Adsorption of U(VI) onto F-Area Sediments from the Savannah River Site

Session: LBNL SFA Research (Laboratory Research Manager: Susan Hubbard)

Wenming Dong[1], Jiamin Wan[1], Tetsu K.Tokunaga[1], Miles Denham[2], James Davis[1]

[1]Earth Sciences Division, Lawrence Berkeley National Laboratory, [2]Savannah River National Laboratory

ABSTRACT

The Savannah River Site (SRS) was a major DOE facility for plutonium production during the Cold War. Waste plumes containing low-level radioactivity and acidic waste solutions were discharged to a series of unlined seepage basins in the F-Area of the SRS from 1955-1989. Although the site has gone through many years of active remediation, the groundwater remains acidic, and the concentrations of U and other radionuclides are still significantly higher than their Maximum Contaminant Levels (MCLs). The overall objective of the multi-disciplinary LBNL/SFA research team is to understand the current and predict the future contaminant fate and transport in the F-Area. As part of this effort, we completed two tasks within this review period. (1) Obtain data on U(VI) adsorption onto representative F-Area sediment samples through laboratory equilibrium experiments. (2) Develop site-specific surface complexation models (SCMs) that can describe U(VI) adsorption behavior in the F-Area. These data and models are needed for the planned plume-scale reactive transport modeling.

Laboratory batch experiments were conducted to evaluate U adsorption behavior over the pH range of 3.0 to 9.5. Ten sorbent samples were selected including six contaminated sediment samples from three boreholes drilled within the plume and along the groundwater flow direction, two uncontaminated (pristine) sediment samples from a borehole outside of the plume, and two reference minerals, goethite and kaolinite (identified as the dominant minerals in the clay size fraction of the F-Area sediments). Sorption experiments show that goethite and kaolinite largely control U partitioning behavior, and thus are the minerals useful for identifying reactive facies in these sediments. The batch experimental data show that in comparison with the pristine sediment samples, U(VI) adsorption onto contaminated sediments have shifted adsorption edges toward lower pH by about 1.0 unit at acidic pH conditions (e.g., from pH ≈ 4.5 to pH ≈ 3.5).

Our modeling results show that using an existing SCM of U(VI) adsorption onto goethite and a modified SCM of U(VI) adsorption onto kaolinite, a component additivity (CA) approach, can successfully predict U(VI) adsorption onto uncontaminated SRS sediments. However, application of the same SCMs to contaminated sediments resulted in under-estimates of U(VI) adsorption at acidic pH conditions. The model sensitivity analyses pointed out that both goethite and kaolinite surfaces are co-contributed for U(VI) adsorption at acidic pH conditions, particularly the exchange sites from clay minerals might play an important role in adsorption of U(VI) at pH < 5.0. These results suggested that the contaminated sediments might either contain other more reactive clay mineral facies such as smectite, or the long-term acid-leaching process might have altered the surface reactivity of the original sediments. Further studies are needed to identify more reactive mineral facies and understand the effects of acid leaching on the surface reactivity of the sediments.

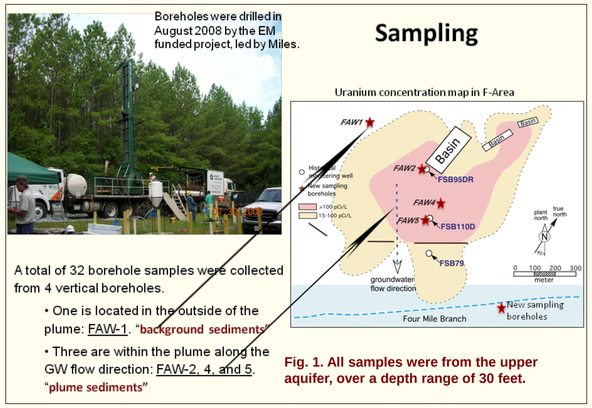

Fig. 1. All samples were from the upper aquifer, over a depth range of 30 feet.

BACKGROUND, OBJECTIVES & APPROACH

Background and Objectives: **The SRS F-Area was a major DOE facility for extracting plutonium during the Cold War. Low-level radioactivity acidic waste solutions were discharged to a series of seepage basins in the area from 1955-1989. The basins were closed and capped in 1991. The contaminant plumes contain U, ^{90}Sr, ^{129}I, and other radionuclides. The site has gone through many years of active remediation including pump-and-treat, barriers, and alkaline solution injection to neutralize the acidic groundwater. However, its groundwater remains acidic with pH values as low as 3.2 near the basins, and the concentrations of U, ^{90}Sr, ^{129}I, are still up to ten times higher than their Maximum Contaminant Levels (MCLs). It is well known that U(VI) is highly mobile under acidic conditions common to many DOE waste plumes (pH 3.0-5.0), however, important research needs remain. We do not quantitatively understand the key factors controlling retention and release of the radionuclides, as well as their capacities and rates under acidic conditions. Therefore, the purpose of this work is to conduct U(VI) adsorption experiments on F-Area sediments and to develop site-specific SCMs that can be used for the plume scale reactive transport modeling.**

Materials and Experimental Method: **Two background sediment samples (1A and 1B, including their bulk and fine fractions), six plume bulk sediment samples (1G, 2C, 2H, 5C, 5E, and 5G) (Fig.1), and two reference minerals (goethite and kaolinite) were used. Laboratory batch equilibrium experiments were used to study U(VI) adsorption under conditions: 1.0 μM U(VI) spiked; 0.01 M $NaNO_3$; solid/liquid ratios = 20 g/L for bulk sediments, and 5 g/L for fine fractions, goethite and kaolinite; room temperature; pH = 3.0 – 9.5: adjusted and in equilibrium with atmospheric P_{CO2} by addition of calculated equilibrium amounts of $NaHCO_3$-Na_2CO_3, and opening to air frequently. The pH values were re-adjusted daily, and samples were shaken for 3 days; 0.2 μm syringe filters were used for separation of solutions from sorbents; aqueous U(VI) was analyzed using ICP-MS.**

Modeling: **A site-specific Component Additivity(CA) approach based on diffuse layer SCMs was selected/developed (Table 1) to predict U(VI) adsorption behavior onto SRS sediments. The SCMs were optimized through testing various existing SCMs of U(VI) with goethite and kaolinite using the PHREEQC geochemical computer code.**

RESULTS

I. Characterization of selected samples (Fig. 2 and Table 1)

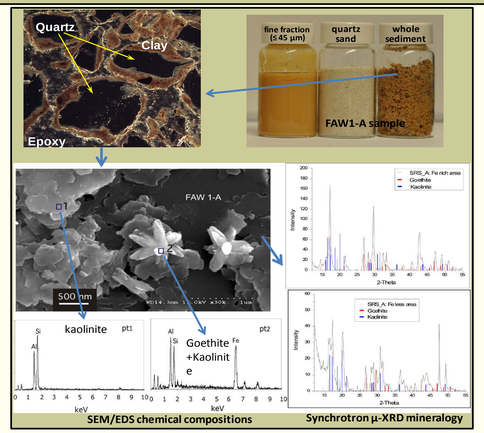

Fig. 2. Kaolinite and goethite are the dominant minerals in the fine fraction from all the samples. Some samples contain small or trace amounts of mica, smectite, and illite.

RESULTS (CON'T)

Table 1. Characterization of selected samples

Sample ID	Description	Fine fraction	BET SSA (m^2/g)	Mineralogy
FAW1-A	Bulk sediment		4.62	K+G, w/ M
	Fine fraction (<45 um)	12%	35.9	
FAW1-B	Bulk sediment		1.88	K+G, w/ M
	Fine fraction (<45 um)	5.50%	33.6	
FAW2-C	Bulk sediment		1.90	K+G, w/M
	Fine fraction (<45 um)	4.80%	36.5	+S(?)
FAW5-G	Bulk sediment		1.90	K+G, w/M
	Fine fraction (<45 um)	7.64%	94.8	+S(?)

II. Comparison of U(VI) Experimental Adsorption Data

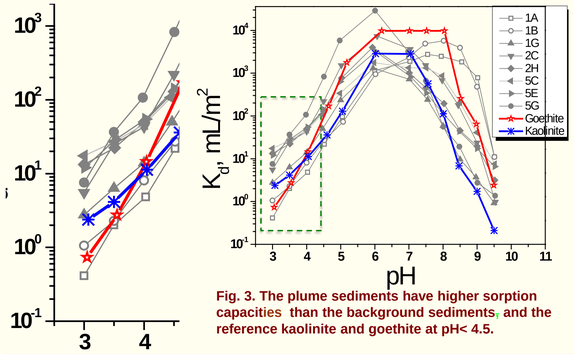

Fig. 3. The plume sediments have higher sorption capacities than the background sediments, and the reference kaolinite and goethite at pH< 4.5.

III. Surface Complexation Modeling (SCM) of U(VI) Adsorption

Table 2. Selected and optimized surface complexation reactions and constants

Goethite	Log K
$2 >GOH^{-0.5} + UO_2^{2+} = (>GOH)_2UO_2^+$ (GOH: site density = 2.2 sites/nm²)	14.11[a]
$2 >GOH^{-0.5} + UO_2^{2+} + H_2CO_3 = (>GO)_2UO_2CO_3^- + 2H^+$	4.64[a]
$>GOH^{-0.5} + H^+ = >GOH^{+0.5}$	9.18[a]
$2 >GOH^{-0.5} + H_2CO_3 = (>GO)_2CO_2^{-1} + 2H_2O$	5.93[a]
$>GOH^{-0.5} + H_2CO_3 + Na^+ = >GOCO_2^{-1.5}Na^+ + H^+ + H_2O$	-3.02[a]
Kaolinite (clay minerals)	
$2 >SOH^{-0.5} + UO_2^{2+} = (>SOH)_2UO_2^+$ (SOH: edge site density = 2.3 sites/nm²)	5.3[b]
$2 >SOH^{-0.5} + UO_2^{2+} + H_2CO_3 = (>SO)_2UO_2CO_3^-$ + 2 H⁺	-0.1[c]
$>SOH^{-0.5} + H^+ =>SO_2^{+0.5}$	4.9[d]
$>SOH^{-0.5} + Na^+ =>SOH\text{-}Na^{+0.5}$	-2.1[d]
$>SOH^{-0.5} + H^+ + NO_3^- =>SOH^2\text{-}NO_3^-$	4.9[d]
$2X^- + UO_2^{2+} = X_2\text{-}UO2$ (X⁻: face exchange site)	7.1[e]
$X^- + Na^+ = X\text{-}Na$	2.9[d]
$X^- + H^+ = X\text{-}H$	4.5[e]
$2X^- + Ca^{2+} = X_2\text{-}Ca$	6.8[e]
$3X^- + Al^{3+} = X_3\text{-}Al$	8.0[e]

[a]Sherman et al. (2008); [b]Estimated from Kowal-Fouchard et al. (2004) and optimized for this work; [c]This work; [d]Heidmann et al. (2005); [e]Obtained by modifying the values of log K with the similar charged metal ion exchange reactions from Heidmann et al. (2005).

RESULTS (CON'T)

SCM of U(VI) Adsorption onto the Reference and Background Samples.

(Note: the relevant parameters in Tables 1 & 2, and the log K values for aqueous species from Guillaumont et al (2003) were applied in Figs. 4 - 7.)

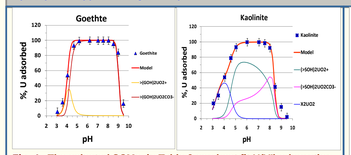

Fig. 4. The selected SCMs in Table 2 can best fit U(VI) adsorption on goethite (SSA=16.2 m²/g), and kaolinite (20.63 m²/g, and (X⁻) = 0.28 sites/nm², [Al]=0.02 mM).

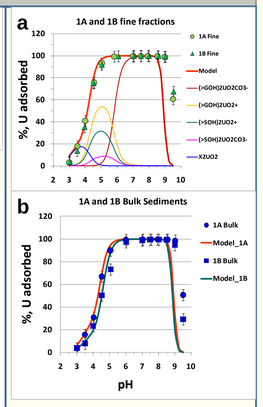

Fig. 5. CA approach of SCMs from Fig. 4 & Table 2 can predict U adsorption onto (a) 1A&B fine fractions with [Na]=15mM, [Ca]=0.1mM and [Al]=0.05mM, and (b) 1A&B bulk sediments with [Na]=15mM, [Ca]=0.03mM and [Al]=0.03mM. Assuming 20%goethite + 80%kaolinite surfaces.

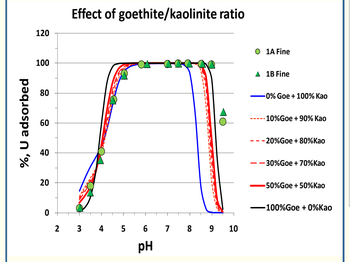

Fig. 6. 20-30% goethite surface plus 80-70% kaolinite surface best fit U adsorption onto 1A and 1B fine sediments. The experimental conditions are the same as in Fig. 5a.

SCM of U(VI) Adsorption onto the Plume Sediment Samples

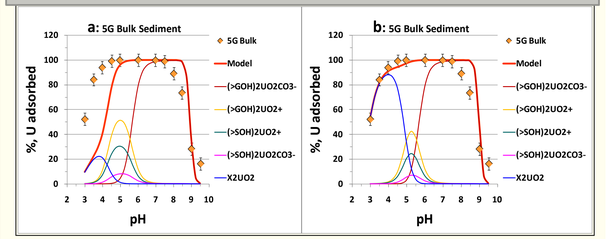

Fig. 7. (a) The application of CA approach using the same SCMs from Fig. 5 resulted in under-estimates of U adsorption onto the plume samples (e.g., 5G). (b) However, increasing exchange site [X⁻] density from 0.28 to 2.8 sites/nm² improves the prediction of U adsorption. Assuming 20%goethite + 80%kaolinite surfaces with [Na] = 10 mM, [Ca] = 0.1mM and [Al] = 0.

REFERENCES

Sherman D.M., Peacock C.L. and Hubbard C.G., *Geochim. Coscochim. Acta*, **2008**, 72(298-310).
Heidmann I.H., Christl I. and Kretzschmar R., *Geochim. Coscochim. Acta*, **2005,** 69(298-310).
Kowal-Fouchard A., Drot R., Simoni E. and Ehrhardt J.J., *Environ. Sci. Technol.*, **2004** , 38(399-1407).
Cataland J.G. and Brown Jr. G. E., *Geochim. Coscochim. Acta*, **2005,** 69 (298-310).

Funding for this study was provided by the U.S. Department of Energy, BER Program Contract DE-AC020SCH11231 to the LBNL Sustainable Systems Scientific Focus Area