

## Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model

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**Abstract**—Uranyl adsorption was measured from aqueous electrolyte solutions onto well-characterized goethite, amorphous ferric oxyhydroxide, and hematite sols at 25°C. Adsorption was studied at a total uranyl concentration of  $10^{-3}$  M, (dissolved uranyl  $10^{-5}$  to  $10^{-8}$  M) as a function of solution pH, ionic strength and electrolyte concentrations, and of competing cations and carbonate complexing. Solution pHs ranged from 3 to 10 in 0.1 M  $\text{NaNO}_3$  solutions containing up to 0.01 M  $\text{NaHCO}_3$ . All the iron oxide materials strongly adsorbed dissolved uranyl species at pHs above 5 to 6 with adsorption greatest onto amorphous ferric oxyhydroxide and least onto well crystallized specular hematite. The presence of Ca or Mg at the  $10^{-3}$  M level did not significantly affect uranyl adsorption. However, uranyl carbonate and hydroxy-carbonate complexing severely inhibited adsorption. The uranyl adsorption data measured in carbonate-free solutions was accurately modeled with the surface complexation-site binding model of DAVIS *et al.* (1978), assuming adsorption was chiefly of the  $\text{UO}_2\text{OH}^+$  and  $(\text{UO}_2)_3(\text{OH})_3^+$  aqueous complexes. In modeling it was assumed that these complexes formed a monodentate  $\text{UO}_2\text{OH}^+$  surface complex, and a monodentate, bidentate or tridentate  $(\text{UO}_2)_3(\text{OH})_3^+$  surface complex. Of the latter, the bidentate surface complex is the most likely, based on crystallographic arguments. Modeling was less successful predicting uranyl adsorption in the presence of significant uranyl carbonate and hydroxy-carbonate complexing. It was necessary to slightly vary the intrinsic constants for adsorption of the di- and tricarboxylate complexes in order to fit the uranyl adsorption data at total carbonate concentrations of  $10^{-2}$  and  $10^{-3}$  M.

### INTRODUCTION

MIGRATION OF URANIUM in water-rock systems is largely controlled by uranium solution-mineral equilibria and sorption reactions. Thermochemical data for aqueous uranium species and minerals (*cf.* LANGMUIR, 1978; KRUPKA *et al.*, 1983) permit accurate modeling of uranium solution-mineral equilibria in low temperature waters (*cf.* LUECK, 1978; LANGMUIR and CHATHAM, 1980; RUNNELLS *et al.*, 1980; RUNNELLS and LINDBERG, 1981; MILLER *et al.*, 1984). However, the role of adsorption reactions in controlling uranium mobility in such waters is only qualitatively understood. In addition, there is no general model that has to date allowed the prediction of the adsorption behavior of uranium for a wide range of solution conditions and sorbent phases. A literature review indicates that uranium adsorption studies have been performed with a variety of sorbents including Ti and Zr oxyhydroxides, and amorphous silica (*cf.* MAYA, 1982a), amorphous ferric oxyhydroxides, goethite and hematite (*cf.* VAN DER WEIJDEN *et al.*, 1976; HSI and LANGMUIR, 1980; HSI, 1981; HSI *et al.*, 1982; HSI and LANGMUIR, 1983), and amorphous silica, clays and organic matter (*cf.* SCHMIDT-COLLERUS, 1967; LANGMUIR, 1978). Among these, the greatest adsorption capacity is observed by amorphous titanium and ferric oxyhydroxides (LANGMUIR, 1978). Uranyl adsorption is most complete in the pH range from 5 to 8.5, regardless of sorbent phase. This is in spite of the fact

that some sorbents, including the ferric oxyhydroxides, have a net positive surface charge within this pH range.

Some of the adsorption data have been modeled using Freundlich or Langmuir isotherm-type equations (VAN DER WEIJDEN *et al.*, 1976; AMES *et al.*, 1983a). Unfortunately, most previous workers did not determine such sorbent properties as surface area, surface charge and potential and the effects on adsorption of complexation, sorbate ion competition and ionic strength, all as a function of pH. Such information is critically needed for the development of general predictive sorption models. In this study, the uranyl adsorption reactions were performed using a well characterized goethite, an amorphous ferric oxyhydroxide, a synthetic hematite and a natural specular hematite. The effect on adsorption of pH, competing cations and carbonate complexing was carefully examined. The experimental data were subsequently modeled with the surface complexation-site binding model of DAVIS *et al.* (1978).

These four materials were selected: (1) because they have a strong sorptive capacity for dissolved uranyl species (VAN DER WEIJDEN *et al.*, 1976; LANGMUIR, 1978), and are common accessory minerals or coating materials found in oxidized soils and sediments where uranyl sorption reactions are most likely to be significant; and (2) because hematite and goethite in particular are common accessory minerals in sandstone-type uranium deposits. Previous studies suggest that these minerals may scavenge uranium from



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subsurface waters and so preconcentrate it. The sorbed uranium may later be released to form nearby roll-front-type uranium deposits (BARTON, 1956; LANGMUIR, 1978).

## MATERIALS AND METHODS

### Sample preparation

Four different ferric oxide or oxyhydroxide sols of relatively uniform shape and narrow particle size distribution were prepared as the sorbents.

A. *Goethite* ( $\alpha$ -FeOOH): A colloidal dispersion of goethite was prepared according to the method of ATKINSON *et al.* (1967). After repeatedly washing with deionized water, the colloidal particles were resuspended in deionized water and kept under a pure oxygen atmosphere.

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). The colloidal dispersion was aged at pH 7 for four hours before beginning titration or adsorption experiments.

C. *Hematite* ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>): A colloidal dispersion of hematite was prepared according to the method of MATJEVIC and SCHEINER (1978). After repeatedly washing with deionized water, the colloidal particles were resuspended in deionized water and kept under a pure oxygen atmosphere.

D. *Natural specular hematite* ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>): A natural specular hematite sample was crushed and ground in a mechanical mill and passed through a 45  $\mu$ m stainless steel sieve. The sample was stored as dry powder in a desiccator.

### Sample characterization

Physical and surface properties of the four materials were carefully determined. Particle size, shape and crystallinity were studied by electron microscopy and X-ray diffraction methods. Specific surface area (A) was obtained on freeze-dried samples by the BET nitrogen adsorption method. Surface charge density ( $\sigma_0$ ) and the pH of zero surface charge (PZC) in NaNO<sub>3</sub> electrolyte solutions were determined using the potentiometric titration method of YATES and HEALY (1980) and the salt titration method of DAVIS and LECKIE (1978). Electrophoretic mobilities and the iso-electric point (IEP; pH at which the net electrophoretic mobility is zero) were measured with a Rank Brothers Mark II microelectrophoresis apparatus (Rank Bros., Cambridge, U.K.). Surface exchangeable site densities ( $N_s$ ) were obtained by the tritium exchange method of BERUBE *et al.* (1967) and YATES and HEALY (1976). Water content was found *via* weight loss upon heating in an oven at 650°C for 15 minutes. The bulk physical and surface properties of the four materials are summarized in Table 1.

### Adsorption measurement

Uranyl adsorption experiments were conducted in batches as follows. A measured amount of previously prepared ferric oxide or oxyhydroxide sol 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 of the solid particles after drying in an oven at 110°C for 15 minutes was taken as the weight of the sorbent in the 125 ml bottle. The ionic strength was adjusted to 0.1 M by the addition of 1.0 M NaNO<sub>3</sub> solution. The pH was adjusted when necessary by the addition of 0.1 N HNO<sub>3</sub> or 0.1 N NaOH solutions. Uranium was added to the suspension from a 0.01 M uranyl nitrate stock solution. Enough CO<sub>2</sub>-free deionized water was then added to bring the total volume of the suspension to 100 ml. After bubbling with purified, H<sub>2</sub>O-saturated oxygen gas to purge dissolved CO<sub>2</sub>, the bottle was tightly sealed and agitated 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 experiment. After the desired reaction period, a 40 ml aliquot of suspension was delivered to a screw-capped polycarbonate centrifuge bottle. A final pH measurement was then made on the remaining suspension and taken as the representative pH of the adsorption run. The 40 ml aliquots were centrifuged at 3,000 rpm for 15 minutes to separate particulates. After centrifugation the clear supernatant was analyzed for its uranium content using a SINTREX UA-3 uranium analyzer which has a detection limit of 0.05 ppb uranium and measurement accuracy of  $\pm 15\%$  at the 1 ppb uranium level and above (ROBBINS, 1978).

## RESULTS

### Adsorption kinetics

To determine the time required for completion of the uranyl adsorption reactions, a series of kinetic studies were conducted. Samples were withdrawn for analysis at selected time intervals. Two-step kinetics were observed for uranyl adsorption onto all four materials. The first step was rapid and complete within a few minutes. The second, slower step often continued for days. The same two-step kinetics was reported for trace metal sorption onto manganese dioxide (LOGANATHAN and BURAU, 1973), amorphous ferric hydroxide (DAVIS, 1977),  $\alpha$ -SiO<sub>2</sub> (BENJAMIN, 1978) and titanium dioxide (BERUBE and DE BRUYN, 1968a,b). Diffusion of adsorbate species into the sorbent matrix and slow alteration of sorbent characteristics are considered the chief causes for the slower reaction (YATES and HEALY, 1980). Since our goal 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 and alteration steps. Based on this study and those reported in the literature, an equilibration time of four hours was chosen for experiments using goethite or amorphous ferric oxyhydroxide as sorbents. For experiments using synthetic hematite or natural hematite, a seven-day equilibration period was used.

Table 1. Physical and surface properties of starting materials

Material	Particle Shape	Particle Size	A (m <sup>2</sup> /g)	N <sub>s</sub> (sites/nm <sup>2</sup> )	PZC	IEP	wt% H <sub>2</sub> O
Fe(OH) <sub>3</sub> (am)	Spherical	2 nm	306	20(a)	7.9 $\pm$ 0.2	—	13
$\alpha$ -FeOOH	Rod-like	1 $\mu$ m length	45	18(b)	8.5 $\pm$ 0.3	8.9 $\pm$ 0.2	11.5
Synthetic $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Spherical	0.3 $\mu$ m	3.1	19	7.5 $\pm$ 0.5	7.2 $\pm$ 0.5	2
Natural $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Irregular	1 $\mu$ m	1.8	15	7.8 $\pm$ 0.5	7.0 $\pm$ 0.5	1

(a) 1.05 $\times 10^{-3}$  mol/g; (b) 1.35  $\times 10^{-3}$  mol/g

### Reversibility of

BARTON (1956) studied the reversibility of uranyl adsorption onto synthetic goethite. In this study, the reversibility was studied by carrying out a series of adsorption-desorption cycles. The remaining uranium was determined by adding HNO<sub>3</sub> to break the equilibrium, then the pH was adjusted to the initial value and the values were determined. The reversibility of ferric oxyhydroxide adsorption between pH 7 and 5 was studied. The reversibility of hematite, three adsorption-desorption cycles were carried out. The new data point for initial adsorption and desorption reversibility of uranyl were obtained.

### Effect of pH on

In order to study the effect of pH on uranyl adsorption, experiments were conducted at various pH values. Figure 2 shows the amount of uranyl adsorbed at different pH values for the four oxyhydroxide materials. The adsorption is strongly dependent on pH, with adsorption being most significant above pH 5. The adsorption of uranyl species

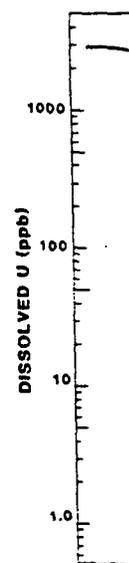


FIG. 1. R = 10<sup>-5</sup> M or free 0.1 M? the initial u pHs follow uranyl adso

### Reversibility of uranyl adsorption reactions

BARTON (1956) reported that the adsorption of uranyl onto synthetic limonite was generally reversible. In this study, the reversibility of uranyl adsorption was studied by carrying out adsorption experiments as previously described. After a small amount of the suspension was withdrawn for uranium analysis, the pH of the remaining suspension was readjusted to a new value with  $\text{HNO}_3$  or  $\text{NaOH}$ . Allowing sufficient time for re-equilibration, the final uranium concentrations and pH values were determined. In the goethite and amorphous ferric oxyhydroxide experiments, four hours elapsed between pH readjustment and the final analysis. For hematite, three days were allowed between pH readjustment and final analysis. Figure 1 shows that the new data points after pH readjustment all lie on the initial adsorption curve for goethite, indicating the pH reversibility of the adsorption reaction. Similar results were obtained for the other oxyhydroxides (Hsi, 1981).

### Effect of pH on uranyl adsorption

In order to study the effect of pH on uranyl adsorption, experiments were carried out in batches with the pH of individual samples adjusted between 4 and 9. Figure 2 shows the percentage of the total uranium adsorbed at different pHs for goethite, amorphous ferric oxyhydroxide, synthetic hematite and natural hematite, respectively. The data demonstrate that uranyl is strongly adsorbed onto all four materials, especially above pH 5. This is in spite of the fact that both the uranyl species (see Fig. 3) and the sorbing oxides or

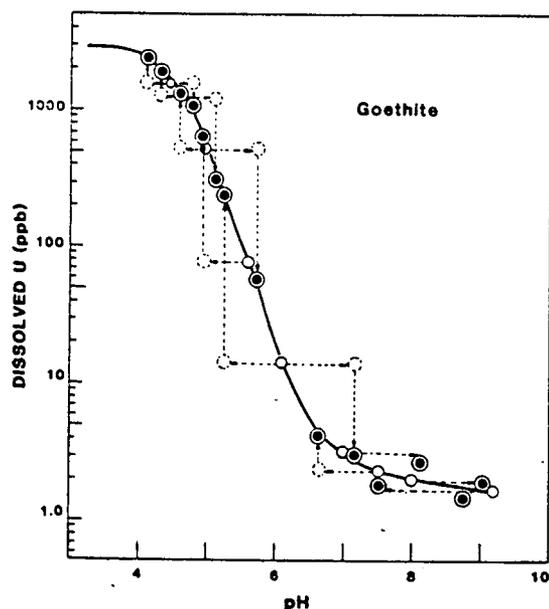


FIG. 1. Reversibility of uranyl adsorption vs. pH at  $\Sigma\text{U} = 10^{-5}$  M onto a 1 g/l goethite suspension in oxygenated  $\text{CO}_2$ -free 0.1 M  $\text{NaNO}_3$  solutions at  $25^\circ\text{C}$ . Open circles represent the initial uranyl adsorption data. Broken circles are solution pHs following pH readjustment, and double circles the final uranyl adsorption data.

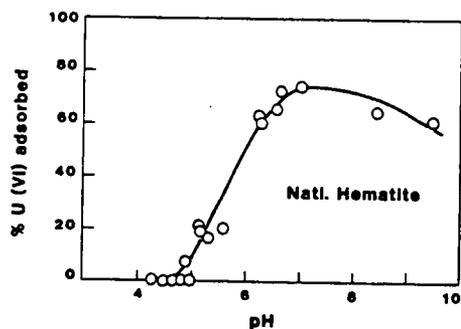
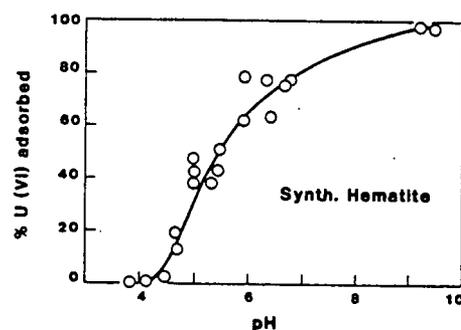
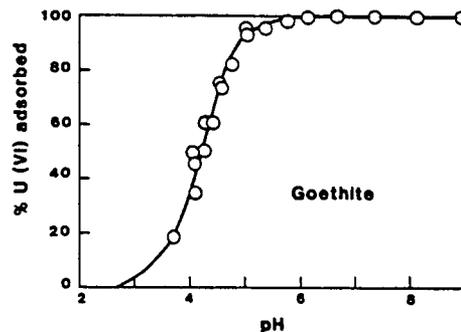
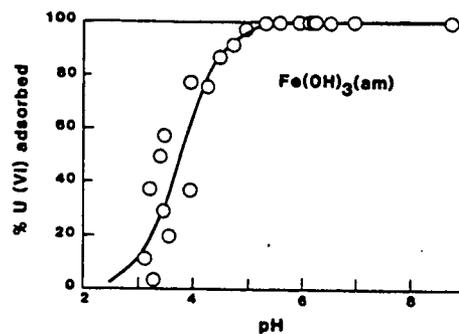


FIG. 2. Adsorption of uranyl vs. pH at  $\Sigma\text{U} = 10^{-5}$  M onto 1 g/l suspensions of ferric oxyhydroxides in 0.1 M  $\text{NaNO}_3$  solutions at  $25^\circ\text{C}$ . Symbols denote the experimental data. Solid curves for  $\text{Fe}(\text{OH})_3(\text{am})$  and goethite only have been model calculated assuming surface parameters given in Table 2, and monodentate surface complexes of  $\text{UO}_2\text{OH}^+$  and  $(\text{UO}_2)_3(\text{OH})_5^+$  with  $p^*K^{\text{int}}$  values of 8.0 and 15.0, respectively.

oxyhydroxides have net positive charges at some of these pHs. The dissolved uranium concentration at each data point was also compared with the calculated

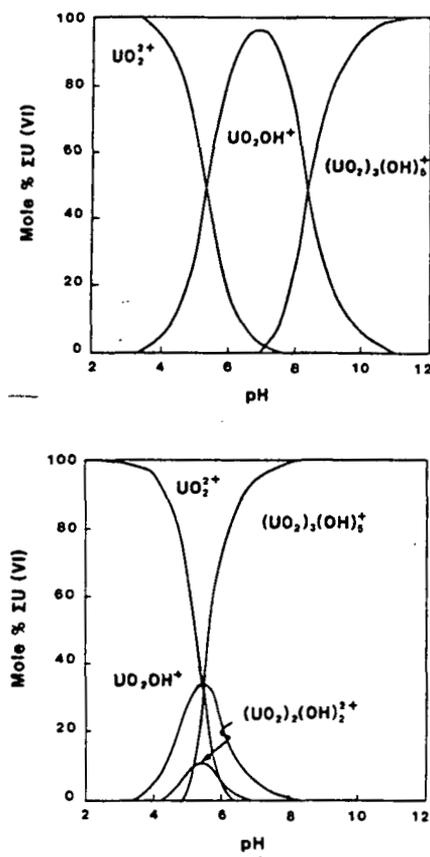


FIG. 3. Distribution of uranyl-hydroxy complexes vs. pH in 0.1 M  $\text{NaNO}_3$  solutions at 25°C: 3a) for  $\Sigma\text{U(VI)} = 10^{-8}$  M; and 3b) for  $\Sigma\text{U(VI)} = 10^{-5}$  M.

solubility of schoepite [ $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{c})$ ] for the same pH conditions. Because most of the concentration data are several orders of magnitude lower than computed for saturation with schoepite, it is evident that they are controlled by adsorption rather than schoepite precipitation. Only a few data points for uranyl adsorption onto synthetic hematite and natural hematite exceeded the computed solubility of schoepite. Uranyl concentrations for these points may be controlled by schoepite solubility as well as adsorption.

#### Effect of competing cations on uranyl adsorption

Fresh natural groundwaters contain calcium and magnesium concentrations typically around  $10^{-3}$  M. To examine the competitive effect of these ions on uranyl adsorption, calcium or magnesium nitrate salts were added to the amorphous ferric oxyhydroxide, goethite, and natural hematite suspensions to give total Ca or Mg concentrations of  $10^{-3}$  M and the same adsorption experiments were repeated. Results indicated that Ca and Mg at  $10^{-3}$  M did not significantly affect uranyl adsorption (Hsi, 1981).

#### Effect of carbonate complexing on uranyl adsorption

STARIK *et al.* (1958) and VAN DER WEIJDEN *et al.* (1976) reported that uranium can be desorbed from

ferric oxyhydroxides and adsorption inhibited by carbonate solutions. To further examine this effect,  $\text{NaHCO}_3$  salt was added to the suspensions to bring the total carbonate concentration ( $C_T$ ) to 0.001 or 0.01 M. Other conditions were the same as previously described. Figure 4 compares uranium adsorption from 0.001 and 0.01 M total carbonate solutions to adsorption from a carbonate-free (oxygenated) solution. The plot indicates that carbonate complexing inhibits adsorption to uranyl onto all four materials. It is also clear that adsorption inhibition is proportional to  $C_T$ . A percentage distribution diagram of uranyl-hydroxy-carbonate complexes vs. pH is plotted in Fig. 5. The diagram has been computed using thermochemical data for uranium species given in the Appendix. A comparison of the uranyl adsorption data in Fig. 4 and the percentage distribution diagrams in Figs. 3 and 5 indicates that the uranyl carbonate and hydroxy-carbonate complexes are weakly adsorbed if at all, relative to strong adsorption of the hydroxyl complexes.

#### MODELING URANYL ADSORPTION REACTIONS

A comprehensive adsorption model is critically needed to explain and predict the adsorption behavior of uranium in water-rock systems. A variety of empirical and theoretical models have been suggested to fit laboratory heavy metal adsorption data. These include simple isotherm equations, such as the Freundlich and Langmuir equations (*cf.* SOLDATINI *et al.*, 1976; and AMES *et al.*, 1983a,b); mass action type equations, including Donnan exchange (KRISHNA-MOORTHY and OVERSTREET, 1950) and more general expressions (TRUEDELL and CHRIST, 1968; LANGMUIR, 1981). However, many of these models determine conditional or apparent equilibrium constants which, strictly speaking, only apply to the given experimental conditions, and not to more complex natural systems. More comprehensive models that can consider the interplay of a multiplicity of independent properties of the solution and sorbent phases are needed. The surface complexation site-binding model of DAVIS *et al.* (1978), which is such a comprehensive model, was chosen to fit the uranium adsorption data. This model can simultaneously predict adsorption behavior of aqueous sorbate species and the development of surface charge at the hydrous oxide interface using a single set of equilibrium constants. It has also been applied with reasonable success to predict the adsorption of simple cations and anions in dilute to moderately concentrated solutions (*cf.* DAVIS and LECKIE, 1978, 1980; BALISTRERI and MURRAY, 1979, 1981). Experimental data for uranyl adsorption onto amorphous ferric oxyhydroxide and goethite were used to test the accuracy of this model.

#### Model background

According to the surface complexation site-binding model, the development of surface charge at the ferric oxyhydroxide/water interface is due to amphoteric ionization reactions of

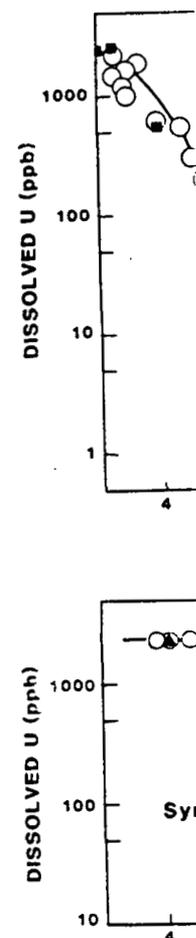


FIG. 4. The effect of carbonate complexing on uranyl adsorption onto 1 g/l synthetic hematite.

surface functional groups and the development of surface potential.

Fe(III) and Fe(II) species.

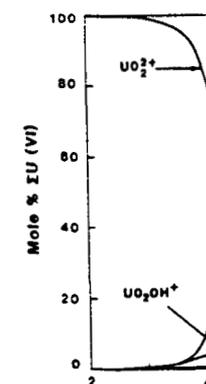


FIG. 5. Distribution of uranyl-hydroxy-carbonate complexes vs. pH at  $\Sigma\text{U(VI)} = 10^{-5}$  M in 0.1 M  $\text{NaNO}_3$  solutions at 25°C.

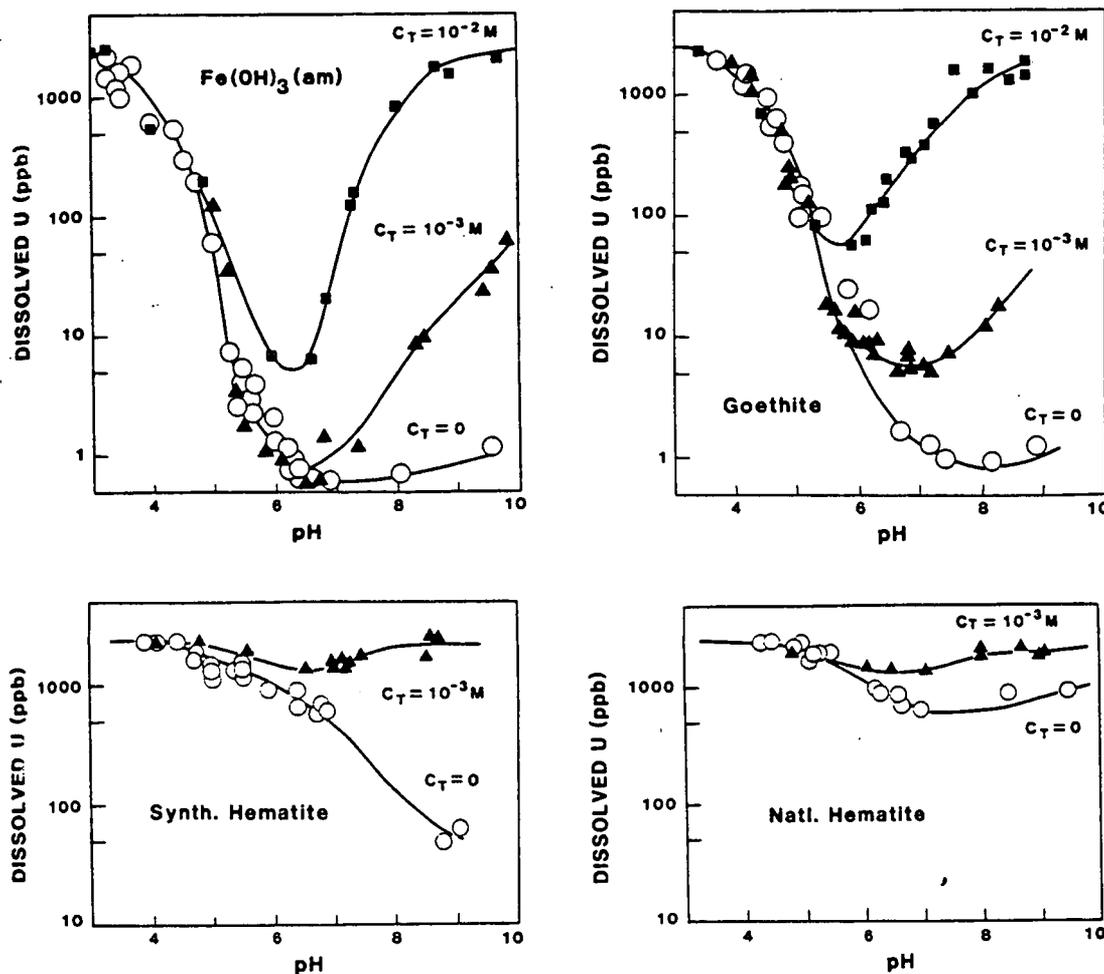
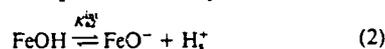
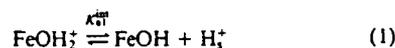


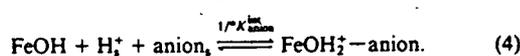
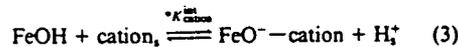
FIG. 4. The effect of changes in total carbonate ( $C_T$ ) on the adsorption of uranyl vs. pH at  $\Sigma U = 10^{-5}$  M onto 1 g/l suspensions of ferric oxyhydroxides in 0.1 M  $\text{NaNO}_3$  solutions at 25°C.

surface functional groups ( $\text{FeOH}$ ) through the uptake or release of potential determining ions (i.e.,  $\text{H}^+$  and  $\text{OH}^-$ ). Thus



where  $\text{FeOH}_2^+$  and  $\text{FeO}^-$  are ionized surface species,  $\text{H}_a^+$  denotes activities of protons on the surface, and  $K_{a1}^{\text{int}}$  and  $K_{a2}^{\text{int}}$  are intrinsic acidity constants determined at zero surface charge and zero potential conditions.

Specifically adsorbed counter-ions, located in the inner Helmholtz plane at a distance of  $\beta$  from the mean surface plane, are assumed to form complexes with the charged surface groups.



Here, the subscript  $s$  denotes activities of individual ions on the surface, and symbols  $K_{\text{cation}}^{\text{int}}$ ,  $K_{\text{anion}}^{\text{int}}$  denote intrinsic complexation constants determined at zero surface charge and zero potential conditions.

For a ferric oxyhydroxide dispersion in a simple  $\text{NaNO}_3$  electrolyte system (see Figs. 1 and 10 in DAVIS *et al.*, 1978), the surface charge ( $\sigma_0$ ) and the charge in the mean plane of specifically adsorbed counter-ions ( $\sigma_\beta$ ) can be defined as:

$$\sigma_0 = 10^6 F/A ([\text{FeOH}_2^+] + [\text{FeOH}_2^+ - \text{NO}_3^-] - [\text{FeO}^-] - [\text{FeO}^- - \text{Na}^+]) \quad (5)$$

$$\sigma_\beta = 10^6 F/A ([\text{FeO}^- - \text{Na}^+] - [\text{FeOH}_2^+ - \text{NO}_3^-]) \quad (6)$$

where  $A$  is the surface area of ferric oxyhydroxide available in solution,  $F$  is the Faraday constant, and  $[\text{FeOH}_2^+]$  and sim-

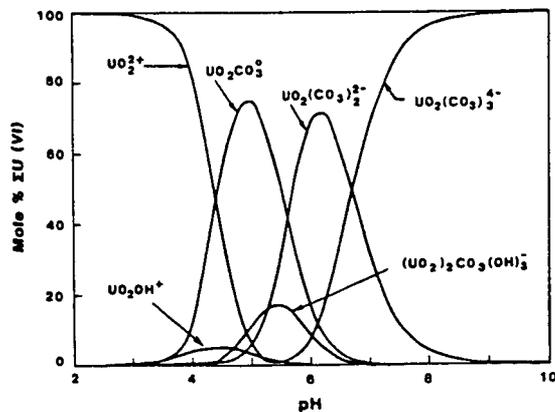


FIG. 5. Distribution of uranyl-hydroxy and carbonate complexes vs. pH at  $\Sigma U = 10^{-5}$  M and  $C_T = 10^{-2}$  M in 0.1 M  $\text{NaNO}_3$  solutions at 25°C.

ilar bracketed surface species are equivalent concentrations of surface species.

Constant integral capacitances  $C_1$  and  $C_2$  are assumed in the regions between the surface plane and the inner Helmholtz plane and between inner and outer Helmholtz planes. Surface potentials at the zero, inner and outer Helmholtz planes are  $\psi_0$ ,  $\psi_\beta$  and  $\psi_d$ , respectively. Thus,

$$\psi_0 - \psi_\beta = \sigma_d / C_1 \quad (7)$$

$$\psi_\beta - \psi_d = -\sigma_d / C_2 \quad (8)$$

The charge at the outer Helmholtz plane or diffuse layer ( $\sigma_d$ ) can be derived from Gouy-Chapman diffuse layer theory.

$$\sigma_d = -11.74 C^{1/2} \sinh \left( \frac{Ze\psi_d}{2KT} \right) \quad (9)$$

where  $C$  and  $Z$  are bulk concentration and charge of the supporting electrolyte cation in the diffuse layer. Finally, electro-neutrality and surface mass balance requirements must also be met, hence,

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

$$N_s = 10^6 F/A ([\text{FeOH}_2^+] + [\text{FeOH}_2^+ - \text{NO}_3^-] + [\text{FeOH}] + [\text{FeO}^-] + [\text{FeO}^- - \text{Na}^+]) \quad (11)$$

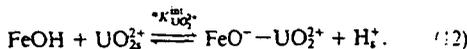
where  $N_s$  is the total number of sites available on the particle surface.

The entire set of equations (Eqns. 1-11) can be solved numerically at any pH and electrolyte concentration provided that values for the parameters  $A$ ,  $N_s$ ,  $K_{a1}^{\text{int}}$ ,  $K_{a2}^{\text{int}}$ ,  $*K_{\text{Fe}^{\text{int}}}$ ,  $*K_{\text{NO}_3}^{\text{int}}$ ,  $C_1$  and  $C_2$  are known. In a series of previous papers (JAMES *et al.*, 1977; DAVIS and LECKIE, 1978, 1979, 1980; BALISTRERI and MURRAY, 1979, 1981; JAMES and PARKS, 1982), others have shown that the intrinsic ionization constants and complexation constants can be determined using potentiometric titration data and graphic double extrapolation methods. Specific surface area ( $A$ ) and site density ( $N_s$ ) can be estimated using the BET nitrogen adsorption method and tritium exchange methods, respectively. The only adjustable parameters that remain are the inner layer capacitance ( $C_1$ ) and outer layer capacitance ( $C_2$ ). By proper selection of a combination of values for these two parameters ( $C_2$  is usually fixed at  $20 \mu\text{F}/\text{cm}^2$ , and only  $C_1$  adjusted), the model can give good agreement between the computed and measured surface charge ( $\sigma_0$ ) and the electrokinetic data in simple electrolyte solutions. Numerical calculations are performed with a modified version of the computer program MINEQL (WESTALL *et al.*, 1976) which includes the surface reactions in model calculations.

Values of the surface parameters for goethite and  $\text{Fe}(\text{OH})_3(\text{am})$  used in this study are listed in Table 2, and agree with those in Table 1, except for the surface area assigned to the amorphous phase. Similar values for ferric oxyhydroxides determined by others are also listed in Table 2. A surface area of  $700 \text{ m}^2/\text{g}$  instead of  $306 \text{ m}^2/\text{g}$  was assumed for  $\text{Fe}(\text{OH})_3(\text{am})$  in order to optimize the fit between the model-computed and measured surface charge of the oxyhydroxide as a function of pH. The higher value is in good agreement with  $600 \text{ m}^2/\text{g}$  similarly derived by DAVIS (1977), and is within the range of published values ( $157\text{--}840 \text{ m}^2/\text{g}$ ; HSI, 1981). Figure 6 shows the excellent agreement between the model calculated and measured surface charge of  $\text{Fe}(\text{OH})_3(\text{am})$  and goethite, assuming the fixed parameters given in Table 2, which are adopted in subsequent modeling calculations of uranyl adsorption.

Modeling uranyl adsorption reactions

The modeling procedure began by assuming that uranyl ion,  $\text{UO}_2^{2+}$ , is the only uranyl species adsorbed and that the simplest surface reaction is followed, *i.e.*,



This single surface reaction was thus assumed in the computer program MINEQL to model uranyl adsorption data onto goethite. Predictably, poor agreement was observed between experimental data and model calculations.

A comparison of the percentage distribution diagram of uranyl-hydroxy complexes in water (see Fig. 3) and the uranyl adsorption data (Fig. 2) reveals that in the pH range where uranyl is most strongly adsorbed (*i.e.*, at  $\text{pH} > 5$ ), the predominant dissolved uranyl species are  $\text{UO}_2\text{OH}^+$  and  $(\text{UO}_2)_3(\text{OH})_5^+$ . It was therefore assumed that  $\text{UO}_2\text{OH}^+$  and  $(\text{UO}_2)_3(\text{OH})_5^+$  hydroxy complexes are also adsorbed and the following surface reactions apply.

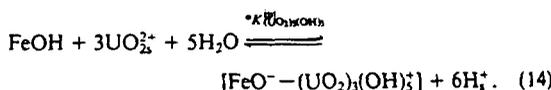
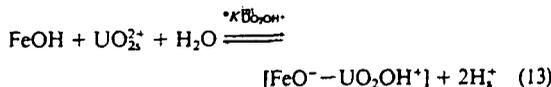


Table 2. Surface parameters for ferric oxyhydroxides assumed in this study and by others in surface ionization and complexation model calculations. The surface area ( $A$ ) for  $\text{Fe}(\text{OH})_3(\text{am})$  adapted in this study, and that of Davis (1977), were both estimated by model-fitting surface charge data (see text). All studies have assumed  $C_2 = 20 \mu\text{F}/\text{cm}^2$ . ND denotes not determined.

Systems	References	A (m <sup>2</sup> /g)	N <sub>s</sub> (sites/nm <sup>2</sup> )	pK <sub>a1</sub> <sup>int</sup>	pK <sub>a2</sub> <sup>int</sup>	*pK <sub>cation</sub> <sup>int</sup>	*pK <sub>anion</sub> <sup>int</sup>	C <sub>1</sub> (μF/cm <sup>2</sup> )
Fe(OH) <sub>3</sub> (am) / NaNO <sub>3</sub>	This study	700	20 (1.05x10 <sup>-2</sup> mol/g)	4.8	11.1	9.3	7.0	130
Fe(OH) <sub>3</sub> (am) / NaNO <sub>3</sub>	Davis (1977)	600	11* (9.85x10 <sup>-3</sup> mol/g)	5.1	10.7	9.0	6.9	140
α-FeOOH / NaNO <sub>3</sub>	This study	45	18	4.5	12.0	10.1	7.0	140
α-FeOOH / NaCl	Hingston et al. (1968)	32	16.8*	4.9	ND	6.6	ND	ND
α-FeOOH / KNO <sub>3</sub>	Yates (1975)	48	16.8	4.2	10.5	9.0	6.2	100
α-Fe <sub>2</sub> O <sub>3</sub>	Breeuwsma (1972)	ND	10	6.7	10.3	9.5	7.5	90

\* from Yates (1975)

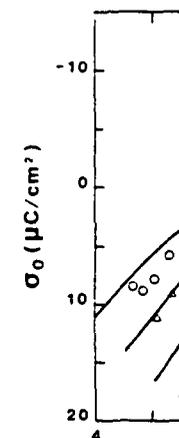
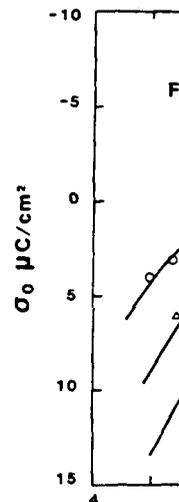
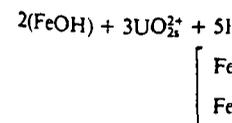


FIG. 6. Surface charge vs pH for Fe(OH)<sub>3</sub>(am) (a) and goethite (b). Solid curves are model calculations.

Excellent agreement was observed between the model calculations and experimental data for both  $\text{Fe}(\text{OH})_3(\text{am})$  and goethite. A combination of the two model calculations and experimental data indicates that the adsorbed uranyl species are bidentate or tridentate



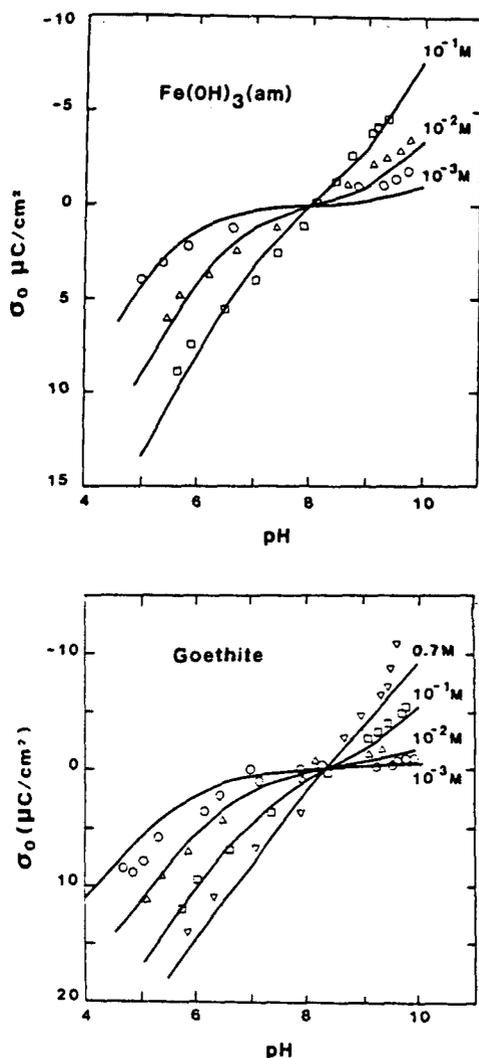
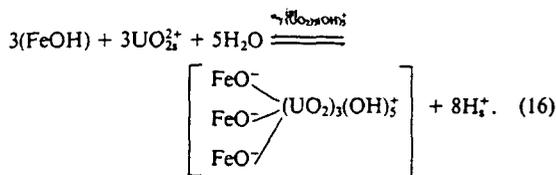
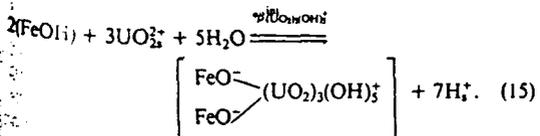


FIG. 6. Surface charge densities as a function of ionic strength and pH in NaNO<sub>3</sub> solutions at 25°C: 6a) Fe(OH)<sub>3</sub>(am); and 6b) goethite. Symbols denote the experimental data. Solid curves have been model calculated assuming the surface parameters given in Table 2.

Excellent agreement was achieved by including these three surface reactions (Eqns. 12-14) in the model calculations. According to these calculations, the contribution of Eqn. (12) to the total surface reaction is always small and can be neglected. In fact, by assuming UO<sub>2</sub>OH<sup>+</sup> and (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>3</sub><sup>+</sup> are the only uranyl species adsorbed, the model adequately explains the uranyl adsorption data onto amorphous ferric oxyhydroxide and goethite. A combination of  $p^*K_{UO_2OH^+}^{int} = 8.0$  and  $p^*K_{(UO_2)_3(OH)_3^+}^{int} = 15.0$  gives the best agreement between the model calculations and experimental results (Figs. 2a and 2b). However, the model reactions proposed above are not the only ones that can accurately fit the experimental data. For example, the adsorbed uranyl hydroxy complexes could form bidentate or tridentate surface complexes, i.e.,



The symbols  $\beta$  and  $\gamma$  in Eqns. (15) and (16) were used to define the stability constants when the surface reaction involves a bidentate or tridentate surface site. It was found that by arbitrarily assuming the dissolved uranyl species are adsorbed as a UO<sub>2</sub>OH<sup>+</sup> monodentate complex (Eqn. 13), and a (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>3</sub><sup>+</sup> bidentate surface complex (Eqn. 15), with  $p^*K_{UO_2OH^+}^{int} = 8.0$  and  $p^*K_{(UO_2)_3(OH)_3^+}^{int} = 20.0$ , model calculations fit the experimental data equally well. The same goodness of fit can also be achieved by assuming a monodentate UO<sub>2</sub>OH<sup>+</sup> complex (Eqn. 13) and a tridentate (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>3</sub><sup>+</sup> complex (Eqn. 16), with  $p^*K_{UO_2OH^+}^{int} = 8.2$  and  $p^*K_{(UO_2)_3(OH)_3^+}^{int} = 23.6$ . Therefore, it is not possible to uniquely identify the predominant reactions on the surface of amorphous ferric oxyhydroxide or goethite based solely on the goodness of the model fit to the data. Although the geometric configuration of the adsorbed (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>3</sub><sup>+</sup> complex and its orientation on the adsorbing ferric oxyhydroxide surface are not known, an estimation based on the crystal radii of uranyl ions suggests that adsorbed (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>3</sub><sup>+</sup> has a minimum cross-sectional diameter of 0.6-0.8 nm on the surface. However, a calculation based on the measured site density (see Table 2) indicates that each surface (FeOH) functional group has a cross-sectional area of only 0.05 nm<sup>2</sup>. It therefore seems likely that each adsorbed (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>3</sub><sup>+</sup> complex is bound to more than one surface functional group. This would support the hypothesis that adsorption forms a bidentate (Eqn. 15) or a tridentate (Eqn. 16) rather than monodentate surface complex (Eqn. 14). Unfortunately, crystallographic arguments alone do not allow one to decide whether a bi- or tridentate model is the more correct. One can argue, however, that a tridentate complex is less likely than a bidentate one because of the greater difficulty the tridentate complex would have finding surface sites with which to bond.

Although the model-calculated curves fit the experimental data very well when plotted on percent U adsorbed vs. pH diagrams (see Figs. 2a and 2b), the same goodness of fit is not obtained when the plots are drawn in terms of total dissolved U vs. pH. As shown in Fig. 7, the model calculated curve deviates from the experimental data points at total dissolved uranium concentrations < 1 ppb. Model calculations predict a continuous decrease in uranium concentrations as the pH increases, whereas the experimental data indicate that adsorption levels off at pH > 7. Unfortunately, concentrations near 1 ppb are typical of those in average groundwater systems, and therefore are of most interest to geochemists. More discussion is needed to explain this apparent failure of the surface complexation site-binding model in dilute uranyl solutions. Several possible explanations are:

(1) The adsorption experiments were contaminated with a trace amount of atmospheric CO<sub>2</sub> during sample transfer and centrifugation. As previously discussed, carbonate complexing inhibits adsorption and favors desorption, especially at alkaline pHs. A comparison of previous data suggests that a high total dissolved carbonate concentration (10<sup>-4</sup> M) is needed to account for the observed discrepancy. This much CO<sub>2</sub> contam-

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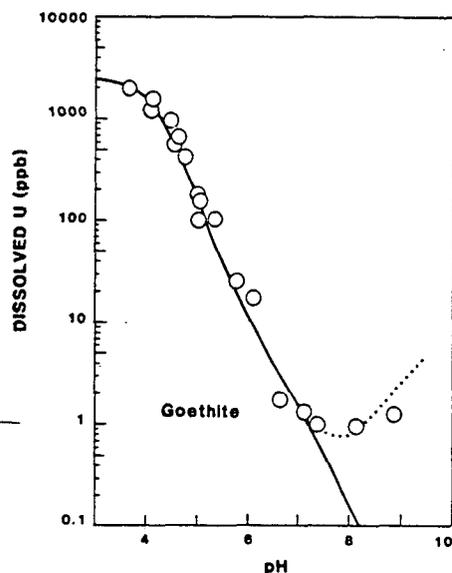
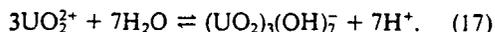


FIG. 7. Adsorption of uranyl vs. pH at  $\Sigma U = 10^{-5}$  M onto a 1 g/l suspension of goethite in 0.1 M  $\text{NaNO}_3$  solutions at 25°C. Symbols denote the experimental data. The solid curve has been model calculated assuming surface parameters given in Table 2, and a  $\text{UO}_2\text{OH}^+$  monodentate surface complex, and  $(\text{UO}_2)_3(\text{OH})_7^-$  bidentate surface complex. The assumed  $p^*K^{\text{int}}$  values for these surface complexes are 8.0 and 20.0 respectively. The dotted curve has been model calculated assuming the presence of a dissolved  $(\text{UO}_2)_3(\text{OH})_7^-$  complex which is not adsorbed.

ination is not likely in view of the experimental care taken in the study.

(2) Anionic uranyl hydroxy complexes were present. 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.*,  $(\text{UO}_2)_3(\text{OH})_7^-$ ) in basic uranyl solutions. They also calculated an equilibrium constant ( $\log K = 31 \pm 4$ ) for the reaction:



We feel that further studies are needed to prove the existence and stability of this complex. Nevertheless, the same modeling procedures were repeated as previously, assuming the presence of  $(\text{UO}_2)_3(\text{OH})_7^-$  and that the complex is not adsorbed by goethite. A  $\log K$  value of  $-29.0$  was assumed for reaction (17) (within the uncertainty of the value given above). Model calculated values are plotted as a dotted curve in Fig. 7. It is evident that significantly better agreement between the empirical data and the model fit is achieved by including this complex in the model calculations. Whether such an approach is valid awaits further confirmation of the presence and stability of  $(\text{UO}_2)_3(\text{OH})_7^-$ .

(3) Trace amounts of goethite particles in the supernatant were not completely separated during centrifugation. Thus, if for example 0.05% of the total goethite remained in the supernatant, its adsorbed

uranium would suffice to account for the apparent leveling off of uranyl adsorption at high pH. In view of the experimental procedures used in this study, this is considered the most likely explanation for the adsorption data above pH 7.

#### Determination of proton release during adsorption

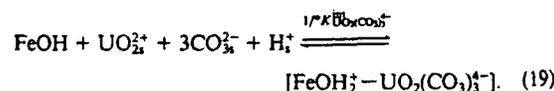
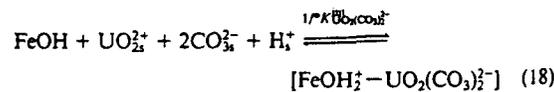
Determination of the number of protons released per uranyl ion adsorbed provides further information on the stoichiometry of the surface reactions. An effort was made to obtain this quantity by carefully measuring the pH shift during adsorption. Results indicated that the number of protons released per uranyl ion adsorbed varied between two and three and averaged about 2.3 in the pH range from four to nine. This is in good agreement with model assumptions, in that all the surface reactions proposed (Eqns. 13-17) release between 2 and 2.66 protons per uranyl 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.

#### Modeling uranyl-carbonate adsorption data

Rigorous modeling of uranyl adsorption from carbonate solutions using the surface ionization and complexation model, requires intrinsic constant values for the adsorption of carbonate and bicarbonate ions, as well as for uranyl carbonate and hydroxy carbonate complexes.

As a first approximation, however, modeling was begun by assuming that none of these species are adsorbed, and thus they do not influence surface charge and potential. The assumption that  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  adsorption can be ignored was not considered a serious source of error in light of values for the intrinsic constants for adsorption of similar ligands onto ferric oxyhydroxides (DAVIS, 1977). However, poor agreement was found between model calculations based on these assumptions and the experimental data, which showed that dissolved uranyl species were more strongly adsorbed than predicted by the model.

As a second approximation, it was assumed that the uranyl di- and tricarbonato complexes were adsorbed according to the reactions:



Adsorption of  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_5^-$  was again considered negligible, in that the species is monovalent, and a minor complex relative to the di- and tricarbonato complexes (see Fig. 5). Combining reactions (13) and (14) for adsorption of the hydroxy complexes, with (18) and (19) for adsorption of the carbonate complexes, with MINEQL the intrinsic constants for the last two reactions were found by trial and error using the uranyl adsorption data onto goethite for  $C_T = 10^{-2}$  M (Fig. 8). The resultant constants, which gave an excellent fit to the adsorption data, were  $p^*K^{\text{int}}_{\text{UO}_2(\text{CO}_3)_2^-} = -30.0$  and  $p^*K^{\text{int}}_{\text{UO}_2(\text{CO}_3)_3^{2-}} = -38.5$ . Unfortunately, the same intrinsic constants were less successful at modeling the uranyl adsorption

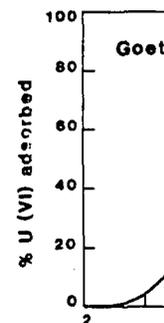


FIG. 8. Adsorption of uranyl (VI) in a 1 g/l suspension as a function of  $C_T$  at 25°C. The solid curve is model calculated using surface parameter values for  $\text{UO}_2(\text{CO}_3)_2^-$  and  $\text{UO}_2(\text{CO}_3)_3^{2-}$ , with  $p^*K^{\text{int}}$  values of  $-30.0$  and  $-38.5$ , respectively.

data for  $C_T = 10^{-2}$  M. In view of these data, it was assumed that  $p^*K^{\text{int}}_{\text{UO}_2(\text{CO}_3)_2^-}$  was not clear. It may be that the stability and surface complexation model from the assumption including the uranyl carbonate complex (MILLER, 1985). This inadequacy.

#### Predictive capability

The surface ionization model accurately predicts uranyl adsorption conditions, provided the complexation reactions are defined, and the adsorption of carbonate and sorbate and sorption have been determined. Intrinsic stability constants (PETERSON *et al.*, 1981) found that the uranyl adsorption at different solid phases. Presumably the parameters could be used in soils and sediments and are the appropriate correction factors for different phases, and for the oxyhydroxy complexes (PETERSON *et al.*, 1981). Adsorption in the complexing, indicated from alkaline conditions, qualitative until in related aquo-complexation conditions.

DAVIS and LANGMUIR (1977) found that the solutes, the chemical species with an oxide surface

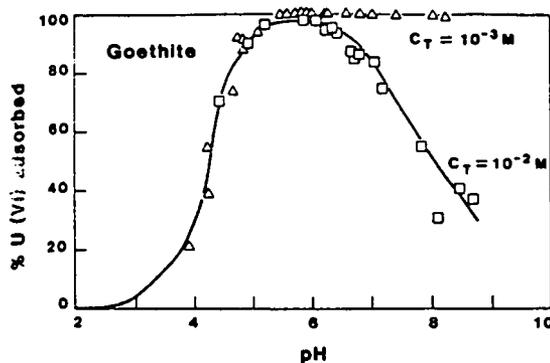


FIG. 8. Adsorption of uranyl vs. pH at  $\Sigma U = 10^{-5}$  M onto a 1 g/l suspension of goethite in 0.1 M  $\text{NaNO}_3$  solutions as a function of  $C_T$  at 25°C. Symbols denote the experimental data. The solid curve has been model calculated assuming surface parameters given in Table 2, and monodentate surface complexes of  $\text{UO}_2\text{OH}^+$ ,  $(\text{UO}_2)_2(\text{OH})_2^+$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$ , and  $\text{UO}_2(\text{CO}_3)_3^{4-}$ , with  $p^*K^{\text{int}}$  values of 8.0, 15.0, -30.0, and -38.5, respectively.

data for  $C_T = 10^{-3}$  M. To obtain the best agreement with these data, it was necessary to assume  $p^*K^{\text{int}}_{\text{UO}_2(\text{CO}_3)_2^{2-}} = -29.5$  and  $p^*K^{\text{int}}_{\text{UO}_2(\text{CO}_3)_3^{4-}} = -42.5$ . The reason for this discrepancy is not clear. It may reflect an accumulation of errors in aqueous stability and surface intrinsic stability constants, and/or derive from the assumption of non-adsorption of carbonate species including the uranyl hydroxy carbonate complex (cf. HO and MILLER, 1985). Failure of the model may also reflect its own inadequacy.

#### Predictive capability

The surface ionization and complexation model can accurately predict adsorption for a wide variety of conditions, provided that the stoichiometry of surface complexation reactions (which may not be uniquely defined), and the intrinsic stability constants and other sorbate and sorbent properties listed in Table 2 have been determined. For example, using a single set intrinsic stability constants and surface parameters, HSI (1981) found that the model could accurately predict uranyl adsorption onto amorphous ferric oxyhydroxide at different solid-to-liquid ratios (1 g/l and 0.15 g/l). Presumably the same intrinsic constants and surface parameters could be used to predict uranyl adsorption in soils and sediments within which ferric oxyhydroxides are the predominant sorbent phases, with appropriate correction for the ratio of predominant sorbent phases, and for the ratio of surface exposed weight of the oxyhydroxides to volume of contacting water (cf. PETERSON *et al.*, 1985). The imperfect modeling of adsorption in the presence of variable carbonate complexing, indicates that prediction of uranyl adsorption from alkaline natural waters must remain somewhat qualitative until or unless further refinements are made in related aquo-complexing constants and/or surface complexation constants.

DAVIS and LECKIE (1978) 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 also showed that when written in terms of charged sites (*i.e.*,  $\text{SO}^-$  or  $\text{SOH}_2^+$ ), 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 to estimate the stability constants for uranyl adsorption by other oxides, such as  $\text{TiO}_2$  and  $\alpha\text{-Al}_2\text{O}_3$ , provided that other surface parameters are available from previous studies.

#### SUMMARY AND CONCLUSIONS

1. Dissolved uranyl species are strongly adsorbed onto amorphous ferric oxyhydroxide and goethite, and less strongly onto synthetic and natural hematite at pHs above 5 to 6. Uranyl adsorption reactions equilibrate rapidly and reach pseudo-reversible equilibrium conditions within a few hours to a few days. Competing cations Ca or Mg at concentrations of  $10^{-3}$  M do not significantly affect uranyl adsorption. However, uranyl carbonate complexing inhibits uranyl adsorption especially in alkaline solutions. The amount of inhibition is directly proportional to the total dissolved carbonate content.

Results of this study and previous work (cf. LANGMUIR, 1978) indicate that, in low temperature oxidized environments sorption is generally a more important control on uranium mobility than is uranium mineral precipitation. This is particularly true in the presence of highly sorptive sedimentary materials such as the amorphous ferric oxyhydroxides. Uranyl sorption onto such phases can pre-concentrate U from surface and subsurface waters. The adsorbed uranium may later be desorbed because of crystallization of the oxyhydroxides to goethite or hematite with aging, and/or an increase in the alkalinity of ground water. Reduction of the uranyl to uranous species at a ground water redox interface ( $E_h < 0$  volts) may subsequently lead to the formation of a sandstone-type uranium deposit of uraninite ( $\text{UO}_2$ ) or coffinite ( $\text{USiO}_4$ ) (cf. LANGMUIR and CHATHAM, 1980).

2. The surface complexation site-binding model, with its several fixed parameters, has been used to successfully model the surface charge as well as adsorption data for uranyl species onto goethite and amorphous ferric oxyhydroxide in carbonate free systems. However, in the more complex uranyl-hydroxy-carbonate system, the modeling was less successful. In general, the model should be viewed as semi-empirical with the correct mathematical form to yield an optimal fit to most experimental data (WESTALL and HOHL, 1981; SPOSITO, 1983). Nevertheless, it can still be a very useful tool for predicting the adsorption behavior of trace metals including actinide ions at the oxide/water interface, and their effect on surface charge and electrokinetic properties. Successful application of the model involves the determination of multiple parameters, including specific surface area, intrinsic adsorption constants, and the surface site density of individual sorbents. These requirements make the model difficult to apply to het-

erogeneous natural environments containing multiple sorbents. In this context, more studies are needed to determine and compile intrinsic equilibrium constants and surface parameters for common sorbents in natural water-rock systems.

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*Editorial handling:* H. Elderfield

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## APPENDIX

Cumulative association constants for uranyl hydroxy and hydroxy-carbonate complexes at  $25^{\circ}\text{C}$  and 1 atm total pressure

Species	Log $\beta$	Source
$\text{UO}_2\text{OH}^+$	8.9	DONGARRA and LANGMUIR (1980)
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	22.38	BAES and MESMER (1976)
$(\text{UO}_2)_3(\text{OH})_3^+$	54.37	BAES and MESMER (1976)
$\text{UO}_2\text{CO}_3^0$	10.1	LANGMUIR (1978)
$\text{UO}_2(\text{CO}_3)_2^-$	17.0	LANGMUIR (1978)
$\text{UO}_2(\text{CO}_3)_3^{2-}$	21.4	LANGMUIR (1978)
$(\text{UO}_2)_2\text{CO}_3(\text{OH})_2^-$	-17.97	MAYA (1982b)*

\* MAYA (1982b) measured  $\beta = 10^{-18.63}$  for  $2\text{UO}_2^{2+} + \text{CO}_2(\text{g}) + 4\text{H}_2\text{O} = (\text{UO}_2)_2\text{CO}_3(\text{OH})_2^- + 5\text{H}^+$  at  $I = 0.1 \text{ M}$  and  $25^{\circ}\text{C}$ , which corrected to  $I = 0$  yields the tabulated value.

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