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Surface Complexation Modeling of UO_2^{2+} Sorption
onto Goethite and Kaolinite

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Abstract

The sorption of UO_2^{2+} showed ionic strength independence for goethite and dependence for kaolinite. In the presence of carbonate, the sorption decreased in the weakly alkaline pH range because of the formation of aqueous U(VI)-carbonate complexes. The sorption of UO_2^{2+} onto goethite and kaolinite under various experimental conditions was successfully interpreted using a surface complexation modeling, named triple layer model (TLM). The best fit to the experimental data was obtained by the FITEQL program, and then evaluated with available spectroscopic data. The results showed the versatility of surface complexation modeling over empirical one to predict UO_2^{2+} sorption behavior.

I. Introduction

Uranium is of fundamental importance in the nuclear fuel cycle, where it starts as a source and results as a final waste component. It is a representative actinide element, and is a potential environmental pollutant. The mobility of uranium in the environment is enhanced in oxidizing environment by the formation of uranyl (UO_2^{2+}). In

environmental groundwater conditions, chemical interactions with solid surfaces act to retard uranyl mobility. The stronger the interaction between the uranyl species and solid surfaces, the greater the retardation in the natural groundwater system.

Traditionally, experimental sorption data have been described by empirical means, including partition coefficients, isotherm equations, etc.¹ In order to fully describe the environmental behavior of U, a quantitative model for the sorption of uranyl on natural surfaces is necessary. Quantitative modeling of uranyl sorption to natural system is still in a developing stage. Recently, SCM (surface complexation modeling) is being developed and applied to certain minerals to gain understanding the sorption mechanism involved and to describe it in a mechanistic way.² The fundamental concepts upon which SCM is based is that sorption on solid surface takes place at specific coordination sites and sorption reactions on solid surfaces can be described quantitatively by mass law equations.

II. Experimental

A number of mixtures were prepared with single minerals (12 g / L), uranyl nitrate 6-hydrate (1.0×10^{-4} M) and potassium nitrate (1.0 to 1.0×10^{-3} M) in 30 ml polypropylene bottles (Nalgene). Goethite was purchased from High Purity Fine Chemical Inc. (Japan), and kaolinite (KGa-1b) was supplied by the Source Clays Repository of the Clays Minerals Society (Washington County, Georgia). All solutions were prepared from AR grade reagents and water with the resistivity of 18.3 M Ω cm (Milli-Q, Millipore).

The mixtures were allowed to stand overnight, and the pH of the samples was then adjusted by the addition of KOH or HNO₃. After a week equilibrium period, the final pH was determined, and an aliquot of the samples was withdrawn with a 10 ml plastic syringe then expressed through a 0.45 μ m syringe filter (Whatman). The uranium concentration in the filtrate was determined using ICP-AES (JY 50 P, Jobin yvon).

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III. Results and Discussion

U(VI) sorption onto goethite: The sorption of UO_2^{2+} as a function of pH and goethite concentration is shown in Figure 1(a). The sorption increased from near zero at pH 3.0 to greater than 99% of the total U(VI) at pH 5.5. At a given pH, the sorption increased when additional goethite was present. This is caused by the increase of surface binding sites. The effect of ionic strength on the sorption of UO_2^{2+} onto goethite is shown in Figure 1(b). The change of ionic strength did not influence the sorption significantly. This means that uranyl ions (UO_2^{2+}) are strongly sorbed onto the goethite surface, thus weakly sorbed ions such as potassium ions (K^+) do not interfere.

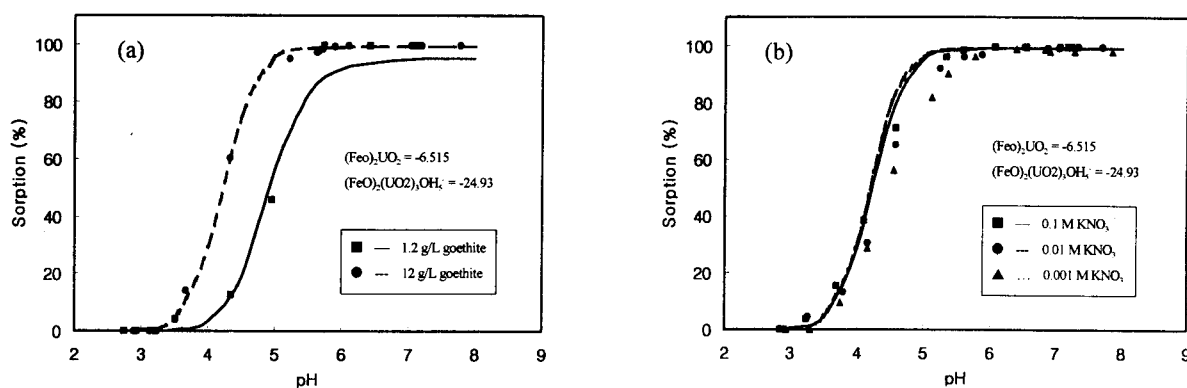


Figure 1. Uranium(VI) sorption onto goethite (a) as a function of pH and goethite concentration at a ionic strength of 0.1 M KNO_3 , (b) as a function of pH and ionic strength at a goethite concentration of 12 g/L. Points are experimental data, and lines are simulation results.

The experimental data were fitted using the FITEQL program.³ A combination of bidentate species $(\text{FeO})_2\text{UO}_2$ and $(\text{FeO})_2(\text{UO}_2)_3\text{OH}_5^-$ gave the best fit to the data. For 12 g/L goethite data, the model gave a good agreement, however, underpredicted the UO_2^{2+} sorption above pH 5 in the case of lower goethite concentration. The same model was applied to predict the effect of ionic strength on UO_2^{2+} sorption. The sorption edge (narrow range where sorption goes from near zero to almost complete sorption) of the

prediction shifted slightly to a lower pH than that of the experimental data. Considering no fitting to the data, however, the model predicts the experimental data extraordinarily well.

U(VI) sorption onto kaolinite: The effect of ionic strength on UO_2^{2+} sorption onto kaolinite is shown in Figure 2(a). Increasing the ionic strength substantially reduced the sorption of UO_2^{2+} in the acidic conditions. This indicates the existence of weakly bound uranyl complexes. Because the kaolinite surface is composed of Al and Si sites, a two-site model was used to fit the experimental data.⁴ The best fit to the experimental data was obtained with a combination of SiO-UO_2^{2+} and $\text{AlO(UO}_2)_3\text{OH}_5$. The model did well explain the effect of ionic strength in the low pH region, however, underpredicted the experimental data above pH 5.

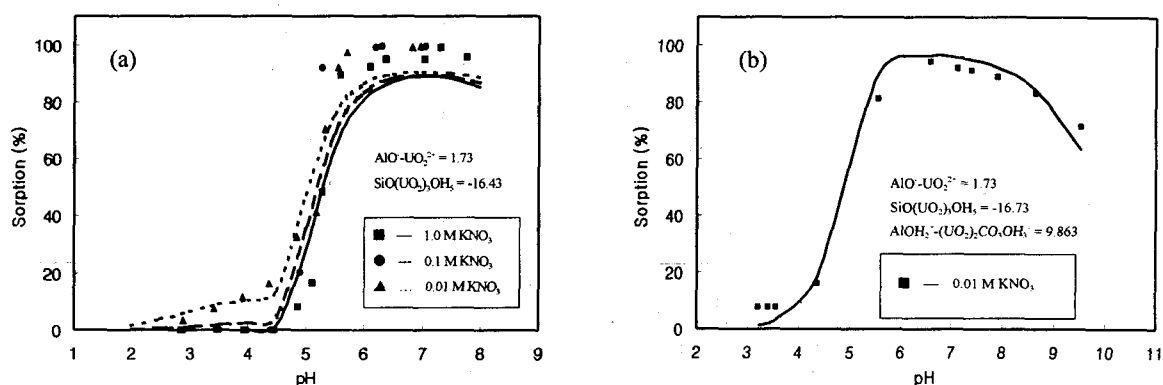


Figure 2. Uranium(VI) sorption onto kaolinite (a) as a function of pH and ionic strength at a kaolinite concentration of 12 g/L. (b) as a function of pH at kaolinite and total carbonate concentrations of 12g/L and 1.0×10^{-3} M, respectively. Points are experimental data, and lines are simulation results.

The effect of carbonate concentration on UO_2^{2+} sorption onto kaolinite is shown in Figure 2(b). The sorption decreased in the weakly alkaline pH range. This is due to the formation of aqueous U(VI)-carbonato complexes. The best fit was obtained with

sorbed species of $\text{AlO}^- \text{-UO}_2^{2+}$, $\text{SiO}(\text{UO}_2)_3\text{OH}_5$ and $\text{AlOH}_2^+ \text{-}(\text{UO}_2)_2\text{CO}_3\text{OH}_3^-$. The agreement between the model and the data is quite good considering no fitting of the $\log K_{\text{sc}}$ values for $\text{AlO}^- \text{-UO}_2^{2+}$ and $\text{SiO}(\text{UO}_2)_3\text{OH}_5$ complexes. These values were predetermined in the study of ionic strength effect.

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