Using the PHT3D Reactive Transport Model for In-Situ Recovery ACL Application Predictions

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The Cake is in the Can
Now What?

- No Longer Generating Revenue
- Restoration Costs Can Be Significant with Some Estimates as High as 50% of the Total Life Cycle Costs
ISR Restoration Goals

• Clean Groundwater to MCLs or Background
  – Groundwater Sweep
  – Reverse Osmosis Water Rinse (and Repeat)
  – Long Term Monitoring

• What if Background or MCLs Cannot be Achieved
  – Alternate Concentration Limit
  – Long Term Monitoring
  – Roughly Equivalent to Monitored Natural Attenuation
Restoration Pitfalls

• TIME ---- It Take Years
• Expensive (Up To 50% of the Production Costs)
• MCLs or Background May Not Be Economically Obtained
• Concentration Rebound Common in ISR Restoration
• The Mine Unit Has Undergone Permanent Changes to Geochemistry
• The Conditions That Generated the Roll Front Are Gone
ACL Approach

Develop a Plan Based on the Concept that a POC Concentration Can Be Developed That Will Result a POE Concentration Lower Than the MCL

- Alternate Concentration Limits Has Not Been Completed For Uranium ISR
- ACL for ISR is Different From a Mill or Mine
- Illustrate Pitfalls In ISR Restoration
- Hydro-Geochemical Models to Develop ACL Concentrations and POE and Reduce the Cost of Closure
<table>
<thead>
<tr>
<th>Uranium Mill ACL</th>
<th>ISR ACL</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Nearly Homogenous Geochemistry</td>
<td>• Variable Geochemistry</td>
</tr>
<tr>
<td>• Non-Reactive Transport Models Commonly Used</td>
<td>• Reactive Transport Model Required</td>
</tr>
<tr>
<td>• POC at Toe of Tailings</td>
<td>• POC at Monitoring Well Ring</td>
</tr>
<tr>
<td>• POE is Typically At Property Boundary of Mining Company</td>
<td>• It May Take Decades for Geochemistry to Stabilize in Mine Unit</td>
</tr>
<tr>
<td>• Property Transferred to DOE upon Acceptance of ACL and License Termination</td>
<td>• POE within Aquifer Exemption Ring</td>
</tr>
<tr>
<td></td>
<td>• No Long Term Custody</td>
</tr>
</tbody>
</table>
Hydro-Geochemical Models and the ACL Process

- Hydro-Geochemical Models Capable of Simulating All of the Chemical Constituents of Mining Unit
- Current Aquifer Exemption Zones are based on Mining and Possible Excursions
- Aquifer Exemption Zones May Require Amendment if ACL Approach is Implemented
- Hydro-Geochemical Models can be Used to Define the Aquifer Exemption Zone Up Front
Hydrogeologic and Geochemical Modeling

Original D&M pH=6, No CO2(g)
Revised K1, K2 pH=6, No CO2(g) atms
4 USC  pH =6, log CO2(g) =
4 USCs & SCs pH =6, log CO2(g) =

Pore Volumes

"Same Transport Model" HFO 0.066 gm/L
No Calcite, pH fixed at 6.0, 1 mg/L U

Uranyl carbonate (K3int, K4int), result in greater retardation
Surface carbonate complexes show slight impact

Original D&M constants (K1int, K2int) produce greater retardation than Revised Constants
Increased CO2 pressures increase mobility
ISR Hydrogeologic Process
ISR Geochemical Process

Reactions Involved in ISR and Restoration

Kinetics
Rate Controlled

Equilibrium Based
Complexation Reactions

\[ O_2(g) + \text{Pyrite} \rightarrow HFO \]

\[ O_2(g) + \text{Hfo}_{wO}UO_2^{+2} \rightarrow \text{HFO} / \text{Goethite} \]

Equilibrium between surface reactions and solution
Post Restoration

Reduced Zone

- Organic Material
- Organic Carbon
- Remineralized Uranium
- Pyrite
- Consumes Residual Oxygen
- Remineralized Uranium

Oxidized Zone

- Mining Zone

Equilibrium between surface reactions and solution:

\[ CO_3^{2-} \rightarrow Hf_{2w}O_2^{12} + UO_2^{2+} \]
Uranium Re-Mineralization

After Claudia Stewart Thesis
2002. University of Wyoming
Uranium Re-Mineralization

Uranium Re-Mineralization

After Claudia Stewart Thesis
2002. University of Wyoming
Regulatory Designations

- Aquifer Exemption Zone
- Exempted Portion of Mining Zone Aquifer
- Ore zone
- Project Area
- Monitor Well Ring
- Lease area

1/4 Mile Area of Review

Area of Review boundary

PROPOSED

not to scale
ACL Process

• Point of Compliance (POC)
• Point of Exposure (POE)
• POC Coincident With the Monitoring Well Ring
• POE Coincident With the Aquifer Exemption Area
• Concentration of Contaminants of Concern (COC) Must Be Below MCL or Background Concentration at the POE
• Use Modeling to Estimate the COC Concentration at the POC that Results in Below MCL At POE
Transport Model Used to Estimate ACL Concentrations

- **MT3DMS**
  - Used where Geochemistry is Stable
  - No Reaction
  - Retardation based on $K_d$
  - Can be Used in Convention Uranium Mill Settings

- **PHT3D**
  - Used where Geochemistry is Variable
  - Fully Reactive Transport
  - Re-precipitation Removes Uranium From the Solution

**NOT** Merely Retard Transport
PHT3D Modeling

• Combines MT3DMS and PHREEQC
• Flow Field Generated By MODFLOW
• Industry Standard Models
• Updated PHREEQC Database
• Fully Three-Dimensional
Modeling Parameters

- Generic Data Collected From Adams (NRC) Using Several Sites in Wyoming and Nebraska
- Organic Carbon Mineralization Inferred From University of Wyoming Claudia Stewart Thesis
- Modified Geochemical Database
  - Uranium Dissolution Calibrated to Site Data
Geochemical Zones
## Zone Definition

<table>
<thead>
<tr>
<th>Zone 1 Oxidized Zone</th>
<th>Zone 2 Mineralized/Mining Zone</th>
<th>Zone 3 Reduced Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Pyrite</td>
<td>Background Oxygen</td>
<td>Pyrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low pe</td>
</tr>
<tr>
<td>No Organic Carbon</td>
<td>Dissolve Pyrite</td>
<td>No Oxygen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Uraninite Precipitates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organic Carbon</td>
</tr>
</tbody>
</table>
Uranium In Solution (ppm)
Sulfate In Solution
Uranium Mineral Dissolution During Mining
ELECTRON ACTIVITY

\[ pe = -\log a_{e^-} \]

- The pe indicates the tendency of a solution to donate or accept electrons.
- If pe is positive, there is a strong tendency for the solution to donate electrons - the solution is oxidizing.
- If pe is negative, there is a strong tendency for the solution to accept electrons - the solution is reducing.
- LEO says GER
Modeled $pe$ Distribution
Uranium Re-Precipitation After Restoration
Conclusions

• Modeled Residual Oxygen In Well Field is Quickly Consumed In Pyrite and Organic Carbon Reactions in Down-Gradient Reduced Zone

• Modeled Residual Uranium In Well Field Quickly Re-Precipitated in Down Gradient Reduced Zone

• Generic Kinetic Rates Were Used In the Model - Actual Kinetic Rates Will Require Calibration
Conclusions

• Calibrated Hydro-geochemical Model Can Be Implemented To Establish Defensible POC Alternate Concentration Limits
• Reduction In Closure Costs
• Excursion Analysis Can Be Implemented To Establish Defensible Aquifer Exemption Boundaries
Thank You
Questions?