# In Situ Immobilization of Uranium in Structured Porous Media via Biomineralization at the Fracture/Matrix Interface

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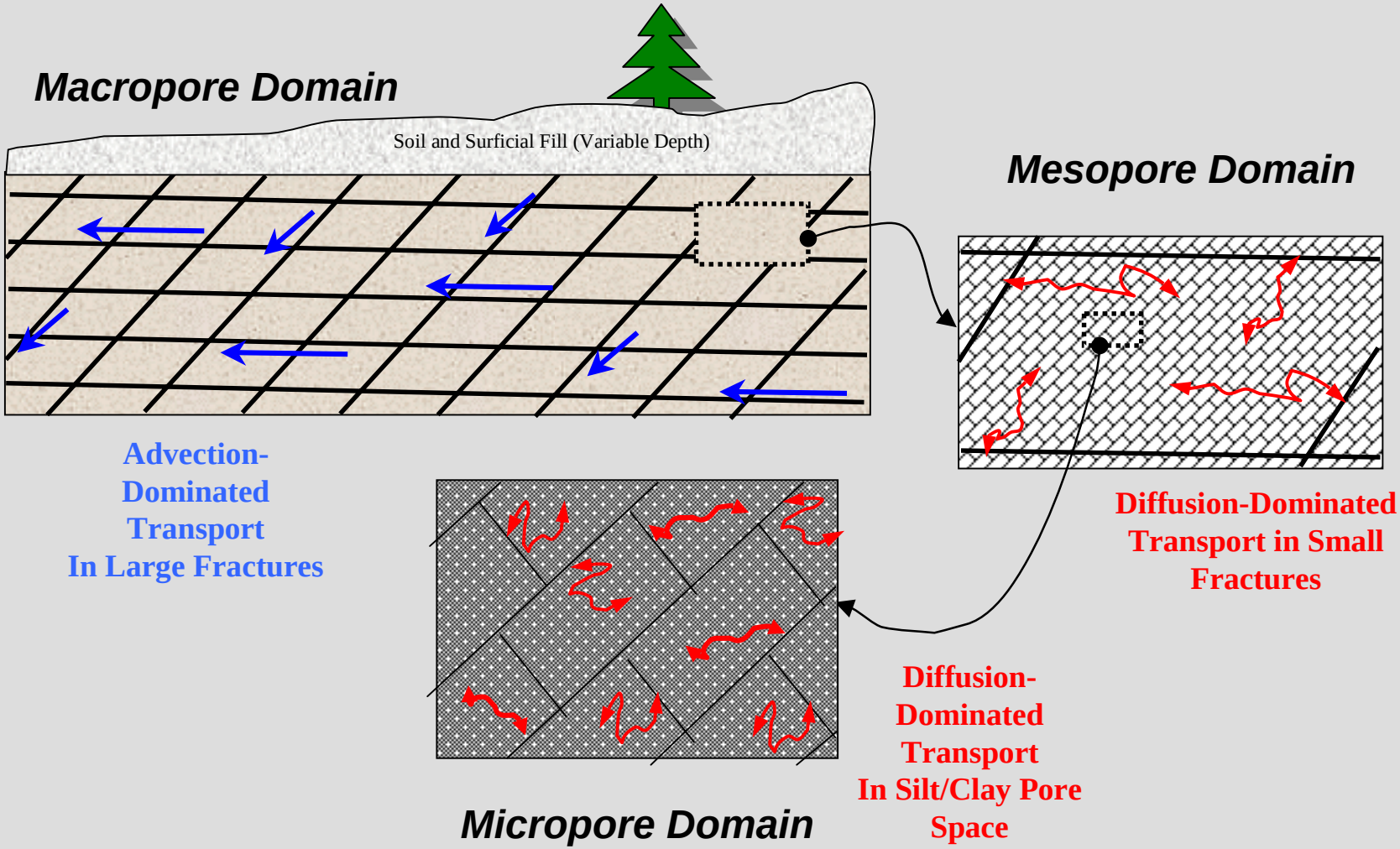
# Structured Porous Media



# Fractured Saprolite

# Remediation Challenges

- Most of the pore space (where contamination resides) is not hydraulically accessible
  - Pump-and-treat quickly removes contamination in macropores but recontamination from meso- and micropores occurs over long time periods.
  - Delivery of chemical reagents or materials needed to support microbial activity (electron donor, nutrients) is ineffective to micropores.
- Most of the pore space is not directly accessible to micro-organisms because of physical size

# Strategic Approach

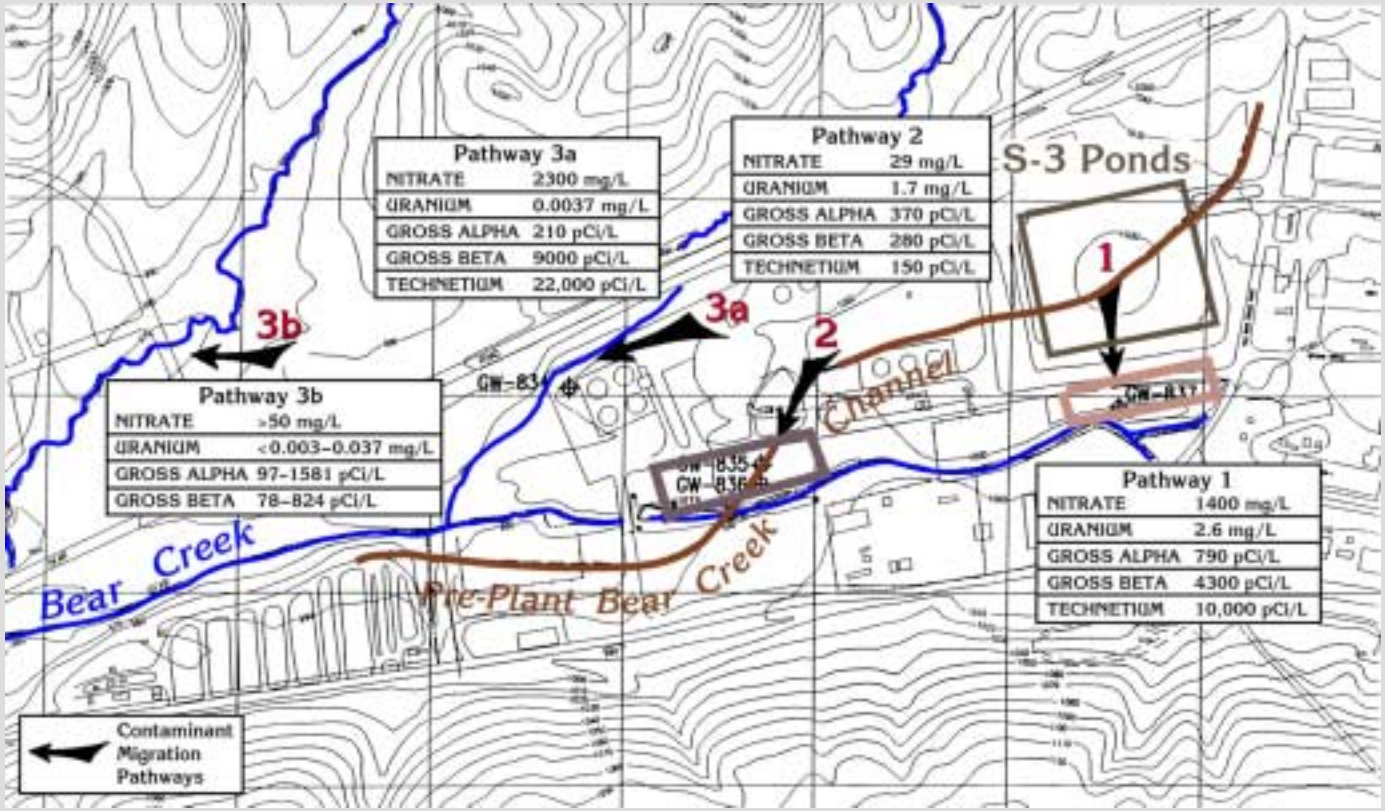
- Use the media structure to advantage
- Isolate radionuclide contaminants in micropore region from free-moving water (macropore) by stimulating biological activity in macropore and mesopore zones
- Effectively create localized distributed reactive barriers around microporous blocks

# Hypothesis

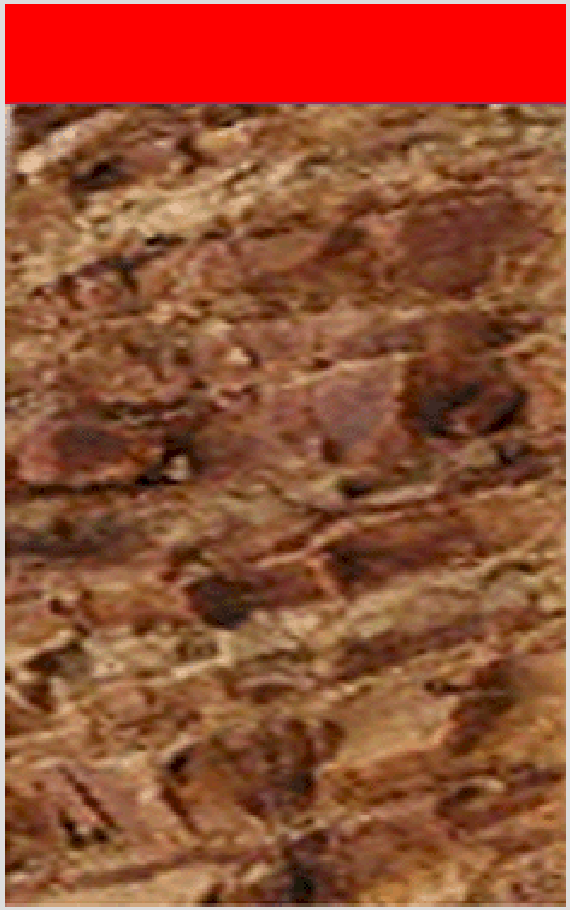
- Mobile radionuclides in low-permeability porous matrix regions of fractured saprolite can be effectively isolated and immobilized by stimulating localized in-situ biological activity in highly-permeable fractured and microfractured zones within the saprolite.

# Illustration

- Conceptual model of contaminant source at FRC Area 2



# Historic Contamination



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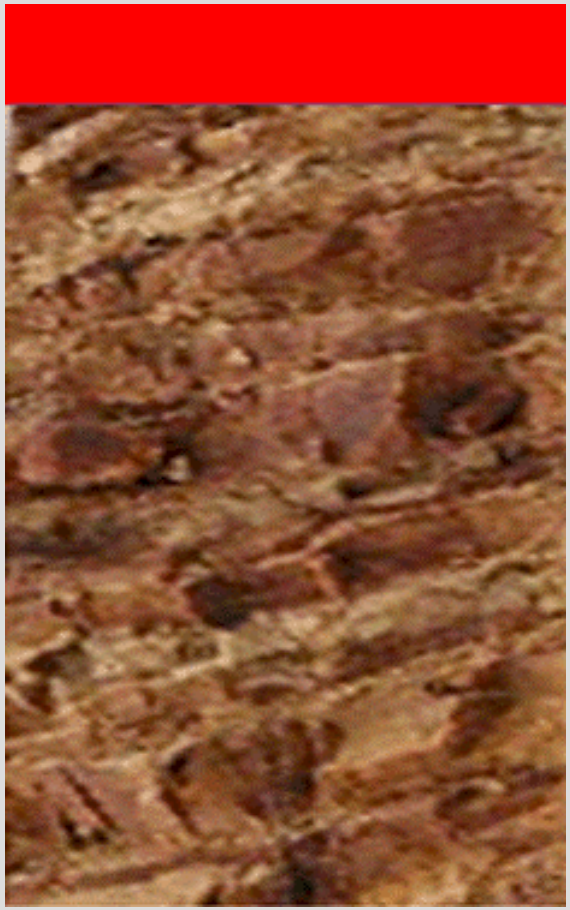

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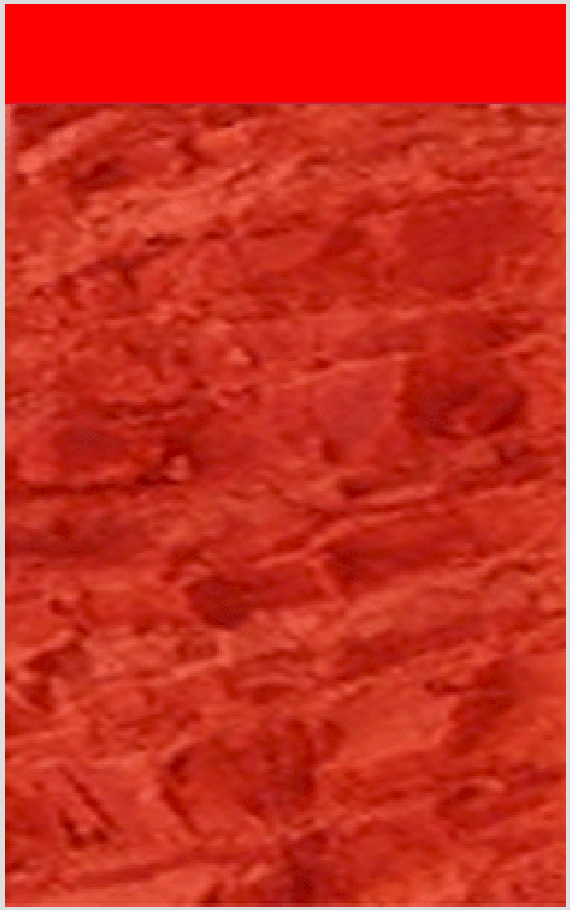
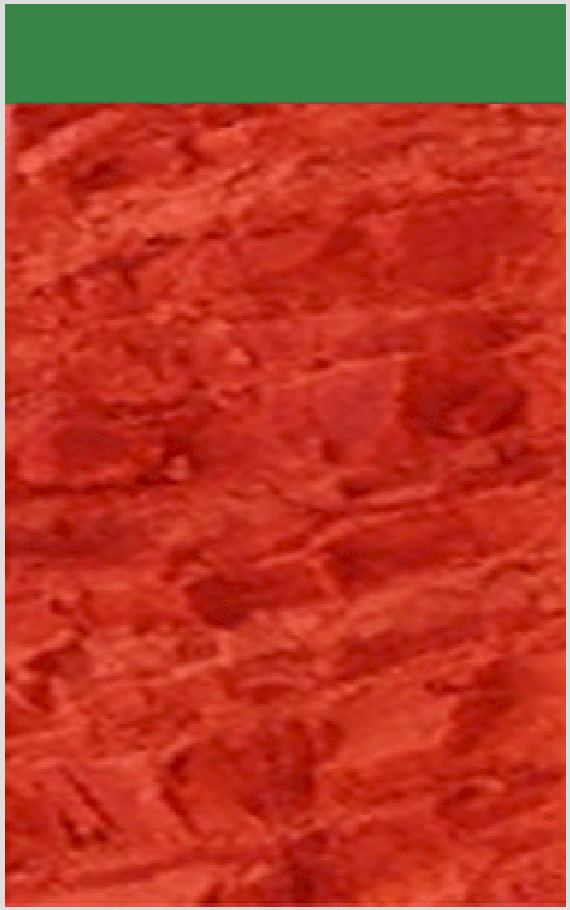


# Current Conditions



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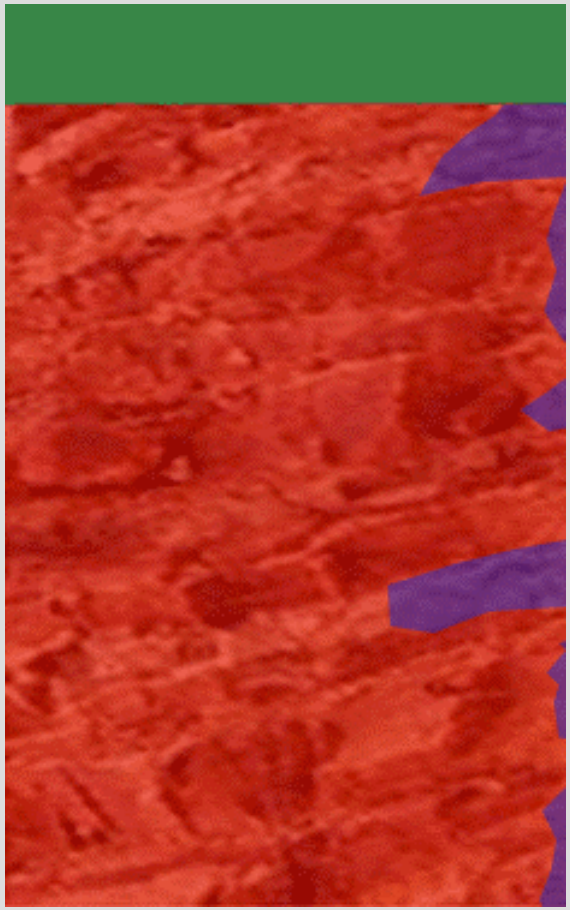

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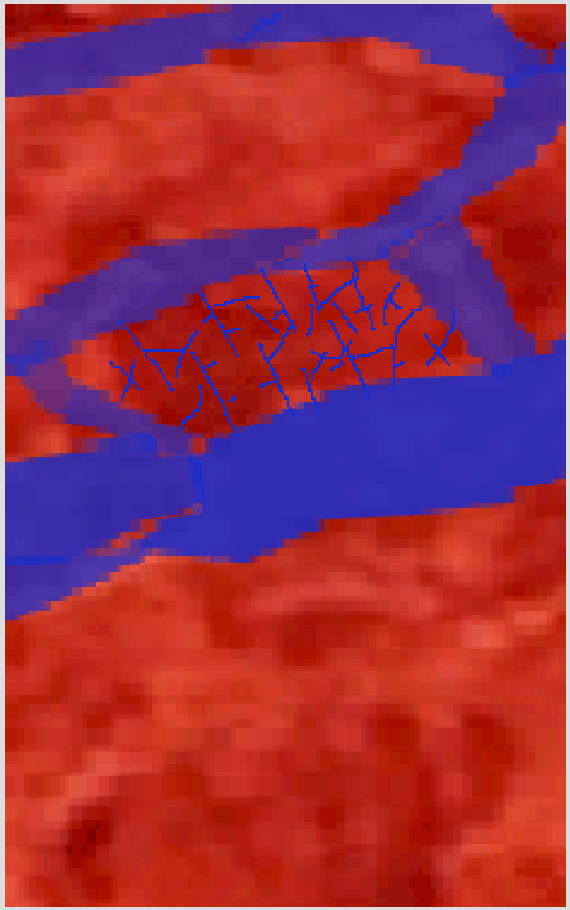
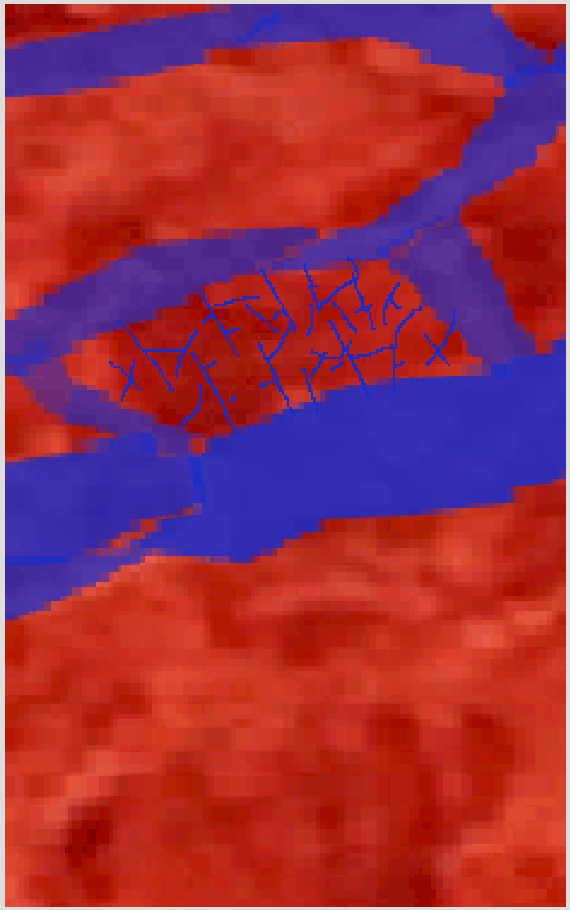


# Biostimulation Scenario



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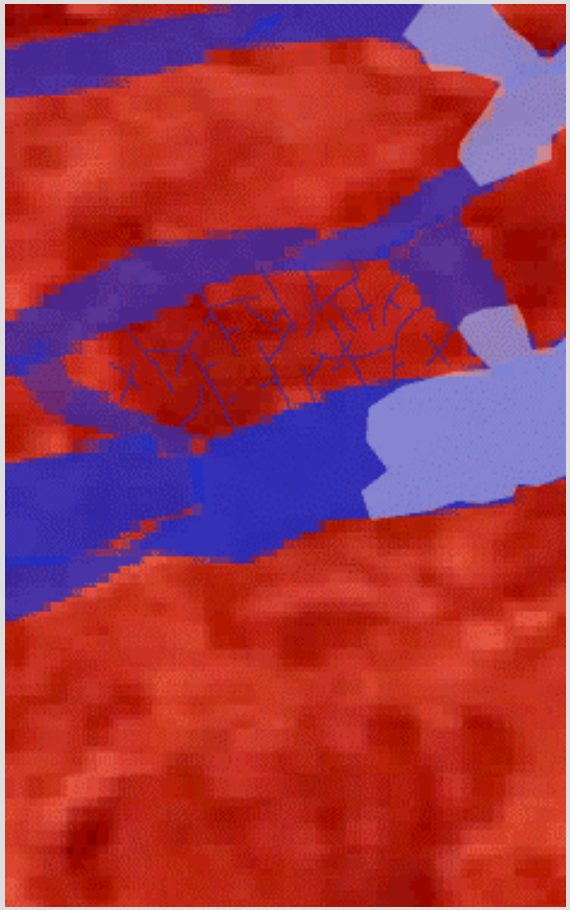

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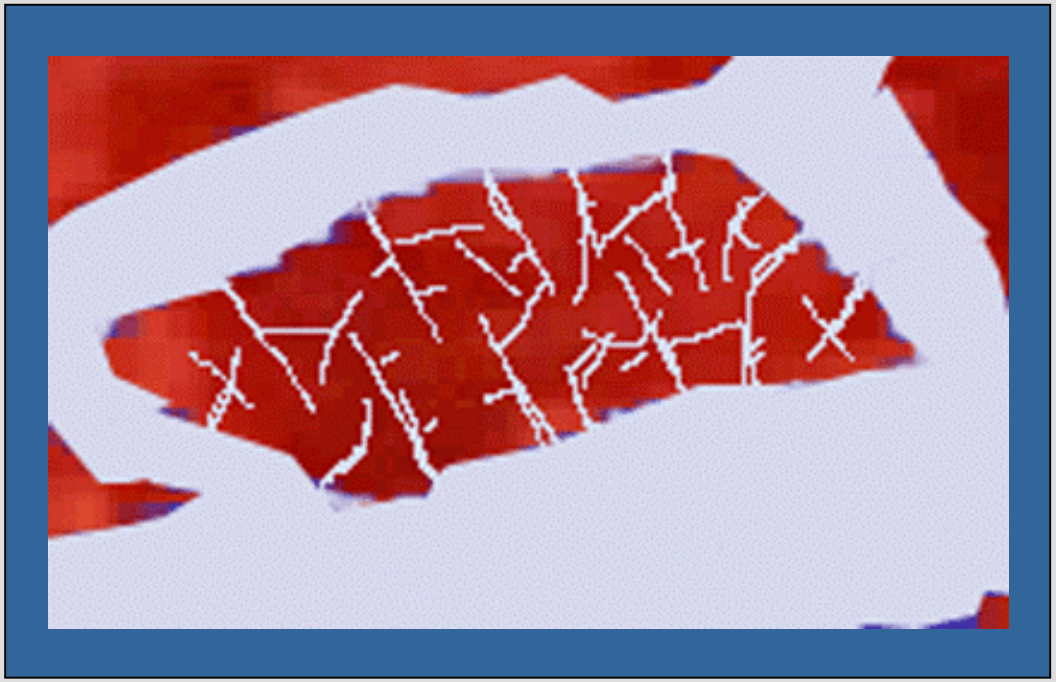

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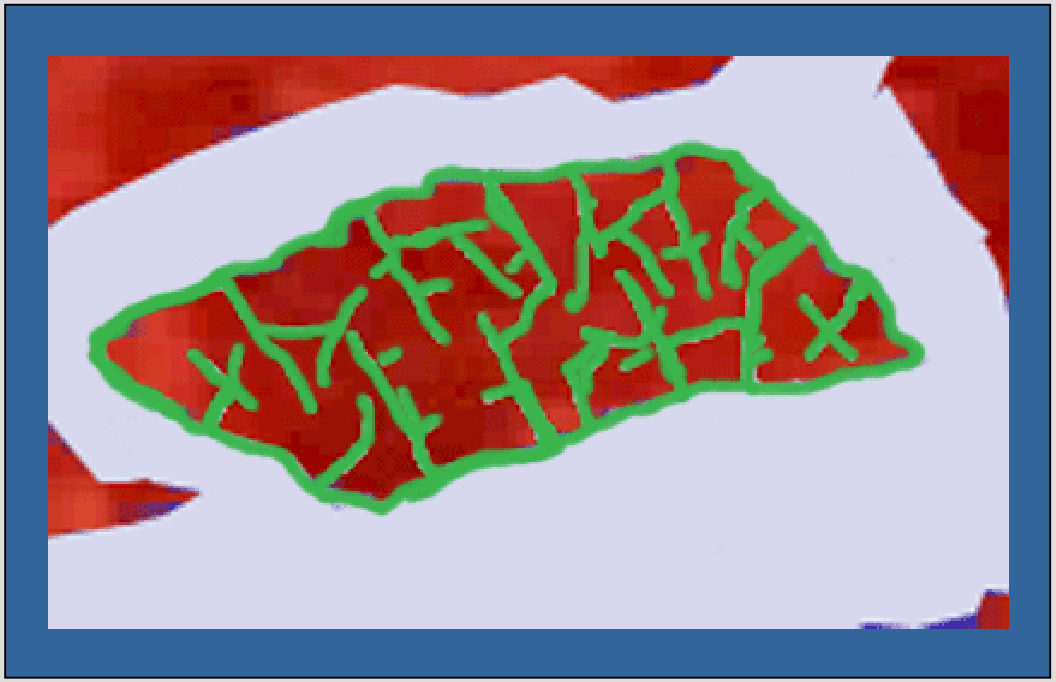


# Feasibility Test: Preliminary Model

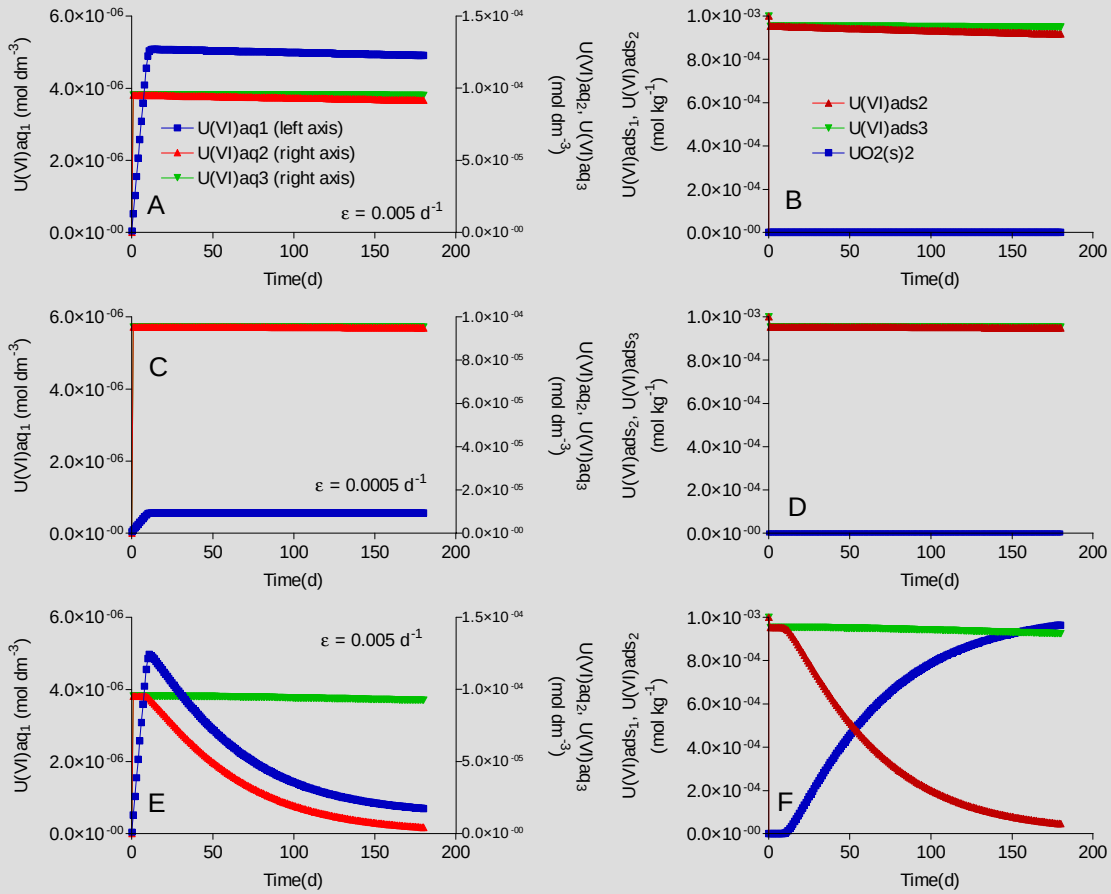


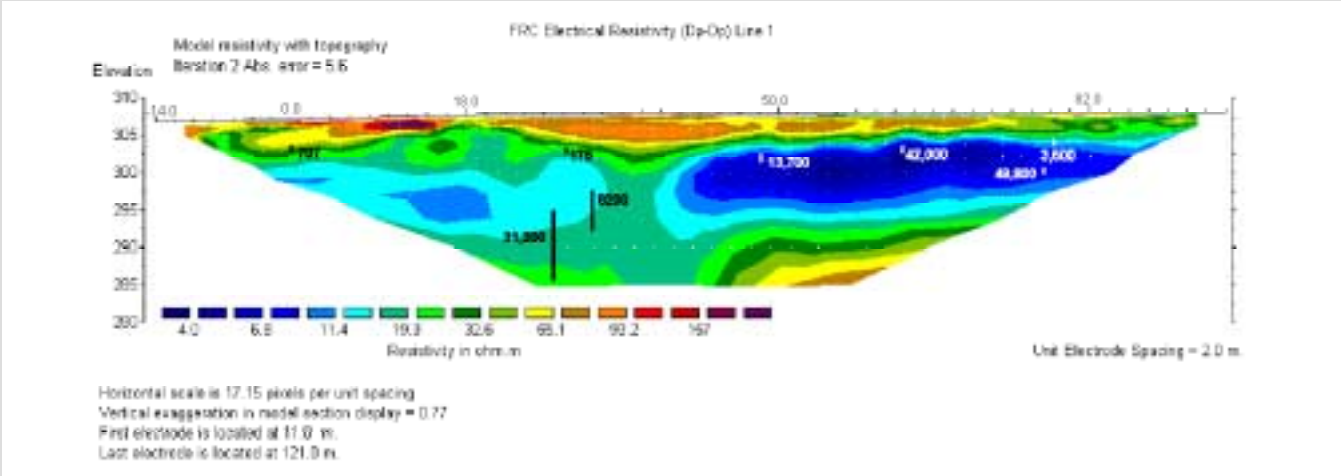

**Figure 6** Breakthrough curves for aqueous U(VI) (A,C,E) in the macro (domain 1), meso (domain 2), and micro (domain 3) pores predicted by the MPR simulation model under abiotic conditions (no enzymatic U(VI) reduction) with first-order mass transfer coefficients (ε values) of 0.005 $d^{-1}$ (A) or 0.0005 $d^{-1}$ (C), or under biotic conditions (active enzymatic U(VI) reduction; DMRB biomass = $10^7$ cells $mL^{-1}$) with an ε value of 0.005 $d^{-1}$ (E). Also shown are the corresponding concentrations of solid-phase (sorbed) U(VI) and U(IV) [$UO_2$(s)] (B,D,F) at the end of the 10-m flowpath during the simulation period.

# Research Elements

- Preliminary Field Studies
- Laboratory Fe/U Reduction Potential Analyses
- Bench-Scale Testing
- Microscopic Biogeochemical Analyses
- Numerical Model Application
- **Field-Scale Biostimulation Experiment**

# Element 1: Preliminary Field Experiments

- Site selection to be guided by geophysical surveys
- Well installation and testing
- Sediment sample collection
- Field-scale tracer tests




Data courtesy of W. E. Doll (ORNL)

# Element 2: Fe/U Reduction Potential

- Sediment laboratory wet-chemical analysis and molecular analysis of sediment and groundwater samples

• Measure concentrations of U(VI) and other constituents in Area 2

• Identify abundance and spatial distribution of DMRB in Area 2 sediments before and during in situ biostimulation

• Define bacterial Fe(III)/U(VI) reduction rates and biomass development during biostimulation in batch sediment slurry experiments

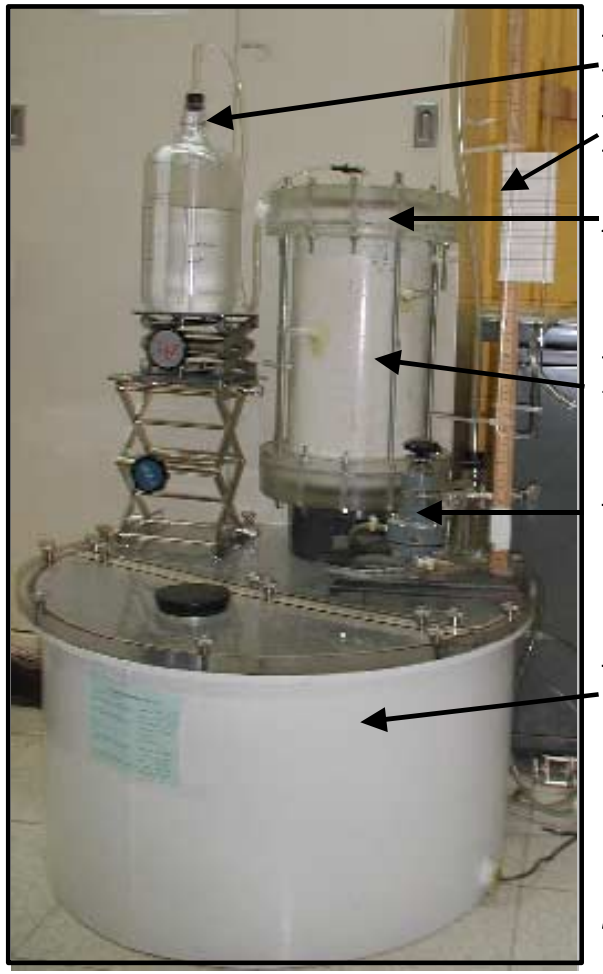
Oxidized Reduced

# Element 3: Bench-scale testing of hypothesized process

Objectives: Proof-of-principle, derive rate expressions for upscaling to field, define reaction network.

- Undisturbed cores – contaminant (U(VI)) introduced to matrix only using unsaturated conditions.
- Biostimulation manipulations:
  - Carrier solution only.
  - Nutrients and electron donor.
  - Nutrients, electron donor, and AQDS (electron shuttle).

# Experimental Apparatus for Unsaturated Flow



**Mariotte device for influent delivery**

**Manometer**

**Acrylic endcaps with glass frits**

**PVC and epoxy-encased soil core (17 cm x 40 cm)**

**Vacuum regulator**

**Vacuum chamber with internal fraction collector**

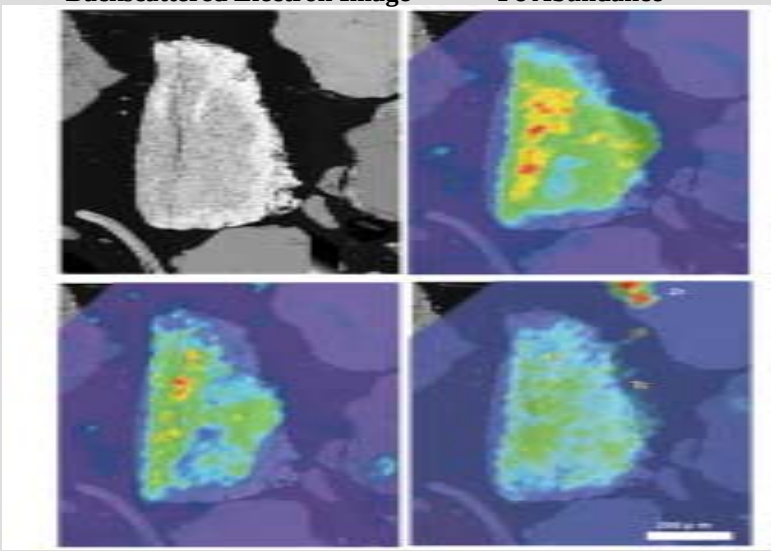
*Jardine et al., 1993; Mayes et al., 2002*

# Element 4: Microscopic biogeochemical analyses

- Determine the spatial distribution of U(IV/VI) and other mineral reaction products in mesopore and micropore domains following biostimulation

- Confirm and/or modify conceptual models of process association with specific pore domains

- Identify the chemical and physical properties of U(IV) fracture precipitates and their association with other biogenic materials.

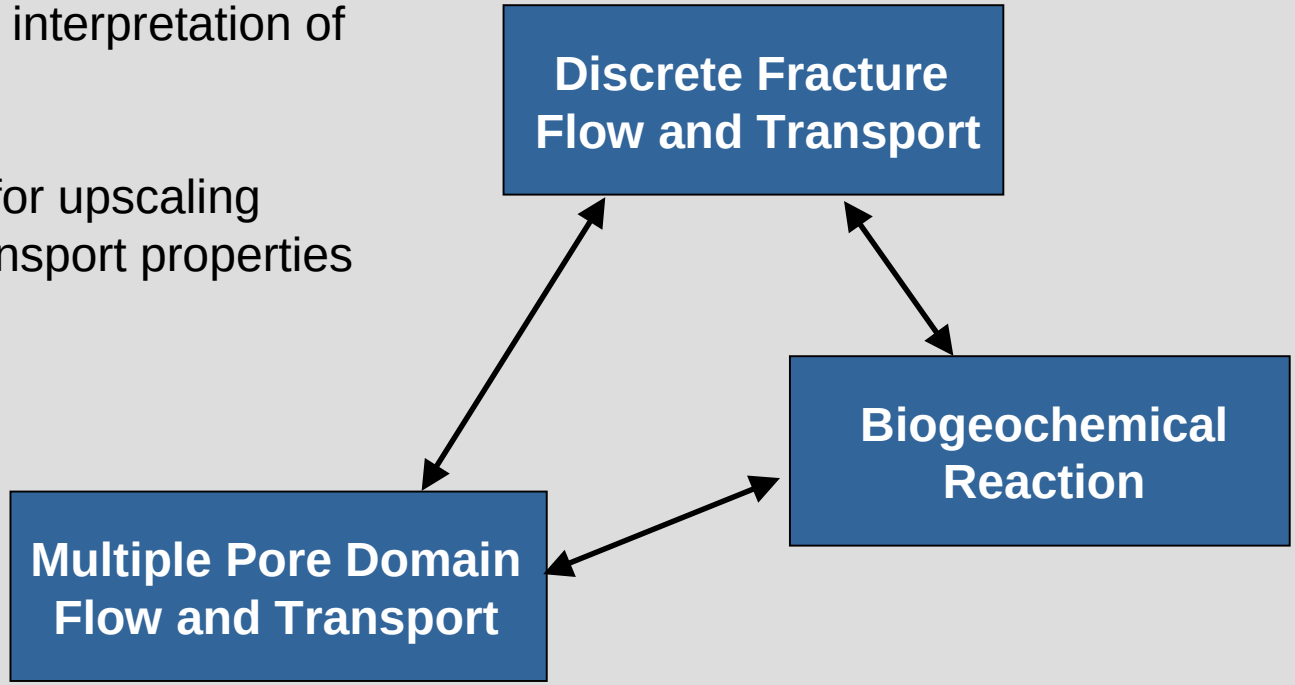



Spatial distribution of Fe, Mn, and Tc(IV) in bioreduced Hanford sediment.

# Element 5: Numerical model application

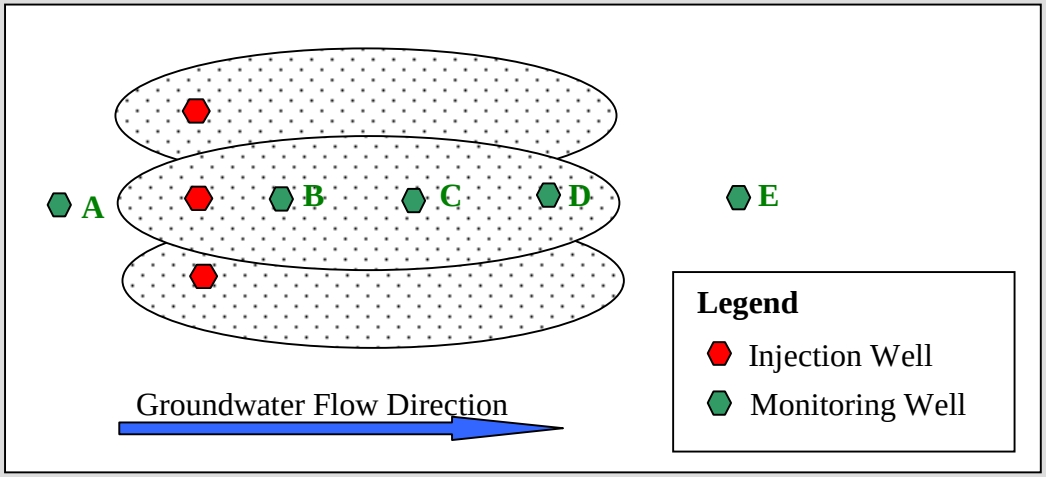
- Provide quantitative basis for iterative design and interpretation of field experiments.

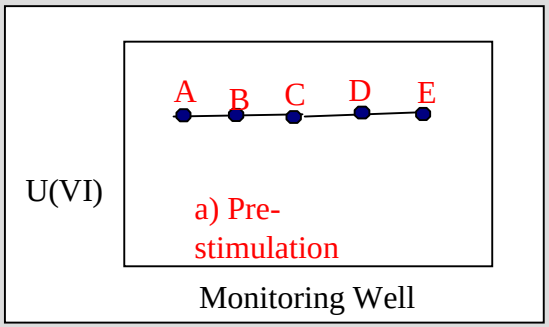
- Assess potential for upscaling laboratory-scale transport properties to field scales.

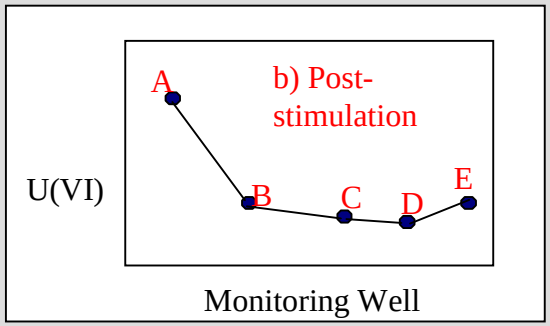


# Element 6: Field biostimulation experiment at Area 2

- Site selection
- Quantitative analysis
- Cross-Validation by multiple observations



# Research Timeline

| Element | Year 1 | Year 2 | Year 3 |
|---|---|---|---|
| Preliminary Field Studies | | | |
| Lab Fe/U Reduction Potential | | | |
| Bench-Scale Biostimulation Experiments | | | |
| Microscopic Analyses | | | |
| Numerical Model Application | | | |
| Field-Scale Biostimulation Experiment | | | |