Realistic Quantification of Radionuclide Retardation under Unsaturated Conditions

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Fracture-Matrix Interactions

Field observation (preferential flow in a fracture network) of dye distribution in unsaturated fractured tuff at Yucca Mt.
$K_d$ Approach under Question

- $K_d$ approach commonly used to describe sorption process in contaminant fate and transport studies and modeling

- Concerns of batch sorption approach for unsaturated rock: “maximum sorption potential”
  - Sorption kinetics; nonlinearity; competition
  - Unrealistically large water/solid ratio
  - Crushed rock used (sample sizes in the range of microns to sub-millimeters; more or less arbitrarily chosen); creating new surface and increasing pore accessibility
  - Well mixed
  - Difficult for fluid-solid-contaminant systems with weak sorption
Comparison of Batch vs. New Approach

Conventional approach

Unsaturated transport-sorption approach

Crushed Rock (μm to mm)

Saturated Batch Sorption Test

Intact Rock (cm scale)

Moisture Front

Nonsorbing Tracer Front

Sorbing Tracer Front

Unsaturated Transport and Sorption Test
### Batch Sorption of Different Sample Sizes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (µm)</th>
<th>Cs</th>
<th>Re / Tc-99</th>
<th>Np-237</th>
<th>Pu-242</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSw34</td>
<td>&lt;75</td>
<td>115±0.75</td>
<td>(-0.053)±0.010</td>
<td>3.13±0.054</td>
<td>1191±372</td>
</tr>
<tr>
<td>TSw34</td>
<td>75-500</td>
<td>59.1±0.93</td>
<td>(-0.067)±0.012</td>
<td>1.26±0.072</td>
<td>144±18.1</td>
</tr>
<tr>
<td>TSw34</td>
<td>500-2000</td>
<td>52.4±0.88</td>
<td>(-0.051)±0.016</td>
<td>1.09±0.039</td>
<td>99.2±5.18</td>
</tr>
<tr>
<td>CHz</td>
<td>&lt;75</td>
<td>73466±46508</td>
<td>(-0.119)±0.009</td>
<td>1.83±0.029</td>
<td>2813±1564</td>
</tr>
<tr>
<td>CHz</td>
<td>75-500</td>
<td>11461±4100</td>
<td>(-0.140)±0.043</td>
<td>1.07±0.041</td>
<td>312±56.9</td>
</tr>
<tr>
<td>CHz</td>
<td>500-2000</td>
<td>11935±7930</td>
<td>(-0.107)±0.032</td>
<td>0.937±0.10</td>
<td>278±65.1</td>
</tr>
<tr>
<td>CHv</td>
<td>&lt;75</td>
<td>677±96.6</td>
<td>(-0.064)±0.036</td>
<td>1.00±0.087</td>
<td>195±23.0</td>
</tr>
<tr>
<td>CHv</td>
<td>75-500</td>
<td>300±11.4</td>
<td>(-0.100)±0.013</td>
<td>0.269±0.025</td>
<td>31.7±6.88</td>
</tr>
<tr>
<td>CHv</td>
<td>500-2000</td>
<td>227±26.3</td>
<td>(-0.098)±0.005</td>
<td>0.162±0.009</td>
<td>17.9±1.87</td>
</tr>
</tbody>
</table>
Unsaturated Transport-Sorption Approach

- Cylindrical rock cores, epoxy-coated along length
- Imbibition rate monitored continuously over time
- Sample size (cm range)
- Different initial water contents
- Tracer solution
Laser Ablation/ICP-MS for Micro-Scale Profiling

ICP-MS

LA

2.1 mm view area

100 µm pit

Vertical height (µm)

Horizontal distance (µm)

1 pulse
- 5 pulses
- 10 pulses
- 25 pulses
- 50 pulses

0 20 40 60 80 100 120 140 160 180 200

Department of Energy • Office of Civilian Radioactive Waste Management
Calibration Curves of LA/ICP-MS

![Graph showing calibration curves for various elements with concentration on the x-axis and intensity ratio on the y-axis.](image)

\[ C_{samp}^{a} = C_{ref}^{a} \left( \frac{C_{samp}^{is}}{C_{ref}^{is}} \right) \left( \frac{I_{samp}^{a}}{I_{a}^{ref}} \right) \left( \frac{I_{ref}^{is}}{I_{is}^{samp}} \right) \]
Unsaturated Transport-Sorption Results: TSw

- Initially dry
- Strong capillarity
- Advection

Initially moist
- High permeability
- Dispersion
Unsaturated Transport-Sorption Results: CHv

Initially 98% RH; exp. duration 1.0 min

Initially dry; exp. duration 2.5 min

Initially 98% RH; exp. duration 1.0 min

Ca-44, Cs-133, Re-185, Np-237, Pu-242
Comparison of Preliminary $K_d$ Results (mL/g)

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Imbibition</th>
<th>Column</th>
<th>Batch</th>
<th>Literature values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>0.37</td>
<td>&gt; 16</td>
<td>20</td>
<td>5 - 30</td>
</tr>
<tr>
<td>Cs</td>
<td>0.44</td>
<td>&gt; 16</td>
<td>50</td>
<td>10 – 700</td>
</tr>
<tr>
<td>Sm</td>
<td>6.8</td>
<td></td>
<td></td>
<td>100 - 1000</td>
</tr>
</tbody>
</table>

Need numerical simulators (e.g., HYDRUS) for transient transport to obtain $K_d$ values.

$R_f = \frac{L_{\text{nonsorbing}}}{L_{\text{sorbing}}} = 1 + \rho_b \times \frac{K_d}{\theta}$

Approach Characteristics Weak sorption Strong sorption

Batch static, crushed +

Column flowing, crushed + +

Imbibition flowing, intact + +
Summary

- Concerns raised about effective $K_d$ approach in unsaturated fractured rock
- Preliminary results indicating that sorption results (batch and/or column) using crushed sample could overestimate the extent of sorption in intact rock
- The new approach, which is especially useful for fluid-solid-radionuclide systems with weak sorption, expected to generate more realistic sorption data (under unsaturated transport conditions) for flow and transport modeling
Acknowledgments

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