Release of aged contaminants from weathered sediments:
Effects of sorbate speciation on scaling of reactive transport

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Context

Plutonium production at Hanford Site (WA)

Wastes contain $^{137}\text{Cs}^+$, $^{90}\text{Sr}^{2+}$, $^{129}\text{I}^-$

stored at pH>13

high ionic strength.

Leaks

fate of radionuclides beneath the tanks?

Distribution of sorbed Cs+ beneath leaked tanks (Zachara et al., 2007)

Schematic diagram of waste discharges to the vadose zone and Columbia river (Gee et al., 2007)


HLRW in underground storage + Salt cake. (Marceau et al., 2002)

Zachara et al., 2007

Plutonium production at Hanford Site (WA)
Transport and Fate of Radionuclides in the Hanford Vadose Zone

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Prior work: *Specimen Clays*

- Studies with specimen clays present at Hanford showed that reaction with caustic waste leads to Si dissolution and neophase (feldspathoid and zeolite) precipitation.
- Neophases sequester Sr$^{2+}$ and Cs$^{+}$ into framework sites.
- Contaminant (Cs and Sr) concentrations affect mineral transformation rates.
- Aging of waste-clay suspensions make contaminants more recalcitrant to subsequent release.
Solid-State NMR at PNNL
Solid-State NMR of $^{27}$Al at High Magnetic Fields

$$\delta_{tot} = \delta_{iso}^{(CS)} + \delta_{iso}^{(2Q)}$$

$$= \delta_{iso}^{(CS)} - \frac{3}{40} \left( \frac{C_Q}{\nu_L} \right)^2 \frac{I(I+1)}{(I(2I-1))^2} \left( 1 + \frac{\eta^2}{3} \right) \times 10^6$$

![Graphs of Al(IV) and Al(VI) at different magnetic fields]

- (a) 7.0 T
- (b) 9.4 T
- (c) 11.7 T
- (d) 17.6 T

Quadruopolar Coupling Constant

$$C_Q = \frac{e^2 qQ}{h}$$

$$P_Q = C_Q \left( 1 + \frac{\eta^2}{3} \right)^{1/2}$$

Kaolinite Dissolution and Neophase Formation

(a) 400 MHz

(b) 500 MHz

(c) 750 MHz

Frequency (ppm from Al$^{3+}$)

(a) basic sodalite

(b) nitrate cancrinite
87Sr and 133Cs Solid-State NMR


$^{87}\text{Sr}$ and $^{133}\text{Cs}$ Solid-State NMR
$^{87}\text{Sr}$ and $^{133}\text{Cs}$ Solid-State NMR

Prior work: *Hanford Sediments*

- Slow strontium uptake to same neophases (sodalite and cancrinite)
- Increasing contaminant recalcitrance (more crystallization) with increased aging time
Questions Driving Our Current Work

• What are the impacts of waste chemistry (particularly contaminant concentrations and CO$_2$ partial pressure) on:
  – mineral transformation reactions
  – contaminant molecular environment
  – contaminant release from the solid phase

• What controls contaminant release from these neophases after re-introduction of native, background pore water (BPW)? At what time scales are desorption or dissolution more important?

• Can we develop reactive transport models of contaminant release from the sorbed state?
Objectives for Our Current Project

• Assess the role of $P_{\text{CO}_2}$ and contaminant concentrations on mineral transformations and contaminant uptake in Hanford sediments.

• Determine the rate and extent of aged contaminant release.

• Develop a reactive transport model based on molecular mechanisms and test this model in macroscopic flow experiments.
2 x 2 x 2 Experimental Matrix

Contaminant concentration

CO₂-atm

CO₂ pressure

CO₂-free

LOW

Contaminant concentration

HIGH

400 g HF sediment reacted with 20 L of synthetic tank waste leachate (STWL) Na-NO₃-Al-OH pH 13.5

6 & 12 month aging

10⁻⁵ m Sr, Cs & 10⁻⁷ m I

10⁻³ m Sr, Cs & 10⁻⁵ m I
Particle Size Transformations

- unreacted
- 6mo
- 12mo

HIGH CO₂

LOW CO₂
Calcite Dissolution Effects on Neophase Formation

- **Sodalite-type:**
  \[ \text{Na}_8\text{(AlSiO}_4\text{)}_6(\text{NO}_3\text{)}_2 \]

- **Calcite:**
  \[ \text{CaCO}_3 \]

- **Chabazite-type:**
  \[ (\text{Ca,K,Sr})\text{Al}_4\text{Si}_8\text{O}_{24}\cdot12\text{H}_2\text{O} \]

- **Stratlingite-type:**
  \[ \text{Ca}_2\text{Al}_2(\text{SiO}_2)(\text{OH})_{10}\cdot2.5(\text{H}_2\text{O}) \]
STWL Reacted Sediments – TEM/EDX

CO₂-atm

sodalite-like

co2 pressure

chabazite-like

sodalite-like

CO₂-free

co2 pressure

Contaminant concentration

LOW

HIGH
Sr EXAFS Linear Combination Fit Results
Sr EXAFS Linear Combination Fit Results
Flow-Through Desorption-Dissolution Experiments

• Unsaturated and saturated column studies were conducted with Hanford sediments reacted under the four STWL conditions.
  – ambient and zero CO₂
  – high and low contaminant (Cs, Sr, I) concentrations

• Sediment columns (6 month weathering) were leached with background pore water (BPW) characteristic of Hanford site:
  pH 7.2 and all following values in mmol kg⁻¹
  3.6 NaCl, 1.7 CaSO₄, 1.0 CaCl₂, 1.0 MgCl₂, 0.3 KCl, 0.1 NaHCO₃

• All dissolution products were measured to develop a mechanistic reactive transport model using CrunchFlow 2008.

• Experiments with 12 month reacted sediments are ongoing.
# Model Constructions

<table>
<thead>
<tr>
<th>Time-Frame Focus</th>
<th>&lt;300 PV’s</th>
<th>&gt;300 PV’s</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mode</strong></td>
<td>Exploratory</td>
<td>Hypothesis testing</td>
</tr>
<tr>
<td><strong>Treatments shown here</strong></td>
<td>Low (+CO₂)</td>
<td>Low(+CO₂) &amp; (-CO₂)</td>
</tr>
<tr>
<td><strong>Minerals Used</strong></td>
<td>Zeolites (Sr &amp; Cs sub.)&lt;br&gt;- (Ca,Sr,Cs₂)Al₂O₄(SiO₂)₄·6H₂O&lt;br&gt;Feldspathoid (Sr-sub)&lt;br&gt;- Na₇.9₈Sr₀.₀₁(NO₃)₂Al₆(SiO₂)₆O₁₂&lt;br&gt;Calcite&lt;br&gt;- CaCO₃&lt;br&gt;Natratine&lt;br&gt;- NaNO₃&lt;br&gt;Analcime-dehydrate&lt;br&gt;- Na₀.₉₆Al₀.₉₆(SiO₂)₂.₀₄O₁.₉₂</td>
<td>Feldspathoid (Sr-sub)&lt;br&gt;- [Na₇(₈₋₂ₓ)Srₓ(NO₃)₂Al₆Si₆O₂₄], with&lt;br&gt;ₓ = 0.₀₁₂(+CO₂) &amp; 0.₀₁₀(-CO₂)&lt;br&gt;Gibbsite&lt;br&gt;- Al(OH)₃&lt;br&gt;Kaolinite&lt;br&gt;- Si₂Al₂O₅(OH)₄</td>
</tr>
<tr>
<td><strong>Ion-exchange formulation</strong></td>
<td>One-site Model</td>
<td>Steefel <em>et al.</em> (2003) Three-site model</td>
</tr>
</tbody>
</table>
### Parameters Used in the Short-term Model

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Log $K_{eq}$ at 25 °C</th>
<th>Log $k_{reaction}$</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chabazite</td>
<td>13.7</td>
<td>-10.8</td>
<td>624 (zeolite X)</td>
</tr>
<tr>
<td>Chabazite-Sr²⁺</td>
<td>12.9</td>
<td>-11.8</td>
<td>624</td>
</tr>
<tr>
<td>Chabazite-Cs⁺</td>
<td>12.9</td>
<td>-12.9</td>
<td>624</td>
</tr>
<tr>
<td>Sodalite-Sr²⁺</td>
<td>-39.2</td>
<td>-14.4</td>
<td>12</td>
</tr>
<tr>
<td>Calcite</td>
<td>1.85</td>
<td>-12.2</td>
<td>0.87</td>
</tr>
<tr>
<td>Natratine</td>
<td>1.04</td>
<td>-8.3</td>
<td>2</td>
</tr>
<tr>
<td>Analcime-dehydrated</td>
<td>12.5</td>
<td>-9.5</td>
<td>2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cs⁺</th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Sr²⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log $K_{for ion exchange}$</td>
<td>-1.45</td>
<td>-0.1</td>
<td>0.18</td>
<td>0.65</td>
<td>1.7</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Short-Term (Pre-Steady State) Release for Sediments Reacted at LOW Contaminant Concentrations with CO$_2$

Saturation level : 75%
Porosity : 0.44 (Bulk density : 1.44 g/cm$^3$)
Flow rate : 11.58 mL/day (0.81 PV / day)
Dispersivity : 1.17 x 10^{-2} cm

Successfully modeled with dissolution/precipitation and ion-exchange reactions
Pre-Steady State Release (continued)

Low + CO₂
Sorption and/or precipitation is thought to be responsible for removal of contaminants from solution after early release (250 < hrs< 1500).

Sr\(^{2+}\) release (> 1500 hrs) is controlled by dissolution of crystalline Sr\(^{2+}\)-containing sodalite as well as ion exchange processes after Sr\(^{2+}\) release from amorphous zeolite (Chabazite-Sr\(^{2+}\)) dissolution.

Cs\(^{+}\) release (> 1500 hrs) is dominantly controlled by ion exchange process after Cs\(^{+}\) release from amorphous zeolite (Chabazite-Cs\(^{+}\)) dissolution.

*Release mechanisms of contaminants in later stage (or long-term release) is affected by short-term releases of the contaminants.*
Long Term (Steady State) Release

- Pseudo steady-state is achieved after ~300 PV’s
- Yet, for Cs this can still be modeled as ion exchange (modeling shown).
- Note the high NO₃ concentrations in the LOW treatments
Cs Release via Ion Exchange in the Low Treatments

- 3-site ion exchange model of Steefel et al. (J. Contam. Hydrol. 2003)
- Adjusted Cs-K selectivity values
- Adjusted CEC site densities.
- Cs\(^+\) loading ~ 30 meq g\(^{-1}\)
NO$_3$-sodalite in the LOW persists with strong reflections after 600PV of BPW infiltration. In the HIGH, the dissolution of the zeolite and possibly some structural modifications are perceptible. In CO$_2$ free contexts (HIGH and LOW), stratlingite is dissolving.
Remaining Fraction of Applied Contaminant After BPW Leaching

 Majority of added Cs and Sr remains bound into the solid phase after > 600 PV of BPW leaching
Conclusions

• Weathering of Hanford sediments in STWL exhibits strong dependence on $P(\text{CO}_2)$ and also on variation in trace contaminant concentrations.

• This results in variation in initial conditions for desorption-dissolution of contaminants when sediments are subsequently exposed to leaching with background pore water.

• The initial sorbate speciation of strontium, for example, varies from sodalite-sorbed at LOW (irrespective of $\text{CO}_2$) to $\text{SrCO}_3$ and sodalite at HIGH + $\text{CO}_2$ to chabazite at HIGH – $\text{CO}_2$.

• Results from column desorption-dissolution experiments show that contaminant release can be effectively simulated with a mechanistic-based reactive transport model that incorporates sorbent dissolution and ion exchange.
Future work

• Column desorption-dissolution studies with 12 month reacted samples.

• *In-situ* column uptake and release data for column STWL infusion followed by BPW leaching (see Nelson Rivera’s poster).

• Mobility studies of secondary precipitates containing contaminants as mobile colloids.

• Ties to reactive surface area measurements using NMR.
Acknowledgements

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SSRL (Beamlines 11-2, 11-3, and 2-3)
Reactive Surface Area Studies

• Identification of dissolution reactive sites on surfaces in the environment

• Scaling of reaction rates to surface areas
  – BET, Geometric, or new methodology?

• Quantification of reactive sites
  – Total reactive species (e.g., -OH groups)
  – Speciation (Al-OH, Si-OH, other)

Penn State Center for Environmental Kinetics Analysis (NSF CHE-0431328)
Solid-State NMR Approach

- Isotopic selectivity
  Selective chemistry

- Molecular-level information
  Chemical shift and other NMR parameters are sensitive to:
  - Type of bonding
  - Coordination environment
  - Motion

- Must overcome low sensitivity – bulk vs. surface probing
  Use nuclei such as $^{19}$F
  - Probe molecule containing CF$_3$ moiety:
    TFS = (3,3,3-trifluoropropyl)dimethylchlorosilane
Reactive Surface Area Measurements via NMR

**New Method: Reactive Surface Area**

- **Surface Chemistry**
  - $\text{CH}_3\text{SiCH}_2\text{CH}_2\text{CF}_3$
  - $\text{Cl}\to\text{CH}_3$
  - $\text{H}_2\text{O}$
  - $\text{HCl}$
  - $\text{CH}_3\text{SiCH}_2\text{CH}_2\text{CF}_3$

- **Bulk Particle**

- **Chemical specificity via covalent bond**
- **Quantitative**

**Specific Information**

![NMR Spectrum](image)
Surface Area on Naturally-Weathered Volcanic Glasses

Rhyolitic & dacitic glasses (Wolff-Boenisch et al., 2004, GCA, 68, 4843)

Geometric

BET

Dissolution conditions: pH 4
Correlation of Dissolution Rate and Hydroxyl Number by TFS

Washton et al. (2008) GCA, 72, 5949
Future Work and Applications

Relevance for base-mediated dissolution of Hanford sediments currently being explored.
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