Effects of Mineral Impurities and Heat on Uranium(VI) Sorption onto Bentonite

R.M. Tinnacher¹, C. Tournassat¹,², P. Huang¹, M. Massey¹, P.S. Nico², P.M. Fox², F. Caporuscio³

1. California State University East Bay, Hayward, California
2. Lawrence Berkeley National Laboratory, Berkeley, California
3. Los Alamos National Laboratory, Los Alamos, New Mexico

SFWST Annual Working Group Meeting
May 22 2018
1. Who we are:
   ⇒ California State University System
   ⇒ Cal State East Bay

2. What we do:
   ⇒ Research motivation
   ⇒ Project tasks
   ⇒ First results and accomplishments
1. California State University System

- 23 campuses across California
- Oldest campus: San José State: 1857
- Youngest campus: Channel Islands: 2002
- ~2,300 faculty members
- ~485,000 students
2. Cal State East Bay

- Founded in 1957
- ~16,000 students
- ~740 academic staff
- Located in Hayward, CA
- Offers bachelors and masters degrees in 50 fields
- Most diverse campus in the continental U.S.
- ~60% of students: 1st generation college students
- “Best in the West” college every year since 2003 (Princeton Review)
- “Top-Tier” institution among master's-granting universities in the West (U.S. News & World Report)
Research Motivation

- U.S.: 61 nuclear power plants, 99 reactors
- ~80,000 metric tons of spent nuclear fuel
- Spent nuclear fuel stored in cooling pools at 75 reactor sites or at 32 independent spent fuel storage installations
- Possible geologic media for long-term storage: granite, clay/shale, salt, and volcanic tuff

1,800 tons of radioactive waste has an ocean view and nowhere to go
Engineered Barrier Systems (EBS)

- **Compacted bentonite** is the proposed backfill material in EBS.
- **Na-montmorillonite** is the main component in bentonite, with:
  - Low porosity
  - Swelling
  - Low permeability
- But bentonite also contains **mineral impurities**: e.g., quartz, feldspars, pyrite, calcium carbonates (calcite).
- **Gradients of chemical solution conditions and temperature** are expected over time and across the EBS.
- **Uranium is an important element** to consider:
  - High abundancy in fuel (96% by weight);
  - Uranium transport away from fuel may affect fuel degradation rates and release of other RNs.

The long-term management of nuclear waste requires reliable predictions of uranium transport through engineered barrier systems (EBS).
Characteristics of Na-Montmorillonite (Clay)

2 types of porosities and diffusion pathways due to clay structure:
- Small (1-3 nm) interlayer spaces within clay particles
- Macropores between clay particles

System conditions affect relevance of each porosity type.

Interlayer porosities dominant at high compaction.

Negative clay surface charges lead to:
- Cation sorption by ion exchange reactions → surface diffusion
- Potential exclusion of anions from interlayer spaces

2 types of montmorillonite surface sites for U(VI) sorption:
- Cation exchange sites in interlayer spaces
- Surface complexation sites at edges of smectite layers

System conditions affect relevance of surf. sites and U(VI) solution speciation.

Still debated: Relevance of uranyl-carbonato surface complexes:
- No (strong) spectroscopic evidence (Marques Fernandes et al., 2012)
- But still included in some U(VI)-montmorillonite surface complexation models
Peculiarities of Montmorillonite Relevant for Development of Surface Complexation Models (SCMs)

• Surface complexation models were originally developed for simple mineral oxides.
• Metal surface complexation reaction:

$$\Delta G_{\text{tot}} = \Delta G_{\text{chem}}^0 + \Delta G_{\text{coul}}^0$$

$$K = \left[ <\text{SOMe}\rangle \left( H^+ \right) \right] / \left[ >\text{SOH} \right] \exp \left( -\frac{F\psi}{RT} \right)$$

• Needed: Knowledge of surface potential as a function of pH, I, electrolyte

• For mineral oxides:
  Determine parameters based on potentiometric titrations of solid

• Montmorillonite: → Spillover effect
  Basal surface potential affects electrostatic potential of edge sites

Edge site: $\equiv\text{Si}_T\text{OH}(\equiv\text{Al}_{oc}\text{-OH}_2)(\equiv\text{Si}_T\text{Al}_{oc}\text{O})$
Interdependence between Parameters & Processes

**Chemical solution conditions**
(pH, Total Inorganic Carbon, Ca, etc.)

**Uranium solution speciation**

**Uranium sorption behavior**

**Clay/bentonite characteristics**

**Uranium diffusion rates**

**Tournassat and Appelo, 2011**
Research Questions and Goals

Overall Goals:

- Develop new U(VI) surface complexation and diffusion models to include impacts of calcite impurities, heat and the spillover effect.
- Decrease uncertainty in actinide sorption / diffusion sub-models that are part of performance assessment models for waste repositories.

Research Questions:

1. How does the presence of calcite impurities affect U(VI) solution speciation, sorption and diffusion?

2. Does the exposure to heat change the effects of calcite impurities?

[Graphs showing the comparison of U(VI) sorption rate with and without calcite impurities under different pH conditions.]

Figure 2. Comparison of U(VI) sorption edge on Na-montmorillonite with (open triangles) and without (squares) 3 mg of calcite added (\([U(VI)] = 10^{-4} \text{ M}, \ i = 0.5 \text{ M}\)). Kowal-Fouchard et al., 2004

Tinnacher et al., unpublished
Overview of Research Tasks

Simulation of U(VI) solution speciation and precipitation reactions
Task 1: U(VI) Sorption Experiments

**Solids:**
- Montmorillonite + dissolved CaCl₂
- Montmorillonite + calcite mixtures → Before and after heat exposure
- FEBEX bentonite → Before and after purification → After various heat exposures

**Varied conditions:** pH, pCO₂, Ca/calcite conc
Overview of Research Tasks

Simulation of U(VI) solution speciation and precipitation reactions

**Task 1: U(VI) Sorption Experiments**

**Solids:**
- Montmorillonite + dissolved CaCl$_2$
- Montmorillonite + calcite mixtures → Before and after heat exposure
- FEBEX bentonite → Before and after purification → After various heat exposures

**Varied conditions:** pH, pCO$_2$, Ca/calcite conc

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*Experimental design*

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*Fibrous illite*

*Analcime*
Overview of Research Tasks

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**Task 1: U(VI) Sorption Experiments**
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- **Varied conditions:** pH, pCO$_2$, Ca/calcite conc

**Task 2: EXAFS Spectroscopy**
- **Characterization of:**
  - U(VI) surface speciation
  - U(VI)-carbonate/U(VI)-Ca-carbonate precipitates/co-precipitates

**Sample prep**
- Experimental design

**Data interpretation**
- Experimental design

EXAFS fit by Shelly Kelly

Ca$_3$UO$_2$(CO$_3$)$_3$
Overview of Research Tasks

Simulation of U(VI) solution speciation and precipitation reactions

**Task 1: U(VI) Sorption Experiments**

Experimental design

**Task 2: EXAFS Spectroscopy**

Experimental design

Data interpretation

**Task 3: U(VI) Diffusion Experiments**

Solids: Montmorillonite + calcite mixtures
Before and after heat exposure

Fixed conditions: pH, pCO₂, calcite conc.
Overview of Research Tasks

Simulation of U(VI) solution speciation and precipitation reactions

**Task 1: U(VI) Sorption Experiments**
- **Experimental design**

**Task 2: EXAFS Spectroscopy**
- **Experimental design**

**Task 3: U(VI) Diffusion Experiments**
- **Solids:** Montmorillonite + calcite mixtures
  - Before and after heat exposure
- **Fixed conditions:** pH, pCO₂, calcite conc.
- **Data interpretation**

**Task 4: Classical MD Simulations**
- **Determine:**
  - Structure & hydration dynamics of U-carbonate / U-Ca-carbonate complexes
  - Access and diffusion of these complexes in clay interlayer spaces
- **Data interpretation**

*Snapshot from MD simulation of UCa₂(CO₃)₃ in water.*
Overview of Research Tasks

Simulation of U(VI) solution speciation and precipitation reactions

Task 1: U(VI) Sorption Experiments
Experimental design

Task 2: EXAFS Spectroscopy
Experimental design

Task 3: U(VI) Diffusion Experiments
Experimental design
Data interpretation

Task 4: Classical MD Simulations
Data interpretation

Task 5: Development of U(VI) Surface Complexation and Diffusion Models
Data and conclusions

- Determine under which conditions the effects of calcite impurities on U(VI) sorption/transport can be neglected, and PA models simplified accordingly.
- For remaining conditions, these new models can predict and quantify these effects.
Overview of U(VI) Solution Speciation Modeling

- Used PHREEQC, a free, geochemical equilibrium program.
- Speciation calculations are based on the chemical reactions listed in the THERMOCHIMIE geochemical database and their equilibrium constants.
- Ionic strength was held constant in all calculations: \( I = 0.1 \text{ M NaCl} \)
- Simulated U(VI) solution speciation as a function of:
  - pH: 3 to 9 or 10
  - Partial pressure of \( \text{CO}_2 \):
    - Zero, atmospheric, 1% and 2% \( \text{CO}_2 \)
  - Total U(VI) concentrations:
    - 1E-7 M, 1E-6 M, 2.4E-6 M, 1E-5 M
  - Calcium/calcite concentrations:
    - Zero, 2 mM \( \text{CaCl}_2 \), 1.5% calcite
- Simulated calcite dissolution as a function of partial pressure of \( \text{CO}_2 \)
Results: Closed Systems (CO$_2$-free Systems)

1E-07 M U(VI)$_{Tot}$

1E-06 M U(VI)$_{Tot}$

2.4E-06 M U(VI)$_{Tot}$

1E-05 M U(VI)$_{Tot}$
Results: Effect of Variable pCO$_2$ at $10^{-7}$ M U(VI)

$pCO_2 = 0$ (Closed system)

$pCO_2 = 10^{-3.45}$ (Atmos. CO$_2$)

$pCO_2 = 10^{-2}$ (1% CO$_2$)

$pCO_2 = 10^{-1.7}$ (2% CO$_2$)
In open system, 2 sources/sinks of CO₂: Calcite and atmospheric CO₂

In closed system, only 1 source/sink of CO₂: Calcite

→ In open systems, there are higher total concentrations of carbonates at lower pH conditions.

→ Calcite starts to precipitate at lower pH with increasing partial pressures of CO₂.
Results:
Effects of 1.5 wt.% Calcite on U(VI) Speciation at 1E-7 M

\[ pCO_2 = 0; \text{1.5 wt.% Calcite} \]

\[ pCO_2 = 10^{-3.45}; \text{1.5 wt.% Calcite} \]

\[ pCO_2 = 10^{-2}; \text{1.5 wt.% Calcite} \]

\[ pCO_2 = 10^{-1.7}; \text{1.5 wt.% Calcite} \]
**Goal:**

- Investigate effects of calcium (CaCl\(_2\)) on U(VI) sorption to Na-montmorillonite.

**Solids:**

- Na-montmorillonite (Swy-2, purified)

**Experimental conditions:**

- 0.5 g/L solid
- I = 0.1 M NaCl/NaHCO\(_3\)
- U(VI)\(_{\text{Tot}}\): 10\(^{-6}\) or 10\(^{-7}\) mol/L (U-233)
- Atmospheric CO\(_2\)
- Sorption equilibration: 48.5 hours
- LSC analysis for U-233
- ICP-MS analysis for Ca, Fe, Si, Al, etc.
- TIC analysis (Shimadzu)
Results: Sorption of 1E-6 M U(VI)

- Sorption of 1.0E-6 M U(VI) in the absence / presence of 2 mM Ca\(^{2+}\)

- Changes in U(VI) solution speciation have no apparent effect on U(VI) sorption.
- No sorption of U(VI)-carbonate or U(VI)-Ca-carbonate species in these systems?
Results: Sorption of 1E-7 M U(VI)

Results

- U(VI) concentration 1.0E-7 M
- Increase in Ca\(^{2+}\)/uranium conc. ratio

- Decrease in U(VI) sorption at low pH, most likely due to a competition between Ca\(^{2+}\) and UO\(_2\)\(^{2+}\) for ion exchange sites.
Other Accomplishments

Organizational:
• Received Radiation Safety License from State of California: November, 2017
• Developed and held radiation safety training for students
• Purchase of Beckman-Coulter Allegra 64R benchtop centrifuge
• Submission of beamtime proposal to SSRL for uranium-EXAFS work
• Application/receipt of 2 scholarships from the Center for Student Research (CSR)
• Application and receipt of a CSR student travel grant

Presentations:
• CSR Student Research Symposium, Cal State East Bay, May 2018: Poster presentation and talk by Nicolas Hall and Jonathan Pistorino
• ACS Undergraduate Research Conference, Oakland, CA, May 2018: Poster presentation by Nicolas Hall
• Cal State Student Research Competition, Sacramento, CA, May 2018: Participation/talk by Nicolas Hall and Jonathan Pistorino
• Goldschmidt Conference, Boston, MA, August 2018: Submission of two abstracts (one invited talk, one student presentation)
• Submission of journal article to *Environmental Science & Technology*, May 2018
Acknowledgements

Funding:

• Department of Energy, Office of Nuclear Energy’s Nuclear Energy University Program. *Federal Grant Number: DE-NE0008683*

• Center for Student Research at Cal State East Bay

• Cal State East Bay, Faculty Support Grant 2017-2018
Additional slides
The long-term management of nuclear waste requires reliable predictions of uranium transport through engineered barrier systems (EBS).

- **Compacted bentonite** is the proposed backfill material in EBS.

- Bentonite largely contains **Na-montmorillonite** clay, but also contains **impurities**: e.g., quartz, feldspars, calcium carbonates, pyrite.

- **Diffusion** will be the dominant transport mechanism in EBS that contributes to radionuclide dose in the environment.

- **Gradients of chemical solution conditions and temperature** are expected over time and across EBS.
Processes Controlling Metal Contaminant Mobility

• Only contaminants in solution can be transported.
  – **Mobile**: Dissolved or suspended with mineral colloids
  – **Immobile**: Precipitated or (ad)sorbed to bulk minerals

• To predict metal mobility, we need to understand:
  – What fraction of metal contaminants is (ad)sorbed?
  – What (ad)sorption processes are involved?
  – What are the resulting surface species?
  – How easily can contaminants be remobilized again?

• What pathways and transport mechanisms are involved?
‘Sorption’ includes **adsorption and absorption** processes.

**Specific surface sites** involved:

(Parking spots)
- Limited number of sites/nm$^2$
- Distribution of site types
  (Good and bad parking spots)
- Different types of surface complexes
  (How well did you park?)

**Surface reactions:**
- Acid/base chemistry of surface sites:
  $$\text{SOH} \Leftrightarrow \text{SO}^- + \text{H}^+$$
  $$\text{SOH} + \text{H}^+ \Leftrightarrow \text{SOH}_2^+$$
- Surface complexation reactions:
  e.g.:  $$\text{SOH} + \text{UO}_2^{2+} \Leftrightarrow \text{SOUO}_2^+ + \text{H}^+$$  \[\text{Log} \ K = 2.08\]

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**Surface speciation influences later metal desorption behavior.**
Montmorillonite Clay

Protonation/deprotonation constants from FPMD calculations (from literature)

Predicted titration curves vs. experimental data
Dent et al., 1992; Chisholm-Brause et al., 1994; Giaquinta et al., 1997; Sylwester et al., 2000; Hennig et al., 2002; Catalano and Brown, 2005; Schlegel and Descostes, 2009; Marques Fernandes et al., 2012; Troyer et al., 2016; Morris et al., 1994; Chisholm-Brause et al., 2001; Kowal-Fouchard et al., 2004; Wolthers et al., 2006; etc.

**Lessons learned from spectroscopy (mainly EXAFS)**

- presence of U(VI) outer-sphere complexes at low pH and/or low ionic strengths, and of U(VI) inner-sphere complexes at other conditions: splitting of the U(VI) oxygen equatorial shell into two distinct contributions at ~2.3 Å and ~2.5 Å in EXAFS spectra

From Schlegel and Descostes, 2009
Lessons learned from spectroscopy (mainly EXAFS)

- presence of U(VI) outer-sphere complexes at low pH and/or low ionic strengths, and of U(VI) inner-sphere complexes at other conditions: splitting of the U(VI) oxygen equatorial shell into two distinct contributions at ~2.3 Å and ~2.5 Å in EXAFS spectra

- considerable uncertainty in the interpretation of second neighbor atoms involved in these surface complexes

Mononuclear bidentate complexes formed at aluminol (Al) sites (Hennig et al., 2002; Schlegel and Descostes, 2009)

Second neighbors = Fe atoms, where Fe has substituted for Al in the octahedral sheets + ternary uranyl-carbonato species formed at the surface (Catalano & Brown, 2005)

Not possible to conclusively distinguish between Fe, Al, and Si as second neighbor atoms in U(VI) EXAFS spectra (Troyer et al., 2016; Marques Fernandes et al., 2012)

No spectroscopic evidence for uranyl-carbonato complexes at the montmorillonite surface (Marques Fernandes et al., 2012)
Effects of Anion Exclusion and Cation Sorption

**Anion exclusion in clay interlayers**

- Ionic strength influences:
  - Diffusion-accessible porosity
  - Diffusive flux

**Fick’s 1st law:**

\[
J_i = -\varepsilon_{a,i} \frac{D_{w,i}}{G_i} \frac{dc_i}{dx}
\]

- \(\varepsilon_{a,i}\)… diffusion-accessible porosity
- \(G_i\)… constructivity/(tortuosity)^2

**Cation exchange reactions**

**Solution conditions (pH, I) influence:**

- Sorption distribution coefficient
- Diffusive flux
- Time to reach steady-state conditions

**Fick’s 1st law:**

\[
J_i = -D_{a,i} \left(\varepsilon_{a,i} + \rho_b K_{d,i}\right) \frac{dc_i}{dx}
\]

- \(K_{d,i}\)… sorption distribution coefficient
Fick’s 1st law:

\[ J_i = -D_{a,i} \left( \varepsilon_{a,i} + \rho_b K_{d,i} \right) \frac{dc_i}{dx} \]

- \( D_{a,i} \) … apparent diffusion coefficient
- \( \varepsilon_{a,i} \) … diffusion-accessible porosity
- \( G_i \) … constructivity/(tortuosity)^2
- \( \rho_b \) … bulk density
- \( K_{d,i} \) … sorption distribution coefficient
Cations, Anions and Neutral Species Diffuse Differently

Fick's 1st law:

\[ J_i = -D_{a,i} \left( \varepsilon_{a,i} + \rho_b K_{d,i} \right) \frac{dc_i}{dx} \]

- Decrease in diffusion-accessible porosity
- Decrease in diffusive flux

Anion exclusion from interlayers

**Tritiated water**

**Bromide**

\[ \begin{align*}
D_{a,i} & \quad \text{apparent diffusion coefficient} \\
\varepsilon_{a,i} & \quad \text{diffusion-accessible porosity} \\
G_i & \quad \text{constructivity/(tortuosity)}^2 \\
\rho_b & \quad \text{bulk density} \\
K_{d,i} & \quad \text{sorption distribution coefficient}
\end{align*} \]
Cations, Anions and Neutral Species Diffuse Differently

Anion exclusion from interlayers

Fick’s 1st law:

\[ J_i = -D_{a,i} \left( \varepsilon_{a,i} + \rho_b K_{d,i} \right) \frac{dc_i}{dx} \]

- Decrease in diffusion-accessible porosity
- Decrease in diffusive flux

Sorption reactions

- Retardation (cation exchange/surf. complex.)
- Weak sorption: Increase in flux
- Strong sorption: No change in flux

\( D_{a,i} \)… apparent diffusion coefficient
\( \varepsilon_{a,i} \)… diffusion-accessible porosity
\( K_{d,i} \)… sorption distribution coefficient
\( G_i \)… constructivity/(tortuosity)^2
\( \rho_b \)… bulk density

Diffusion in Na-montmorillonite is controlled by:

- **Clay pore structure:** → 2 types of diffusion-accessible porosity
- **Negative clay surface charge:** → anion exclusion from interlayers
- **Solute characteristics:** → charge, size and sorption properties
- **Effects of chemical solution conditions and clay compaction**

Results from CaBr$_2$ through-diffusion experiment show:

*Normalized flux:*

\[
\text{Br}^- < \text{HTO} < \text{Ca}^{2+}
\]

Calcium-bromide diffusion rates are affected by:

- **Charge of solutes:** → Anion-exclusion of Br$^-$ from interlayer spaces
- **Solute sorption affinities:**
  → Retardation of Ca$^{2+}$ due to ion exchange reactions with clay
Setup: Surface Complexation Modeling

**Surface model:**

- Mean-field approach to describe relationship between surface charge and surface potential (Bourg, et al., 2007; Tournassat et al., 2013):

\[
\frac{F \psi_{\text{edge}}}{RT} = A_1 a \sinh\left(A_2 \left(Q_{\text{edge}} + A_3\right)\right)
\]

\(A_1, A_2, A_3\) … fitted parameters, \(f(l)\)

\(Q_{\text{edge}}\) … surface charge of edge site

- Protonation/deprotonation constants from first-principle molecular dynamics (Liu et al., 2015)

**Uranium(VI) sorption:**

- Modification of PHREEQC to include clay surface potential model.
- No ion exchange reactions considered due to high ionic strength in sorption experiments.
- Modeling steps:
  1. Fitting of surface complexation constants with U(VI) sorption data from ‘CO₂-free’ exp.
  2. Blind fit of U(VI) sorption under atmospheric \(P_{\text{CO}_2}\): This study and literature data
  3. Evaluation of relevance of ternary U(VI)-carbonato surface complexes
Step 1: Fitting of surface complexation constants using U(VI) sorption data from ‘CO₂-free’ experiment only

>SOH₃ + UO₂⁺² = >SOH₃UO₂⁺² \[ \log K = 3.8 \]
>SOH₃ + UO₂⁺² = >SOHUO₂ + 2 H⁺ \[ \log K = -5 \]
>SOH₃ + UO₂⁺² + 2 H₂O = >SOUO₂(OH)₂⁻³ + 5 H⁺ \[ \log K = -25.4 \]
Step 2: Blind fit of U(VI) sorption under atmospheric $P_{CO_2}$: This study

Model predicts response to an error in NaHCO$_3$ additions

Results: Surface Complexation Modeling

Step 2: Blind Fit of Atmospheric $P_{CO_2}$ Data
Results: Surface Complexation Modeling

Step 2: Blind Fit of Atmospheric $P_{CO2}$ Data

**Step 2:** Blind fit of U(VI) sorption under atmospheric $P_{CO2}$: *Literature data*

- **Turner, 1996**
- **Hyun, 2001**
- **Troyer, 2016, pH 4**
- **Troyer, 2016, pH 6**
Blind fit:
U(VI) sorption at elevated $P_{\text{CO}_2}$

$U(\text{VI})_{\text{Tot}} = 1 \times 10^{-6}$ M
$P_{\text{CO}_2} \sim 1\%$

Addition:
U(VI)-carbonato surface complexes

$> \text{SOH}_3 \text{UO}_2 (\text{CO}_3) \log K = 5$
$> \text{SOH}_2 \text{UO}_2 (\text{CO}_3)_2^{-3} \log K = -1.5$

- Ternary U(VI)-carbonato surface complexes not supported by electrostatic SCM.
- Parameter estimation is highly sensitive to actual (bi)carbonate concentrations: 
  → Experimental measurements needed; assumptions not sufficient.
- U(VI) adsorption reaction stoichiometry + constant
  - Adsorption on most abundant groups (Si-Al-Si)
  - Parsimony rule

Step 1.
- Reactions stoichiometry and associated constants for the « CO₂ free » experiment
- DIC was taken into account

**U(VI) adsorption reactions on Si₅-Al₅c-Si₅ sites**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiteH⁺ + UO₂²⁺ = SiteH⁺UO₂²⁺</td>
<td>4.8</td>
</tr>
<tr>
<td>SiteH⁺ + UO₂²⁺ = SiteHUO₂⁺ + 2 H⁺</td>
<td>-4.8</td>
</tr>
<tr>
<td>SiteH⁺ + UO₂²⁺ +2 H₂O = SiteUO₂(OH)₂⁻³ + 5 H⁺</td>
<td>-25.3</td>
</tr>
</tbody>
</table>

**Graphical Representation**

- pH vs. 
  - $K_D (L \cdot kg^{-1})$
  - DIC (mol L⁻¹)

- DIC = 0
Results: Various U(VI) Conc. at Atmospheric CO₂
Calcite Dissolution at various CO₂ Conditions (U(VI) = 1.5E-6 M, I = 0.1 NaCl)
Summary of Results

How will the presence of a calcite impurity alter:

- The chemical form of U(VI) in solution (chemical speciation)
- Sorption onto the clay

Most likely due to the increase competition for sorption sites (parking spaces) between uranium species and Ca$^{2+}$
Uranium(VI) diffusion experiments: Setup

**Diffusion cell and setup:**
- PEEK cell, stainless-steel filters
- D=1.0 cm, L=0.5 cm
- High and low-concentration reservoirs
- Flow-rate: ~0.7 ml/min

**Clay characteristics:**
- Pretreated Na-montmorillonite
- Dry density: 0.77 g/cm³

**Solution conditions/analysis:**
- U(VI) diffusion: pH~8.69 or pH~8.87
- I=0.1 M NaCl/NaHCO₃
- Solute: 2.35 μM U(VI) (U-233, LSC anal.)
- Monitoring: Ca, Fe, Si, Al, etc. (ICP-MS)

**Experimental steps:**
- pH-equilibration of clay (batch): 3 weeks
- Saturation of dry, packed clay: ~3 ½ weeks
- Through-diffusion of HTO tracer: ~2 weeks
- Through-diffusion of U(VI): 11 weeks
Uranium(VI) Diffusion Experiments: Results

- Estimated U(VI) $K_d$ values:
  - pH-8.75: 2.0 [L/kg]
  - pH-8.95: 1.3 [L/kg]

- Uranium(VI) retardation under both pH conditions: $K_d$, pH-8.75 > $K_d$, pH-8.95.
- U(VI) sorption due to (strong) surface complexation, not (weak) cation exchange.
- Apparent kinetic limitations for U(VI) sorption at pH-8.75 relative to pH-8.95.