate complexing effects. Modeling procedures were begun by assuming that none of the dissolved carbonate species or uranyl carbonate complexes are adsorbed, and thus they do not influence surface charges and potentials. With the intrinsic complexation constants derived in Fig. 51 and other surface parameters listed in Table 3, the model was used to calculate U(VI) adsorption curves for goethite in the presence of $10^{-2}$ and $10^{-3} \text{M}$ total dissolved carbonate ($C_T$). As shown in Fig. 63, the model calculated curves do not agree well with the experimental data. Dissolved U(VI) species are more strongly adsorbed than the model predicts at and above pH=5.

Percentage distribution diagrams for uranyl-hydroxy-carbonate complexes vs pH for $\Sigma U(\text{VI}) = 10^{-5} \text{M}$ and $C_T = 10^{-2} \text{M}$ and $10^{-3} \text{M}$ (see Figs. 33 and 34) indicate that $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are the predominant dissolved uranyl species from pH 5 and up. It was therefore assumed that uranyl carbonate complexes are also adsorbed, according to the following reactions:
Figure 63. Adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃ solutions. Squares and triangles are the experimental data for $C_T = 10^{-2}$ and $10^{-3}$ M, respectively. Solid curves are model calculated assuming dissolved carbonate species and dissolved uranyl carbonate complexes are not adsorbed.
It was found that by combining these two reactions with Eqs. (15) and (16), and by arbitrarily selecting $pK_{\text{UO}_2(\text{CO}_3)_2}^{\text{int}} = -30.0$ and $pK_{\text{UO}_2(\text{CO}_3)_3}^{\text{int}} = -38.5$, model calculations give the best fit to the uranyl adsorption data for $C_T = 10^{-2}$ M (Fig. 64). However, the same set of equilibrium constants cannot model the uranyl adsorption data for $C_T = 10^{-3}$ M. In order to obtain the best agreement with these data, it was necessary to change $pK_{\text{UO}_2(\text{CO}_3)_2}^{\text{int}}$ to -29.5 and $pK_{\text{UO}_2(\text{CO}_3)_3}^{\text{int}}$ to -42.5. The reason for this discrepancy is not clear. However, based on the intrinsic constants for other similar ligands sorbed onto ferric oxyhydroxides reported by Davis (1977), it is unlikely that the neglect of the adsorption of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ ions can account for the discrepancy. More likely the disparity results from an inadequacy in the model itself.
Figure 64. Adsorption of uranium (VI) onto goethite at 25°C in 0.1M NaNO₃ solutions. Symbols are experimental data. The solid curve is model calculated considering $^{\text{UO}_2\text{OH}}^+$, $(\text{UO}_2\text{)}_3(\text{OH})_5^+$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ surface equilibria.
An attempt was made to determine the adsorption reactions for $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ onto the surface of goethite and amorphous ferric oxyhydroxide. The sorption experiments were conducted in a manner similar to those described in preceding sections. A 40 ml screw-capped polycarbonate centrifuge bottle was used as the reaction vessel. The desired amount of NaHCO$_3$ salt was added to the suspensions to give an initial $C_T = 10^{-4}$ M. The bottle was tightly sealed and the empty space above the suspension was kept at minimum to reduce the possible degassing of the dissolved CO$_2$. After the desired reaction period, the sample was centrifuged. The clear supernatant after centrifugation was analyzed for its dissolved carbonate content by acid titration (Brown et al., 1970). Unfortunately, in many cases, the carbonate content was close to or below detection limit, and no consistent or reproducible results were obtained. A more sensitive chemical analytical technique, such as liquid scintillation counting together with the use of radioactive tracers (e.g. C$^{14}$ labeled sodium carbonate salts) is suggested for future studies.

**Predictive Capability**

As with other proposed adsorption models, the surface ionization and complexation model presented here can be used
to predict adsorption, provided that the stoichiometry of surface complexation reactions and the intrinsic stability constants have been determined from other studies. An example is given in Fig. 65, using intrinsic stability constants estimated from preceding sections (see Fig. 52), and surface parameters listed in Table 3, the model was used to predict U(VI) adsorption onto amorphous ferric oxyhydroxide suspensions at different solid to liquid ratios. As shown in Fig. 65, the model calculated curves agree very well with the experimental results.

Davis and Leckie (1978) have suggested that, for many solutes, the chemical component of the bond energy with an oxide surface site may be approximately the same from one oxide to another. They have also shown that, when written in terms of charged sites (i.e., SO\(^-\) or SOH\(_2^+\)), the intrinsic complexation constants are often of the same order of magnitude for different oxide surfaces. If this is also the case for dissolved uranyl species, then, the intrinsic surface complexation constants determined in this study may be used as a first estimate of the stability constants for oxides such as TiO\(_2\) and \(\gamma\)-Al\(_2\)O\(_3\), provided that other surface parameters are available from previous studies.
Figure 65. Adsorption of uranium (VI) onto amorphous ferric oxyhydroxides at 25°C in 0.1M NaNO₃ solutions at two different solid to solution ratios. Circles are experimental data. Solid curves are model calculated considering UO₂OH⁺ and (UO₂)₃(OH)⁵⁺ surface equilibria.
Summary of the Surface Ionization and Complexation Model

The surface ionization and complexation model, with its several fixed parameters (e.g., $N_s$, $pK_{al1}^{int}$, $pK_{al2}^{int}$, etc.) and two adjustable parameters ($C_1$ and $C_2$), has been shown to successfully model the surface properties and uranyl adsorption data over a wide range of solution conditions. However, this model is still basically a curve fitting, semi-empirical approach. It should be viewed as having the correct mathematical form to yield an optimal fit to the experimental data. The model does not necessarily indicate the actual physical or chemical interactions at the interface (Westall and Hohl, 1981). Nevertheless, it is still a very useful predictive tool for modeling the adsorption reactions of ions at the oxide/water interface. The other important advantage of this model is that surface charge and diffuse layer potential are also calculated and may be compared with potentiometric titration results or electrokinetic measurements, if available. Thus, the effect of adsorbing ions on the interfacial electrostatic field and on colloid stability can be predicted. The model can also provide an estimate of the stoichiometry of the adsorbed ions. Such an estimate, a simpler, strictly chemical model usually cannot make. However, the successful application of this model involves the determination of several parameters, such as specific
surface area, intrinsic constants, and the surface site density of individual sorbents. These requirements make the model difficult to apply to heterogeneous natural environments which contain multiple sorbents. More studies are needed to determine and compile intrinsic equilibrium constants and surface parameters for common sorbents in natural sediments. The applicability of the model to more complex solution/colloid systems also needs to be verified before it can be applied with confidence to field conditions.
C. The Power Exchange Function Model

The power exchange function model, proposed recently by Langmuir and Ozsvath (Ozsvath, 1979; Langmuir, 1981) is a simpler mass action type sorption model. It is an empirical model, which as yet does not have a sound theoretical basis that applies to the full concentration range of competing sorbate species. However, the model has been used to model metal adsorption behavior with success over a wide range of sorbate concentrations, pH values, surface charges, competing ion activities and temperatures. The simplicity of the model and its remarkable success in predicting cation exchange reactions make it attractive for application to a variety of natural and pure laboratory systems. In this section, the uranium adsorption data will be tested by this model.

Model Background

According to Langmuir and Ozsvath (Ozsvath, 1979; Langmuir, 1981), the exchange behavior of many major and minor cations on a variety of adsorbents (montmorillonites, beidellite, illite, ferric oxyhydroxides, zeolites, soils and humic materials) can be systematized in terms of power exchange functions. For example, for a homovalent binary
exchange reaction occurring on sorbent site $x^{2-}$

$$A + BX = B + AX$$

(24)

the measured experimental data for this reaction can often be fitted into one or more of the following empirical expressions (called power exchange functions)

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

(25)

where the square brackets denote molal activities of the solute species, AX and BX are mole fractions of A and B on the sorbent, $K_{ex}$ is the exchange constant of the reaction and n is a constant. Based on the cation exchange data so far available, Langmuir (1981) indicated that, the adsorption of alkali and alkaline earth cations at about $10^{-2}$ to $10^{-4}$ M often follows power exchange function-type behavior with n=1 (i.e., equivalent to a simple ion exchange reaction). Adsorption of heavy metals (between $10^{-3}$ to $10^{-7}$ M) is usually more complex and can be fitted with power exchange functions having n=0.8 to 2.0.

Linerization of the power exchange function for an A-B exchange gives:
$\log \frac{[A]}{[B]} = -\log K_{ex} + n \log \left(\frac{AX}{BX}\right)$ \hspace{1cm} (26)

so that a plot of $\log [A]/[B]$ versus $\log (AX/BX)$ has a slope of $n$ and intercept of $-\log K_{ex}$. Langmuir (1981) so examined many published and unpublished binary exchange data and showed that such plots are usually highly linear, with correlation coefficients ($r$ values) between 0.98 and 1.00.

**Application of the Power Exchange Function Approach to Cation Exchange on Amphoteric Oxide/Oxyhydroxide Surfaces**

The successful application of the power exchange function model to fit metal ion-$H^+$ exchange data on amphoteric metal oxide or oxyhydroxide surfaces requires knowledge of the cation exchange capacity (CEC) and/or base exchange capacity (BEC) of the sorbent. The cation exchange capacity (CEC) is defined as the sum of all the readily exchangeable cations on the surface, whereas the base exchange capacity (BEC) refers to the sum of all the readily exchangeable cations other than protons on the surface. The cation exchange capacity (CEC) equals the sum of base exchange capacity (BEC) plus the proton exchange capacity (PEC), which is defined as the sum of all the readily exchangeable protons on the surface.
The CEC, BEC and PEC are all functions of pH.

A review of the literature shows that there are very few data available for metal-H\(^+\) exchange reactions occurring on amphoteric metal oxide or oxyhydroxide surfaces, that can be used to test the applicability of the power exchange function (Langmuir, 1981). Two such sets of data from Gadde and Laitinen (1973) and van der Weijden and Langmuir (1976), were tested and found to fit the power exchange function. However, both of these studies were carried out at constant pH. For example, the experimental data of Gadde and Laitinen (1973) for Pb\(^{2+}\)-H\(^+\) exchange on 'ferric oxide' were performed at pH = 5. For these data, a constant cation exchange capacity of 300 meq/100gm was arbitrarily assumed so as to employ the power exchange function (Ozsvath, 1979; Langmuir, 1981). The experimental data of van der Weijden and Langmuir (1976) for uranyl-H\(^+\) exchange onto different ferric oxides or oxyhydroxides under constant pH conditions, also fit power exchange functions. Constant CEC values estimated from an acid-base titration curve, and from a Langmuir isotherm plot were both found to fit the power exchange function equally well (Hsi, 1978; Langmuir, 1981). However, the uranyl-H\(^+\) exchange data of van der Weijden and Langmuir (1976) obtained at
variable pH values could not be fitted with a power exchange function. Hsi (1978) suggested that incorrect estimation of the CEC could be one cause for the poorness of the fit.

The purpose of this study was therefore, to further test the applicability of the power exchange function model to uranyl-H⁺ exchange on ferric oxide and oxyhydroxide surfaces, especially under variable pH conditions.

Determination of Cation Exchange Capacity on Amphoteric Oxide/Oxyhydroxide Surfaces

Ozsvath (1979) suggested a titration method to experimentally determine the BEC of calcium-montmorillonite for different pH conditions. The BEC vs pH curve, thus determined, was used as the basis to model Cd²⁺-Ca²⁺ and Pb²⁺-Ca²⁺ exchange reactions occurring on the surface of calcium-montmorillonite (Ozsvath, 1979). However, the same titration technique cannot be applied directly to determine the CEC of an amphoteric oxide/oxyhydroxide surface. This is because of the simultaneous presence of several amphoteric ionization reactions of the surface functional groups (SOH). Therefore, the CEC of the amphoteric ferric oxide/oxyhydroxide surface must be estimated using less direct methods.
Uranyl Adsorption at Constant pH

Data for uranyl-H⁺ exchange onto amorphous ferric oxyhydroxide at constant pH 7.23 were fitted to the power exchange function. The data, which are from van der Weijden and Langmuir (1976), are included in the Appendix. It was found that the uranyl-H⁺ exchange data measured at constant pH also obeyed the Langmuir isotherm equation. A linearized form of the Langmuir isotherm equation is:

\[
\frac{1}{N} = \frac{1}{N^\infty} + \frac{1}{N^\infty \times K} \times \frac{1}{C}
\]  

(28)

where

- \( N \) : is the amount of the adsorbate adsorbed (micrograms/gram)
- \( N^\infty \): is the adsorption maximum at monolayer coverage (micrograms/gram)
- \( C \): is the concentration of the adsorbate in solution (micrograms/liter)
- \( K \): is the equilibrium constant

If the adsorption data obey Langmuir isotherm behavior, a plot of \( 1/N \) vs \( 1/C \) yields a straight line with intercept equal to \( 1/N^\infty \) and slope of \( 1/(N^\infty \times K) \). The linearized Langmuir isotherm plot of the uranyl adsorption data of van der Weijden
and Langmuir (1976) are plotted in Fig. 66. As shown in
the figure, the plot exhibits two linear segments. The
reason for the presence of two linear segments is not clear.
The usual interpretation would be that each segment cor­
responds to a different adsorption mechanism. In any case,
extrapolation of each linear segment to the \(1/C = 0\) condition,
theoretically yields the value for \(N_\infty\); the adsorption maximum
at monolayer coverage. The \(N_\infty\) values thus estimated were
50.6 meq/100 gm and 8.5 meq/100 gm for segments (a) and (b)
respectively. The larger value was arbitrarily selected as
the CEC of amorphous ferric oxyhydroxide at \(pH = 7.23\), and
was used in model calculations. Computer calculation of
dissolved uranyl speciation showed that practically all (>99%) of
the uranyl is present as \(\text{UO}_2\text{OH}^+\) ion. It was therefore
assumed that this is the adsorbed species, and that the
following exchange reaction occurs:

\[
[\text{UO}_2\text{OH}^+] + (\text{HX}) \rightarrow (\text{UO}_2\text{OHX}) + [\text{H}^+] \tag{29}
\]

where the \([\text{UO}_2\text{OH}^+]\) and \([\text{H}^+]\) are activities of the aqueous
species and \((\text{HX})\) and \((\text{UO}_2\text{OHX})\) are mole fractions of the
adsorbed species on the exchange sites. The same data cast
in power exchange form according to Eq. (29) are plotted in
Fig. 67. As shown in the plot, a single function fits
Figure 66. Linearized Langmuir isotherm plot of uranyl adsorption onto amorphous ferric oxyhydroxide. Data are from van der Weijden and Langmuir (1976).
Figure 67. Power exchange function plot of uranyl adsorption onto amorphous ferric oxyhydroxide. The line without data points denotes Donnan exchange behavior. Data are from van der Weijden and Langmuir (1976).
all the data, regardless of the adsorption mechanism or mechanisms. The Donnan-type exchange line (i.e., \( n=1, K=1 \)) is also plotted in Fig. 67 for comparison. It is evident that adsorption of \( \text{UO}_2\text{OH}^+ \) is increasingly favored over that of protons at total uranyl concentrations down to \( 10^{-9.6} \) M (0.056 µg/l).

**Uranyl Adsorption at Variable pH**

The data for uranyl adsorption onto synthetic hematite (Figs. 18-19) and natural hematite (Figs. 20-21) from pH 4-9 were also tested using the power exchange function model. Since there was no direct method to experimentally determine the CEC, it was estimated indirectly. Examination of Figs. 57 and 58 shows that the neutral surface functional group (SOH), comprises from 95-98% of all surface sites between pH 4-8. It was therefore assumed that the mole fraction of the SOH groups remained constant in this pH range, and that all were available for exchange with the dissolved uranyl species. This of course also implies that the SOH sites correspond to the CEC. Constant values of 10 meq/100g and 4 meq/100g were selected as the CEC for synthetic hematite and natural hematite, respectively, based on the surface site density data determined by the tritium exchange method. \( \text{UO}_2\text{OH}^+ \) was taken as the only adsorbed
species, and the exchange reaction in Eq. (29) was also assumed. Corresponding results have been calculated and are plotted in Figs. 68 and 69. The data are more scattered than those observed for constant pH conditions (Fig. 67). It was further noted that an increase or decrease of the CEC does not significantly improve linearity, and simply changes the slope and the intercept of the best fit line.

Summary of the Power Exchange Function Model

The power exchange function model is a simple two-parameter equation that can accurately model the behavior of many major and minor cation exchange reactions. The simplicity of the model makes it potentially attractive for application to a variety of natural and laboratory systems. The results of this study indicate that the uranyl adsorption data onto amorphous ferric oxyhydroxide at constant pH fit the power exchange function very well, assuming a constant CEC value estimated from the Langmuir isotherm equation. However, the same goodness of fit was not observed for uranyl adsorption data at variable pH conditions, assuming an arbitrarily assigned constant CEC value. This suggests that the applicability of the model to amphoteric oxide/oxyhydroxide surfaces at variable
SYNTHE TIC HEMATITE
CEC = 10 meq/100g

$K_{ex} = 0.0007$
$n = 1.93$
$r = 0.97$

Figure 68. Power exchange function plot of uranyl adsorption onto synthetic hematite. The line without data points denotes Donnan exchange behavior.
Figure 69. Power exchange function plot of uranyl adsorption onto natural hematite. The line without data points denotes Donnan exchange behavior.
pHs is questionable. The lack of a good estimation of the CEC at various pHs has been suggested as a main cause. More research is needed to develop methods for better estimation of these values. One possible approach is to determine uranyl adsorption isotherms at several constant pH conditions. Then, using the Langmuir isotherm plot technique described in the preceding section, one can estimated the CEC values for these pHs and construct a CEC versus pH diagram.
CONCLUSIONS AND RECOMMENDATIONS
FOR FUTURE STUDIES

A. Conclusions

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

1. At pHs above 5 to 6, dissolved uranyl species are strongly adsorbed onto all four phases tested (i.e., goethite, amorphous ferric oxyhydroxide, synthetic hematite and natural specular hematite). Uranyl adsorptive capacity is directly proportional to the specific surface areas of the adsorbents, with adsorption greatest onto the amorphous phase, and the least onto well crystallized specular hematite.

2. Uranyl adsorption reactions equilibrate rapidly and reach pseudo-reversible equilibrium conditions within a few hours to a few days.

3. Uranyl carbonate complexing inhibits uranyl adsorption and favors desorption especially in alkaline solutions. The amount of desorption is directly proportional to the total dissolved carbonate.

4. The presence of competing cations such as Ca$^{2+}$ or Mg$^{2+}$ at the concentration level of $10^{-3}$M does not signifi-
cantly affect uranyl adsorption.

5. The presence of $10^{-5}$M and $10^{-3}$M total phosphate concentration levels may slightly enhance adsorption at acidic pHs.

6. The surface ionization and complexation model of Davis and Leckie successfully modeled uranyl adsorption data in simple electrolyte systems. However, when systems were more complicated, and involved multiple-ligands for example, modeling procedures become difficult and uncertain.

7. The n-power exchange function successfully modeled uranyl adsorption data at constant pH conditions. The function was less successful modeling adsorption for variable pH conditions possibly because of a lack of good data on cation exchange capacities at different pHs.

B. Recommendations for Future Studies

Experimental Studies

1. Experimental studies similar to those described in this work are suggested for other potential uranium sorbents in natural environments such as titanium and manganese oxides. The uranium adsorption data and surface
parameters determined from these studies would be of great value in understanding the relative importance of these materials as controls on the migration of uranium in natural environments, and for the development of comprehensive uranium sorption models.

2. The results of this study indicate that complexation of uranium significantly affects uranyl adsorption. However, the strong uranyl aquo-complexes formed with carbonate and phosphate species are differently adsorbed, to extents that cannot be predicted from their relative stabilities. Adsorption studies are needed involving other common ligands in natural ground waters including sulfate, fluoride, and organics to further test these effects.

3. Field-oriented studies of groundwaters and geological materials around known uranium deposits are also needed. These should include the collection of data on the relative and absolute amounts of uranyl and other adsorbed species on the natural geological materials. This work would further improve our understanding of the importance of sorption-desorption reactions in the formation of sandstone-type uranium deposits.

Model Developments
a. The surface ionization and complexation model

Several important problems remain to be solved to improve the scientific basis of this model. These include:

1. Determination of the stoichiometry of surface reactions: As shown in this study, the stoichiometry and pK values for simple electrolytes (e.g., Na\(^+\), NO\(_3^-\)) can usually be obtained from extensive potentiometric titration studies and the use of double extrapolation techniques. However, for more complex ions (e.g., UO\(_2^{2+}\), UO\(_2\)OH\(^+\)), the modeling process is based strictly on guess-work, followed by trial and error use of sophisticated computer calculations to test the "goodness of the fit" of the model to the experimental data. This approach is rather inefficient, and as systems become more complicated, it can become impossible to decide which choice of reactions is the correct one. More basic research is needed so as to develop methods to permit an unambiguous determination of the stoichiometry of surface reactions. Possibly other non-thermodynamic data (e.g., electrokinetic data, and infrared spectrometry data) may also be used as additional criteria to test the "goodness" of the model calculations.

2. Application of the model to more complex electrolyte and/or heterogenous systems: The model has so far been tested only in simple electrolyte systems. More experimental
studies are needed to test the applicability of this model to complex natural rock-water systems containing a mixture of different well characterized sorbents.

3. Interfacial calculations involving the formation of surface coatings on original surfaces: There are several systems in which the original colloid surface may be coated with a thin layer of new material which then exhibits its own characteristic ionization behavior. Examples include the formation of a porous hydrous oxide coating on hematite samples. This precludes the accurate estimation of surface charges and intrinsic constants. More research is needed to study the extent and the rate of formation of such coatings, their influence on the release and uptake of trace metals, and what kind modifications are needed in model calculations that consider such sorbent materials.

b. Power exchange function model

1. More research is needed to develop a sound theoretical basis for its remarkable success in fitting empirical data.

2. More empirical adsorption data is needed so that we can better generalize about and predict exchange constants and n values for a wide variety of competing ions and sorbents, and at different temperatures for future applications to natural systems.
APPENDIX

EXPERIMENTAL DATA FOR URANYL ADSORPTION ONTO
AMORPHOUS FERRIC OXYHYDROXIDE AT CONSTANT pH CONDITIONS

The experimental data are from van der Weijden and Langmuir (1976). 51.3 mg of amorphous ferric oxyhydroxide was suspended in 50 ml 0.01M KCl solutions. The desired amount of uranium was added to the suspensions from stock uranyl nitrate solutions to give initial total uranyl concentrations ($C_i$) of: 1, 2, 4, 6, 8, 10, 12, 14, 16, and 20 ppm. The suspensions were allowed to equilibrate at ambient temperature and atmospheric CO$_2$ pressure, and a constant pH of about 7 was maintained throughout the experiment. After a seven-day equilibration period, the suspensions were centrifuged. The pH was measured and the total dissolved uranyl concentration ($C_f$) left in the supernatant solution was analyzed using a Jarrel-Ash Model 26-000 Fluorometer. The experimental data are listed in Table A.
Table A. Experimental Data for Uranyl Adsorption onto Amorphous Ferric Oxyhydroxide at a constant pH of 7.23

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<th>pH</th>
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<th>C_f (ppb)</th>
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<tr>
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<td>8</td>
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</tr>
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REFERENCES CITED


Hsi, C.D., 1978, Application of the \( n \)-power exchange function to available data on uranyl sorption by ferric oxyhydroxides. Unpublished manuscript.


Langmuir, D., 1980, Verbal communication (Professor, Colorado School of Mines).


Ozsvath, D., 1979, Modelling Heavy Metal Sorption from Subsurface Waters with the n-power Exchange Function. M.S. Thesis in Geochemistry, The Pennsylvania State University, University Park, Pennsylvania, 61p.


