Geochemical Fate and Transport of Dissolved Uranium in an ISR Wellfield using Kinetic-based Modeling Approach and PHREEQC and PHAST

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PRESENTATION OUTLINE

- Project History and Detection of Elevated Indicator Parameters across Lease Boundary
- Operator Response to Issues
- Geochemical Fate & Reactive Transport Modeling Approach
- PHREEQC and PHAST (John Mahoney)
  - Introduction to PHREEQC and PHAST
  - Kinetic Rate Law and Calibration
  - Dual Naming of Uranium Sources
PRESENTATION OUTLINE (CONT’D)

- Objectives of Modeling and Model Domain Setup
- Modeling Calibration
- Simulation Results
- Additional Applications of this Reactive Transport Tool
- Summary/Questions

* This work is significant because this is a real world example where modeling was used to assess actual conditions, predict results, and compare to recovery data.
Operating ISR uranium facility; 5-spot patterns at ~100’ spacing; sodium bicarbonate lixiviant

Guard monitor wells installed on adjacent lease boundary at operating ISR facility. Lease boundary ~100 feet from well patterns.

Elevated concentrations of indicator parameters (U, Cl, Bicarb, Conductivity) observed at several guard wells; not an NRC or WDEQ excursion but concern with regard to mineral lease

Wellfield operations modified to reduce concentrations at guard wells

Operational changes resulted in decreased concentrations at 2 of 3 guard wells

One guard well had higher and more persistent concentrations; specific constituent of concern was dissolved uranium
PROJECT HISTORY AND ISSUES ON ADJACENT LEASE AREA

Perimeter Monitor Wells

Guard Well

Wellfield, Lease Boundary, and Guard Well

Guard Wells - Uranium Concentrations

Uranium Concentration (mg/L)

Date


Injection Well
Recovery Well
Perimeter Monitor Well
Guard Well
Lease Boundary

2018 NMA Uranium Recovery Workshop
RESPONSE TO ISSUES

- Reviewed hydrologic testing, geologic logs/cross-sections, injection/extraction rate data, and water level data

- Constructed MODFLOW models (single-layer and multi-layer) to simulate groundwater flow; evaluate flow and transport via particle tracking (MODPATH) and flow vector analysis

- MODFLOW/MODPATH modeling alone could not reasonably simulate observed concentrations away from wellfield

- Geochemical fate & transport modeling approach was proposed to attempt to simulate observed conditions
OBJECTIVES OF GEOCHEMICAL F&T MODELING

- Simulate observed concentrations of dissolved uranium at the guard well on adjacent lease
- Determine wellfield operating conditions and aquifer properties for input to model observed concentrations
- Determine and quantify the source of dissolved uranium (ore on ISR property vs. ore on adjacent lease) that may have been mobilized across lease boundary
- Estimate time frame for concentration reduction
Conducted fate & transport modeling in immediate vicinity of guard well using PHAST (PHREEQC And Solute Transport; USGS)

- Input data based on hydrologic tests, bottle roll (leach) tests, breakthrough curves, mineralogy data, ore (GT) maps
- Define uranium dissolution by kinetic processes (rate law), calibrated to site-specific data
- Delineate two uranium “types”, U and Ux
  - U = Uranium ore on ISR Facility
  - Ux = Uranium ore on adjacent Lease
PHREEQC AND PHAST

- **PHREEQC** and **SOLUTE TRANSSPORT**; Developed by USGS (Denver) as reactive transport code
- Fully 3-D, flow defined using finite differences
- Fully functioning PHREEQC program to define chemical reaction(s)
  - Equilibrium processes, sorption, and dissolution kinetics can be included in model
- Injection and Pumping well options; incorporate geologic/hydrologic characterization
- Different volumes (boxes) can have different properties
FLEXIBILITY IN PHREEQC/PHAST

- Modified thermodynamic database by adding alternative uranium component and corresponding reactions
- Called the alternative form of uranium – Ux
- Ux reactions are identical to regular Uranium (U) reactions already in database
- Similar exercise conducted for Radium/Barium solid solution in a deep disposal well
URANINITE / UXRANINITE

- Uraninite assumed as primary source of dissolved uranium; dissolution controlled by kinetic processes

- Uraninite (U)
  \[ UO_2 + 4H^+ = U^{4+} + 2H_2O \]
  \[ \log_k = -4.8 \]
  \[ \Delta_h = -18.610 \text{ kcal} \]

- Uxraninite (Ux)
  \[ UxO_2 + 4H^+ = U^{4+} + 2H_2O \]
  \[ \log_k = -4.8 \]
  \[ \Delta_h = -18.610 \text{ kcal} \]

- Applied to Kinetics and Rate Laws
In ISR wellfield, presence of lixiviant produces geochemical conditions far from equilibrium. Chemical kinetics, which produce concentration as function of time, ideally suited for ISR wellfield.

\[ \frac{d(U)}{dt} = k(SA / V)^n(\text{terms}) \]

Where:

- \( \frac{d(U)}{dt} \) = change in uranium (U) concentration with respect to time;
- \( SA \) = surface area (usually in terms of cm\(^2\) or m\(^2\));
- \( V \) = volume of solution (Liters), and
- \( k \) = rate constant (1/time)
Same rate laws apply, but different kinetic reactant (names) for Uraninite (U) and Uxraninite (Ux) for dual naming convention.
• Lixiviant used 23.5 mg/L dissolved O₂
  • Corresponds to maximum U concentrations
• 0.011 Moles NaHCO₃; ~ additional 670 mg/L bicarbonate
• After 40 days
**U/Ux PROOF OF CONCEPT**

- Several assumptions/approximations used in the proof of concept model
- PHAST models demonstrate that the dual naming convention works
- Straightforward method to differentiate between different sources of ore
- This approach could be applied to other issues such as wellfield performance.
  - Could be expanded to more than two uranium sources
  - Define uranium ore bodies in space \((x, y, z)\) and with varying ore properties
$Rate = k \cdot parm(1) \cdot (O_2)^{\frac{1}{2}} \cdot (1 - SR("Schoepite")) \cdot (m/m_0)$

- $parm(1)$ term represents surface area (SA) to volume term
- SA is often first parameter to be adjusted in reactive transport model and can be adjusted in calibrations to site data
- Parameters to calibrate PHAST model include concentrations of uraninite, pyrite, dissolution rate constant of $UO_2$, and SA terms for uraninite and pyrite

**Calibration Phases**
- Bottle roll tests for initial rate constant of $UO_2$
- Single five-spot pattern to evaluate concentrations at recovery well compared to “breakthrough” data and maximum observed concentrations during operations
PHAST CALIBRATION

- Bottle roll tests provide reasonable starting value of dissolution rate
- Single five-spot pattern model used to adjust surface area of uraninite
  - Simulated ore zone in production zone aquifer assigned average thickness and grade (as U); lixiviant composition of 150 mg/L oxygen and 0.03 mol/L NaHCO₃
  - Calibration goal of 50 ppm dissolved uranium in ~8 – 12 days based on breakthrough curves at recovery wells
- At later times, uranium concentrations too high based on site-specific data, suggesting too much oxygen in system
- Pyrite was added (consumes O₂ and produces sulfate) and adjustments made to rate constant
Calibration target of 50 mg/L successfully achieved in ~8 – 12 days

Time = 8.25 d
PHREEQC KINETIC CALIBRATION

- Uraninite and Pyrite

**Batch Dissolution Model of Uraninite - Lower Surface Area**

- **Uraninite Only**
  - Formula: Uraninite 1
  - m: 0.026
  - m0: 0.026
  - parms: 0.00213
  - steps: 8640000 in 50 steps

- **Uraninite and Pyrite**
  - Formula: Pyrite
  - m: 0.366
  - m0: 0.366
  - parms: 0.70 0.67 0.5 -0.11

Time in Days: 0 to 100
Uranium Concentration: 0 to 400 mg/L
OBJECTIVES OF GEOCHEMICAL F&T MODELING

- Simulate observed concentrations of dissolved uranium at guard well on adjacent lease
- Determine wellfield operating conditions and aquifer properties to simulate elevated concentrations
- Determine and quantify the source of dissolved uranium (ore body on ISR property vs. ore body on adjacent lease) that may have been mobilized across lease boundary
- Estimate time frame for concentration reduction
Reactive solute transport model used is PHAST (PHREEQC And Solute Transport)

U and Ux ore bodies located on either side of lease (zone) boundary
Uraninite ($\text{UO}_2$) assumed as primary source of dissolved uranium

Kinetic rate law calibrated to bottle roll data, breakthrough curves, and maximum concentrations during operations

Aquifer parameters include Hydraulic Conductivity ($K$, ft/d), Specific Storage ($S_s$), dispersivity, porosity, head

Apply injection and extraction rates within simulated 5-spot patterns
Guard well exhibited elevated concentrations of Uranium

Two five-spot patterns were constructed in PHAST and observation point placed at guard well

Mass flux (U vs Ux) can be evaluated across lease (zone) boundary or at observation/recovery well
Operational modifications successful in reducing concentrations at 2 of 3 wells

Uranium concentrations at guard well continued to rise, indicating potentially larger plume had migrated from wellfield due imbalance and/or some level of preferential pathways in production zone.
- 100 ft thick production zone, completed across 30 ft interval, with a zone defined simulating the presence of uranium ore body (ore body based on site-specific average ore thickness and grade data)
Dissolved uraninite can be traced to source area (Box U vs. Box Ux) to assess mass flux of each to recovery wells or across zone boundary, or evaluate component of each at observation well.
GEOCHEMICAL MODEL CALIBRATIONS

- Initial calibrations for rate kinetics result in early-time uranium concentrations that match observed data (breakthrough) for “Life-of-Mine” simulation

- A combination of anisotropy ($K_x \neq K_y$) and wellfield imbalance required to replicate guard well U concentrations (not a unique solution)

- Final model inputs
  
  - Hydraulic conductivity: $K_x = 0.9$ ft/day; $K_y = 2.7$ ft/day (preferential flow north @ 3:1 ratio)
  
  - Specific Storage: $1.7 \times 10^{-6}$/ft
  
  - Porosity: 23%
  
  - Longitudinal/transverse/vertical dispersivity: 20 ft / 10 ft / 1 ft
Utilizing anisotropy (3:1), and a duration of wellfield imbalance and recovery only, can match concentrations observed at guard well.

- Concentration of Ux (adjacent leaseholder ore body) to U (ISR operator ore) very small in guard well.
- Subsequent sampling confirmed simulated decline in dissolved uranium.
GEOCHEMICAL MODELING RESULTS

10 days

30 days

250 days

750 days (Cease Injection)

875 days

1,150 days

1,515 days

| Recovery Well |
|Injection Well|
|Guard Well|
|Lease Boundary|

Uranium Concentration (mg/L)

10 50 100 200 300

0 ft 100 ft 200 ft
GEOCHEMICAL MODEL RESULTS

- Total mass flux across zone boundary during first 750 days (concurrent injection and recovery); only ~0.4% of total mass of dissolved uranium sourced from Ux.

- At 1,150 days, the total mass of Ux represents only 2.3% of total mass of U + Ux across lease boundary.
GEOCHEMICAL MODEL RESULTS

- Model indicates some combination of wellfield imbalance and/or geologic preferential pathways explains elevated concentrations of U.
- Concentration gradient of dissolved uranium is sharp at leading edge of plume and likely extended no more than 100 feet beyond lease boundary.
- As ore body continues across lease boundary, it is most likely that ore from ISR operator from has been mobilized and migrated north to adjacent lease.
- The area where Ux component (adjacent lease) was potentially mobilized is small.
- The vast majority (>95%) of mobilized ore originated from ISR operator lease property.
3-D geochemical model can be very useful to assess current conditions and predict operational changes

PHAST model demonstrates that the dual naming convention for uranium “types” works to differentiate ore bodies

Approach could be applied to other issues such as optimization of wellfield performance

Could expand to more than two uranium sources

Could define varying properties of ore body in x, y, and z directions

Cost/benefit/risk evaluation to optimize reserve recovery when ore bodies approach lease lines
QUESTIONS/CONTACT INFORMATION

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