

Surface Complexation Modeling of Uranyl (UO_2^{2+}) Adsorption by Hematite

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1. INTRODUCTION

Sorption by geological media is a main retardation mechanism in radionuclides migration in the mineral-water reaction system (Thomson *et al.*, 1986).

Uranium is a representative actinide element that is of fundamental importance in the nuclear fuel cycle, where it starts as a source and results as a final waste component (Turner *et al.*, 1996). It is mobilized by forming uranyl ion (UO_2^{2+}) in the oxidizing condition and becomes potentially hazardous pollutant to the environment (Hsi and Langmuir, 1985).

Hematite is a common mineral of ferric iron oxide. It has large affinity for uranyl and is believed to be one of primary sources and sinks controlling U(VI) reactive transport (Hobart, 1990).

Experimental sorption data has been described by various empirical means, including partition coefficients, isotherm equations, and conditional binding constants (Dzombak and Morel, 1990). But they contain no mechanistic information on sorption. Therefore models to gain understandings on the sorption mechanisms involved were needed to be developed. Resulting surface complexation modeling (SCM) has successfully explained adsorption of various cations and anions onto many oxide and hydroxide minerals in a mechanistic way.

In this paper, mechanism of uranyl adsorption onto hematite was interpreted through surface complexation modeling approach. The diffuse double layer model was employed to depict electric double layer at the hematite-water interface.

2. EXPERIMENTAL

Aldrich 99.98% α - Fe_2O_3 reagent was used in the uranyl batch sorption experiment. It shows typical XRD peak pattern of hematite. Specific surface area was measured to be $20.1\text{m}^2/\text{g}$ by N_2 sorption-B.E.T. method.

Batch sorption experiments were conducted under different concentrations of background electrolyte, total dissolved carbonate and pH.

Background electrolyte solutions were 0.1, 0.01 and 0.001M potassium nitrate solutions. Two different conditions for dissolved carbonate were adopted: a closed system with 10^{-5} M total dissolved carbonate and a system open to the atmosphere.

Hematite powders were put into background electrolyte solution and equilibrated for 1 day. Adsorbent concentration was 0.79845g hematite per one liter solution. Uranyl was added to the hematite suspension and was kept in reaction for 5 days in polypropylene bottles. pHs of solution were adjusted with 0.1M or 1M nitric acid and potassium hydroxide solutions. Initial concentration of uranyl was 10^{-6} M.

pH of solution was measured after 5 days of reaction and an aliquot of 10ml was filtered through $0.2\mu\text{m}$ membrane filter for chemical analysis. Uranium in solution was analyzed by ICP-MS (inductively coupled plasma-mass spectrometry). The best fit to the experimental data was obtained by surface complexation modeling using FITEQL code for the determination of equilibrium binding constant for uranyl adsorption onto hematite.

3. RESULTS AND DISCUSSION

Uranyl uptake by hematite surface as a function of pH, ionic strength and carbonate condition is shown in Fig. 1 to 3. Adsorption increases from near zero at pH 4 to almost 100 % of total U(VI) at pH 6 and more. Considering experimental error, uranyl adsorption is independent of ionic strength. It means uranyl forms inner-sphere surface complex with hematite.

In Fig. 1, mono- and bidentate bindings of uranyl are calculated for uranyl adsorption onto hematite surface in 0.01 M KNO_3 solution with 10^{-5} M total dissolved carbonate. Monodentate surface complexation model underestimates uranyl uptake in high pH ranges. Fig. 2 shows surface complexation modeling of uranyl adsorption from 0.001M KNO_3 solution with 10^{-5} M total dissolved carbonate. In this case both mono- and bidentate complexations of UO_2^{2+} describe experimental data well. The fitting result for uranyl adsorption in the system open to the atmospheric CO_2 is presented in Fig. 3. The simulation with bidentate binding of UO_2^{2+} and $\text{UO}_2(\text{CO}_3)_2^{2-}$ gave best fitting result. But the identity of adsorbed uranyl-carbonato complex is not in accordance with the predominant aqueous species, namely, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$.

The optimal equilibrium binding constants from each experimental run were weight-averaged. Average $\log K$ values for $\equiv(\text{FeO})_2\text{-UO}_2^{2+}$ and $\equiv(\text{FeO})_2\text{-UO}_2(\text{CO}_3)_2^{2-}$ were -6.079 and 4.891 respectively. Final simulation results employing weighted average of optimal surface complex formation constants are given in Fig. 4.

4. CONCLUSION

1. SCM approach successfully explains experimental uranyl adsorption onto hematite in a consistent manner.
2. Uranyl adsorption is not affected by ionic strength, which means uranyl is strongly bound to hematite surface by forming inner-sphere complexes.
3. SCM results suggest that uranyl be adsorbed onto hematite surfaces by forming bidentate surface complexes.
4. It is supposed that hematite surface-uranyl-carbonate ternary complex is formed in the open system, but its identity is not same as the predominant aqueous uranyl-carbonato species.

5. REFERENCES

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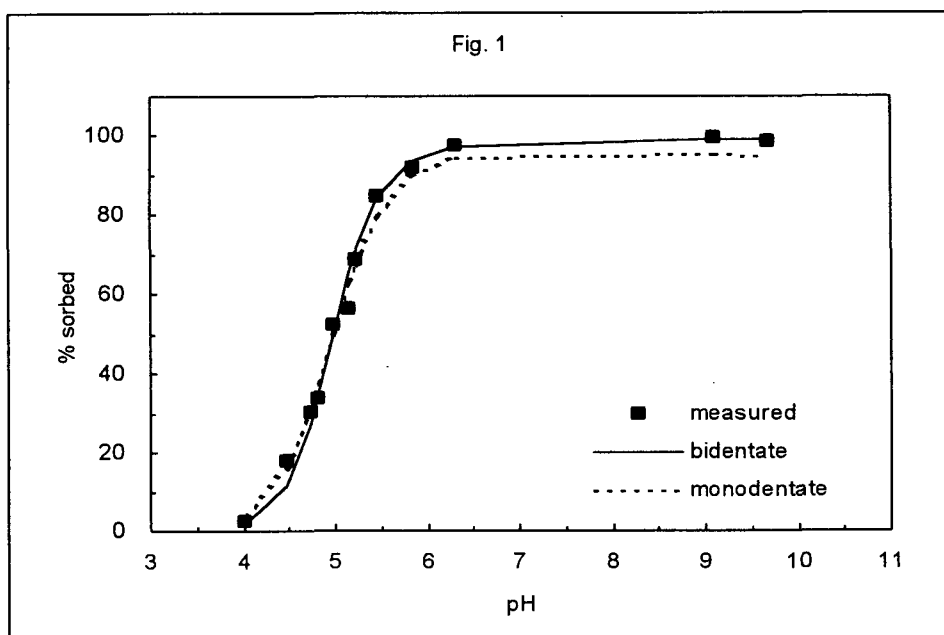


Fig. 1. Uranyl adsorption onto hematite surface as a function of pH. $[UO_{22+}]_{Tot} = 10^{-6}M$ in 0.01M KNO_3 solution with $10^{-5}M$ total dissolved carbonate. Monodentate binding of uranyl underestimates uranyl uptake at high pH ranges.

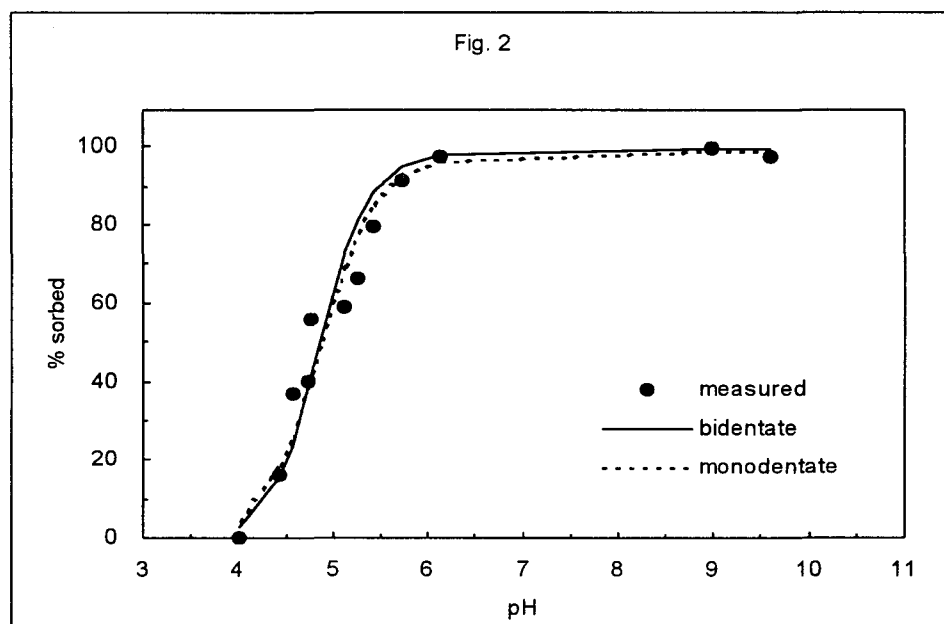


Fig. 2. Uranyl adsorption onto hematite surface as a function of pH. $[UO_{22+}]_{Tot} = 10^{-6}M$ in 0.001M KNO_3 solution with $10^{-5}M$ total dissolved carbonate.

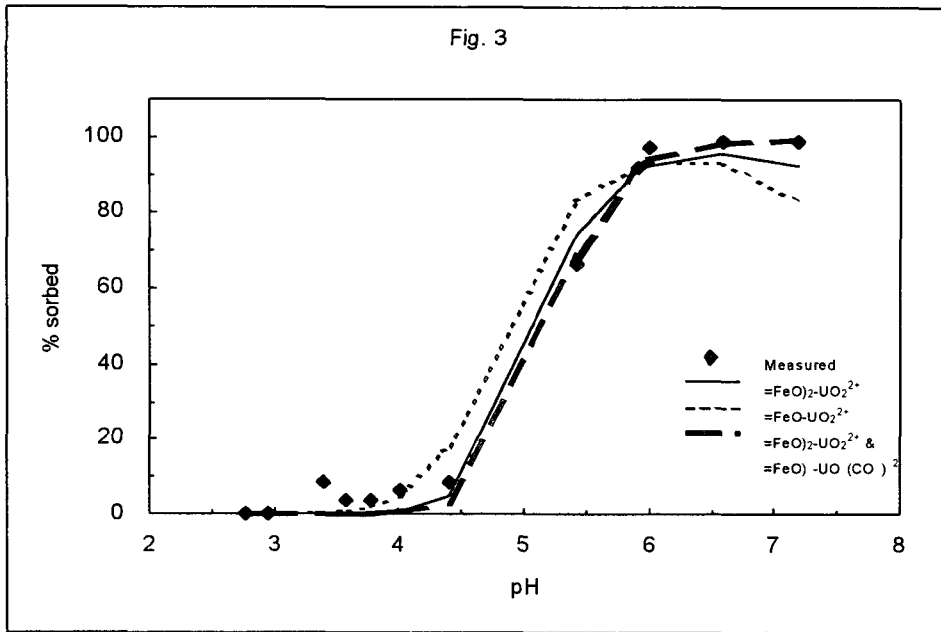


Fig. 3. Uranyl adsorption onto hematite surface as a function of pH. $[UO_2^{2+}]_{Tot} = 10^{-6}M$ in 0.1M KNO_3 solution open to the atmosphere. Adsorption of UO_2^{2+} only is insufficient to explain the experimental adsorption behavior. Simulation with bidentate binding of $UO_2^{2+} + (CO_3)^{2-}$ together with UO_2^{2+} gives the best fitting result.

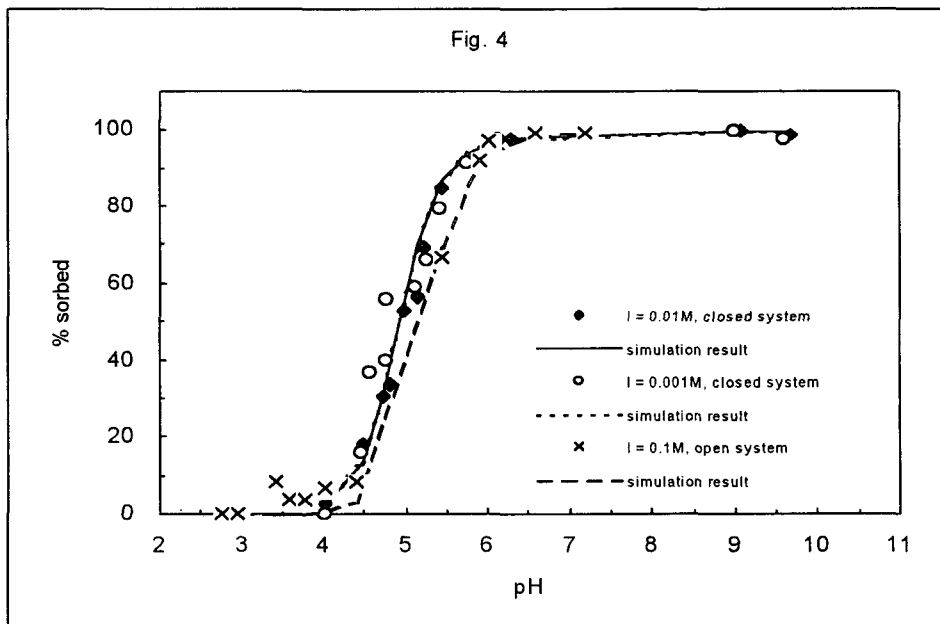


Fig. 4. Surface complexation modeling of uranyl adsorption on hematite surface as a function of pH, and dissolved carbonate using average binding constant. Average $\log K$ value is the weighted sum of surface complexation constants obtained from each experimental data set.