Hyphenated Techniques for Determining pH Dependent Pore-Scale Uranium (VI) Speciation: FFF-ICP-MS

PIs
James F. Ranville and Bruce D. Honeyman
Department of Chemistry and Geochemistry
&
Division of Environmental Science and Engineering
Colorado School of Mines
Golden, CO 80401

Graduate Student Investigator
Emily K. Lesher

Presented at DOE-ERSP PI Meeting
April 9, 2008
Lansdowne, VA
Talk Outline

• Introduction
  – Project relevance
  – Aqueous speciation

• Field Flow Fractionation
  – Theory & instrumentation
  – Application for U characterization (previous work)
    • Laboratory bacteria U sorption
    • SREL soil leachate
    • Aquitard pore water
  – Quantitative application for U speciation
    • Well-defined ligands

• Future work
INTRODUCTION: Project Relevance

U.S. Department of Energy
Office of Science
Office of Biological and Environmental Research
Environmental Remediation Sciences Division

ENVIRONMENTAL REMEDIATION SCIENCES PROGRAM

1. Provide the scientific

3. Develop new monitoring tools to manage complex approaches for chemical and natural environment

Figure 1. DOE’s remediation challenges occur in the field where highly interactive natural processes occur over a broad range of scales control the fate and transport of contaminants. The ERSD goal is to help provide the basis for development of innovative remediation measures and to support decision making critical to long-term site stewardship.
INTRODUCTION: Project Hypotheses

- **Geochemical**
  - Uranium solution speciation in groundwater will depend on solution composition and will respond to changes in composition
  - Geochemical process such as sorption and biotransformation will be affected by U speciation

- **Analytical**
  - Hyphenated techniques that combine separation (field flow fractionation) and detection (ICP-MS) can provide a means of speciation measurement
  - Developed techniques, which utilize small volume samples (micro liter), will allow examination of U solution phase speciation with high spatial resolution in heterogeneous systems
INTRODUCTION: Speciation

Solution Speciation Influences Contaminant Behavior

Complex formation with aqueous and surface ligands

Macromolecular, nanoparticulate, and colloidal ligands

Stanford Environmental Molecular Science Institute (EMSI)

Studying chemical and microbial interactions at environmental interfaces
Field flow fractionation
Theory & Instrumentation

FFF is a separation method that when combined (hyphenated) with ICP-MS will allow measurement of aqueous phase U(VI) speciation

Analogous to chromatography
(no stationary phase)
Field flow fractionation - ICP-MS

- Injection port
- Channel flow HPLC pump
- Cross flow HPLC pump
- Carrier solution
- UV detector
- Fluorescence detector
- ICP – sample introduction, plasma generation
- Mass spec: element detection
- Calibration standards (connected at T for standardization runs)
- Internal standard: 50 ppb Bi in 4% HNO3
- Waste
- Injection port
Flow FFF: Channel Configuration

- Separates colloids (inorganic or organic solids from ~2 nm – 1 μm size range)
- Supra-micron particles can also be analyzed using alternate Fl FFF modes (1-20 μm)
High field FFF for separation of DOC

Separation of PSS molecular weight standards (Da)

High field: 3.0 ml/min  Carrier flow: 1.0 ml/min
Low field for nanoparticles

- Low field: 0.9 ml/min
- Carrier flow: 1.0 ml/min
- PSS standards (Duke)
- 20 μL injection
- FI detector

![Graph showing time versus diameter with peaks at 26 nm, 90 nm, and 138 nm.](image)

\[ y = 5.2262x - 3.598 \]

\[ R^2 = 0.993 \]
Normal-Mode FFF Theory

Experimental Measurement

Computing $d$ from retention time

$$R = \frac{t^0}{t_R}$$

$t^0 =$ retention time for void volume
$t_r =$ retention time for sample component

FFF Theory

$$R = 6\lambda \left[ \coth \left( \frac{1}{2\lambda} \right) - 2\lambda \right]$$

Flow FFF

$$\lambda = \frac{D V^0}{V_c w^2} = \frac{k T V^0}{3\pi \eta V_c w^2 d}$$

Sedimentation FFF

$$\lambda = \frac{6kT}{d^3 \pi \Delta \rho (\omega^2 r_o) w}$$

$D =$ diffusion coefficient
$U =$ field velocity
$w =$ channel thickness (0.25 mm)

$V^o =$ void volume
$V_c =$ volumetric cross-flow rate
$\eta =$ viscosity

$d =$ diameter
$\Delta \rho =$ density difference
$\omega =$ rpm
$r_o =$ radius of centrifuge
Field flow fractionation: Uranium characterization applications
Laboratory Investigation of U(IV) Sorption to Bacteria

- Culture of *Shewanella oneidensis* (~10^6 cells/mL)
- pH 5 linear isotherm by FFF-ICP-MS
Investigation of U Sorption to Bacteria

- pH dependence of sorption

- Suspected high MW exopolymer competes with cells for U
- Proton competition is different for cells vs exopolymer
- FFF can be useful in studies of mixtures

Jackson et al., Anal. Chem., 2005
U and Ni porewater characterization at Savannah River Site, Aiken SC

- Examined filtered (0.2 μm) soil extracts (water-dispersible colloids) from SREL
- High levels of DOC suggest that metal-DOC binding might be important in Ni and U speciation
- Mildly acidic pH
- Interface FI-FFF on-line with ICP-MS for (multi-) element-specific chromatograms
SP5 water extract:

<table>
<thead>
<tr>
<th>Sediment</th>
<th>pH</th>
<th>DOC (mg l(^{-1}))</th>
<th>Al (µg l(^{-1}))</th>
<th>Fe (µg l(^{-1}))</th>
<th>Ni (µg l(^{-1}))</th>
<th>U ((µg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP5</td>
<td>5.94</td>
<td>200</td>
<td>4370</td>
<td>2060</td>
<td>407</td>
<td>237</td>
</tr>
</tbody>
</table>

**low field Fl-FFF ICP-MS**

Jackson et al., ES&T, 2005
SP5 water extract:

High Field FI FFF
ICP-MS

Al, Fe, Ni, U, ICP-MS cps

Particle size (µm)

UV response

Jackson et al., ES&T, 2005
Environmental significance at SRS
- ‘dissolved’ U may be partially non-available, associated with colloids and DOC
- Soil/groundwater reactive transport models should include speciation
Compare to: Clay-rich glacial till aquitard

- Located in western Canada
- 80 m thick
- Mildly alkaline
- High in carbonate
- High in DOC
- Well-instrumented with piezometers
- Natural U source

Ranville et al., J. Contam Hydrol, 2007
Depth = 2.3 m
U = 460 μg/L
DOC = 136 mg/L

Depth = 4.5 m
U = 430 μg/L
DOC = 77 mg/L

Depth = 11.9 m
U = 38 μg/L
DOC = 19 mg/L

Ranville et al., J. Contam Hydrol, 2007
Comparison of speciation model and FFF results

<table>
<thead>
<tr>
<th>Water composition (mM)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Mg</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
</tr>
</tbody>
</table>

Uranyl species percentage distribution

<table>
<thead>
<tr>
<th>Species</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca₂UO₂(CO₃)₃⁰⁻</td>
<td>66.2</td>
</tr>
<tr>
<td>CaUO₂(CO₃)₃⁻</td>
<td>2.2</td>
</tr>
<tr>
<td>UO₂(CO₃)²⁻</td>
<td>0.8</td>
</tr>
<tr>
<td>UO₂(CO₃)₃⁴⁻</td>
<td>28.9</td>
</tr>
<tr>
<td>-FA₂UO₂</td>
<td>1.9</td>
</tr>
</tbody>
</table>

FFF results
- DOC was low in MW
- 50% recovery of DOC
- % Organic bound U measured = 0.62 %
- Assuming lost DOC contained U
  - 0.62 % x 2 = 1.24 %
Field flow fractionation
Quantitative applications
Why develop measurement methods when we have models?

- Are the models accurate for complex water compositions?
  - Compare predictions to measurements
- What about complex ligands for which thermodynamic data are lacking?
  - Uncharacterized NOM
  - Natural nanoparticles
- Separation-based approach
  - Differentiation of “free” vs complexed
  - Mixtures
    - Competitive reactions (e.g. cells and mineral particles)
- Development begins with well-characterized ligands
U(VI) solution complexes can be predicted by computer modeling

- For example-Visual MINTEQ (Gustafsson, 2006)
- Uses thermodynamic data on uranium association with
  - Database likely “good” for complexes with dissolved inorganic and simple organic ligands (subject of new ERSP project: K. Hatfield PI)
U(VI) solution complexes predicted by computer modeling: DOC vs carbonate

- **U=10^{-6} M, DOC = 1 mg C/L**
  - Increase organic complexes

- **U=10^{-6} M, DOC = 10 mg C/L**
  - Decrease organic complexes

- **Ca^{2+} = 10^{-3} M, atmospheric CO_{2},**
  - U=10^{-6} M, DOC = 1 mg C/L
  - Increase organic complexes
  - Ca^{2+} = 10^{-3} M, atmospheric CO_{2},
  - U=10^{-6} M, DOC = 10 mg C/L
  - Decrease organic complexes
  - Ca^{2+} = 2 \times 10^{-3} M, 10 X atmospheric CO_{2},
U(VI) solution complexes predicted by computer modeling: Soil pH variations
Well-characterized ligand: Nanoparticulate Hematite

Table 3. Surface reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log $K$ ($I = 0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{FeOH} + \text{H}^+ = \text{FeOH}_2^+$</td>
<td>8.25**</td>
</tr>
<tr>
<td>$\text{FeOH} = \text{FeO}^- + \text{H}^+$</td>
<td>-10.25**</td>
</tr>
<tr>
<td>$\text{FeOH} + \text{Na}^+ = \text{FeO}^- - \text{Na}^+ + \text{H}^+$</td>
<td>-8.46**</td>
</tr>
<tr>
<td>$\text{FeOH} + \text{H}^+ + \text{ClO}_4^- = \text{FeOH}_2^+ - \text{ClO}_4^-$</td>
<td>10.18**</td>
</tr>
<tr>
<td>$\text{FeOH} + \text{H}_2\text{CO}_3 = \text{FeHCO}_3^- + \text{H}_2\text{O}$</td>
<td>6.00b**</td>
</tr>
<tr>
<td>$\text{FeOH} + \text{H}_2\text{C} = \text{FeCO}_3^- + \text{H}^+ + \text{H}_2\text{O}$</td>
<td>-3.30b**</td>
</tr>
<tr>
<td>$\text{Fe}_2(\text{OH})_3 + \text{UO}_2^{2+} = \text{Fe}_2\text{O}_3\text{UO}_3^- + 2\text{H}^+$</td>
<td>-0.087c</td>
</tr>
<tr>
<td>$\text{Fe}_n(\text{OH})_2 + \text{UO}_2^{2+} = \text{Fe}_n\text{O}_2\text{UO}_2 + 2\text{H}^+$</td>
<td>-3.43c</td>
</tr>
<tr>
<td>$\text{Fe}_n(\text{OH})_2 + \text{UO}_2^{2+}\text{H}_2\text{CO}_3 = \text{Fe}_n\text{O}_2\text{UO}_2\text{CO}_2^- + 4\text{H}^+$</td>
<td>-12.14**</td>
</tr>
</tbody>
</table>

All SCM simulations used $C_1 = 1.4 \text{ F/m}^2$ and $C_2 = 0.2 \text{ F/m}^2$, after Katz and Hayes, 1995.

* Determined from FITEQ simulation of potentiometric titration data (Murphy et al., 1999).

b Determined by modeling pH_{ep} from electrophoretic mobility experiments (Fig. 5a).

c From simulation of U(VI) sorption data (Figs. 1 and 2).

** Assumes to be the same for weak and strong site types.
Well-characterized ligand:
Nanoparticulate Hematite

Existing thermodynamic surface complexation sufficient to allow predictions

What about natural nanoparticles?

Experimental results and FITEQL model simulations of fraction uranium sorbed onto 0.09 g/l, 0.9 g/l and 9.0 g/l hematite at variable pH. Ionic strength = 0.1, U(VI)$_T$ = 10$^{-6}$ M and atmospheric concentrations of CO$_2$. Lenhart and Honeyman (1999).
Batch Sorption Experiments

Uranium sorption onto hematite: [hematite]=0.09 g/L, [U]=1 uM (238 ppb), I=0.1 M, atmospheric CO2

Phase separation using filtration
Volume for ICP-MS ~10 ml
Sorption Experiment: FI FFF-ICP-MS

20 uL injected into FI FFF-ICP-MS
• Smaller [Fe]/[U] ratio in void peak. Indicates some dissolved U.

• Increasing [Fe]/[U] ratio over peak. Function of sorbed [U] being surface area dependant, [Fe] being volume dependant.
• Void peak ratio close to peak ratio, indicates U present in hematite that was not fully injected/equilibrated
Comparison of sorption results: FFF vs batch

<table>
<thead>
<tr>
<th>pH</th>
<th>% Sorbed</th>
<th>Log Kd</th>
<th>% Sorbed</th>
<th>Log Kd</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>4.5</td>
<td>1.7</td>
<td>5.1</td>
<td>1.8</td>
</tr>
<tr>
<td>4.2</td>
<td>58.4</td>
<td>3.2</td>
<td>29.2</td>
<td>2.7</td>
</tr>
<tr>
<td>4.2</td>
<td>50.4</td>
<td>3.1</td>
<td>29.2</td>
<td>2.7</td>
</tr>
<tr>
<td>5.3</td>
<td>96.1</td>
<td>4.4</td>
<td>99.1</td>
<td>5.1</td>
</tr>
<tr>
<td>6.1</td>
<td>100</td>
<td>5.3</td>
<td>99.6</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Future Work

• Method Validation
  • Complete Hematite work
  • Examine IHSS HA

• Up-scaled Lab Experiments
  • Construct small tank with layered heterogeneous materials
    • Carbonate, organic matter
  • Sample at high spatial resolution, utilizing the small sample volume requirements of FFF-ICP-MS to examine U speciation

• Field-scale
  • Examine U speciation at field sites (part of new ERSP project)
Acknowledgements

Funding

DOE ERSP Grant: ER64419
Edna Bailey Sussman Fellowship

Student Investigators

Ph.D. Opportunities

The Colorado School of Mines has opportunities for graduate students and faculty interested in Ph.D. research and teaching. The School of Mines has a strong focus on environmental science and engineering, with particular emphasis on groundwater protection and remediation.

Benefits:
- Annual stipend of up to $30,000
- Payment of tuition and fees
- Conference travel allowance

This program is open only to U.S. citizens and permanent resident aliens studying at a U.S. university.

This is an equal opportunity program and is open to all qualified persons without regard to race, sex, creed, age, physical disability or national origin.

Applications are due by February 15, 2008.

Graduate Programs:
- Chemistry & Geochemistry
- Environmental Science & Engineering

For More Information Contact:
Dr. Linda Figueroa
ESNR Program Coordinator
Environmental Sci. and Engin. Division
Colorado School of Mines
Golden, CO 80401
Phone: 303.273.3491
Email: lfiguero@mines.edu
http://www.mines.edu/fs_home/figuero/ESNR.html

Updated 12/21/07

Contact: Linda Figueroa
Lfiguero@mines.edu