3D Field-Scale Reactive Transport Modeling of In Situ Immobilization of Uranium in Structured Porous Media

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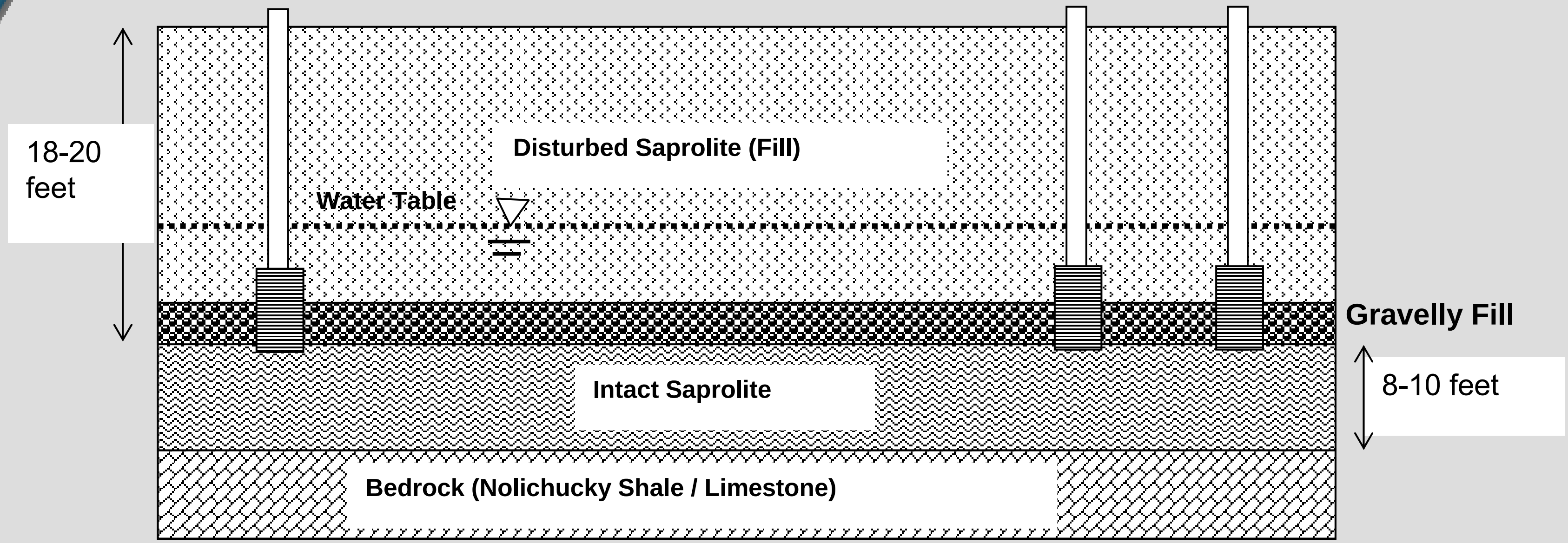
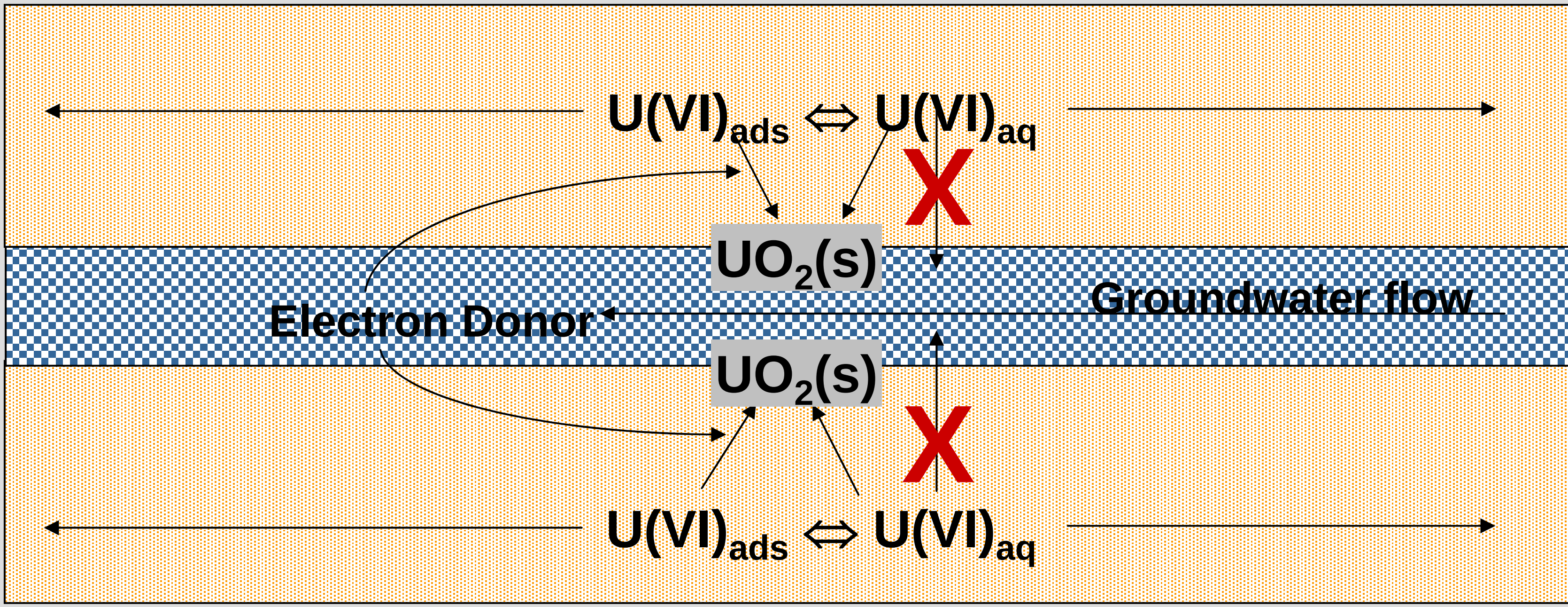
Introduction



- Three geologic materials
- Gravel layer at the bottom of the historically excavated and replaced fill zone
- High Uranium concentration at the interface b/w gravel zone and saprolite zone

Introduction



Hypothesis - The injection of electron donor into the gravel layer will result in:

- ►Dispersive mass transfer into the adjacent fill/saprolite zones
- ►Formation of a microbarrier at the interface
- ►Immobilization of uranium

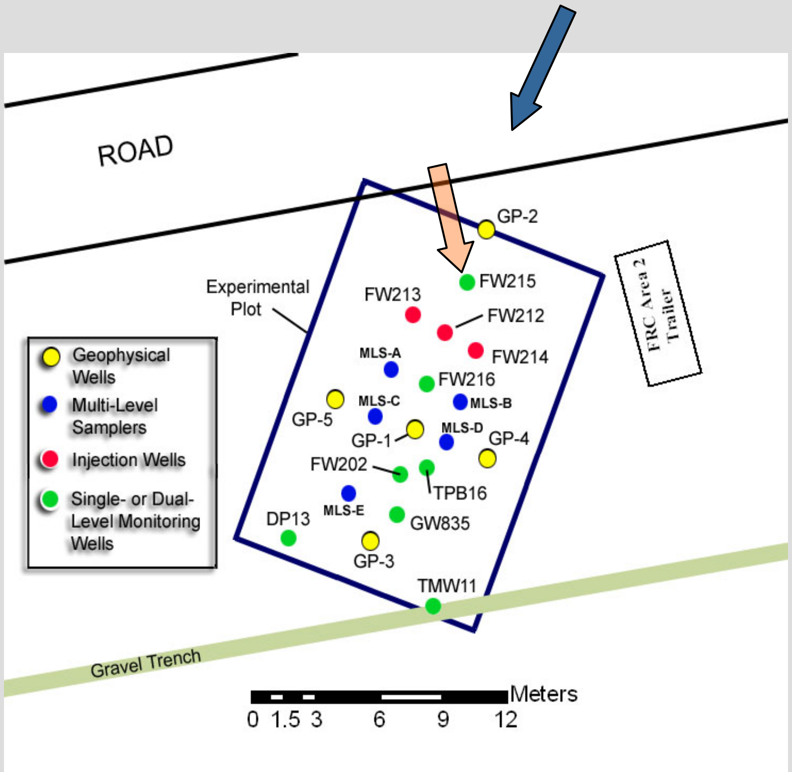
Conceptual Model

- Water table 4 meters below ground surface
- Model Domain:

  Lx = 20 m, Ly = 10 m, Lz = 4 m
- Hydraulic Gradient 0.03, specified head in the x direction
- Well screen depth: 4.5m-6m

	Thickness (m)	Porosity	K (cm/s)
Disturbed Saprolite Fill	1.5	0.3	1.3e-2
Gravelly Fill	0.5	0.3	3.8e-2
Intact Saprolite	2	0.1	4.1e-5

Tracer Test Analysis



Experimental Plot Layout

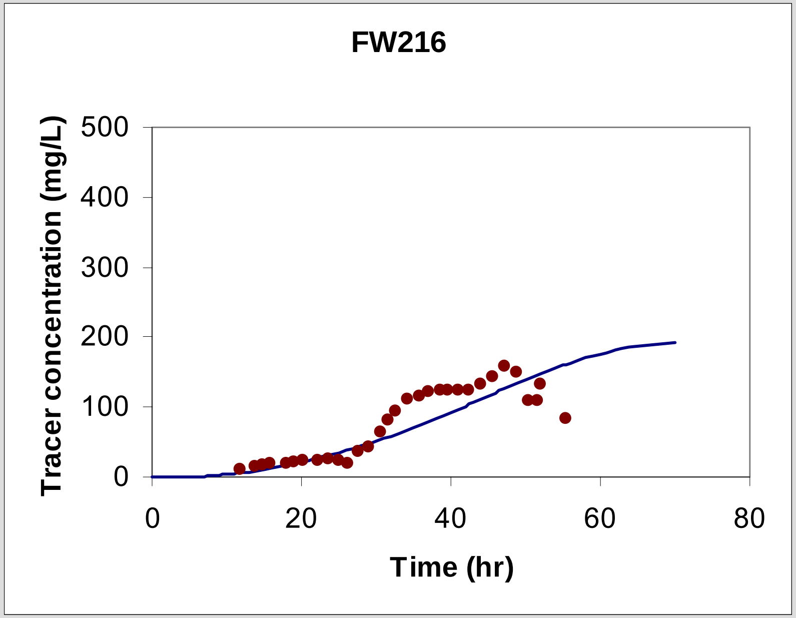
- Confirm the general direction of groundwater flow
- Quantify groundwater flow rate
- Investigate mass transfer between gravel and saprolite layers

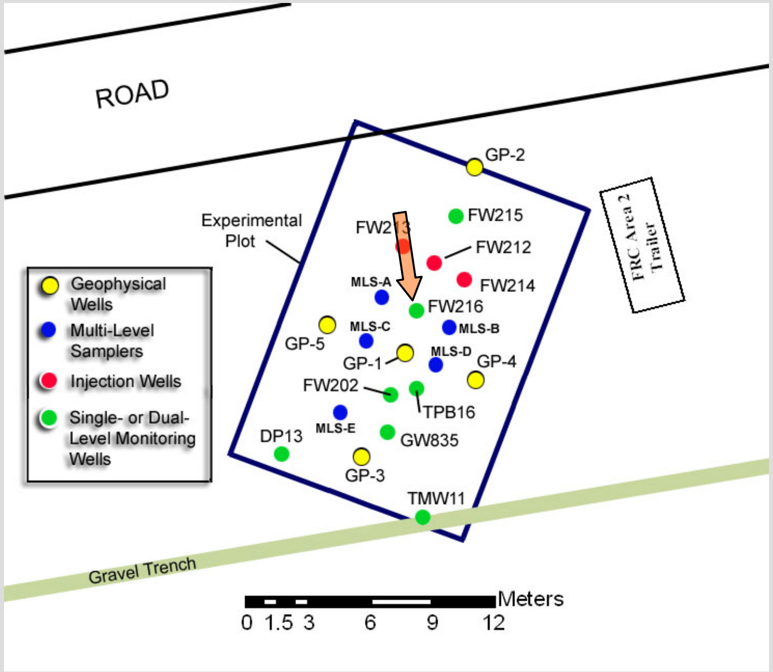
Tracer Test Analysis

- **Dispersivity:**

  $\alpha_L = 1.0$ m

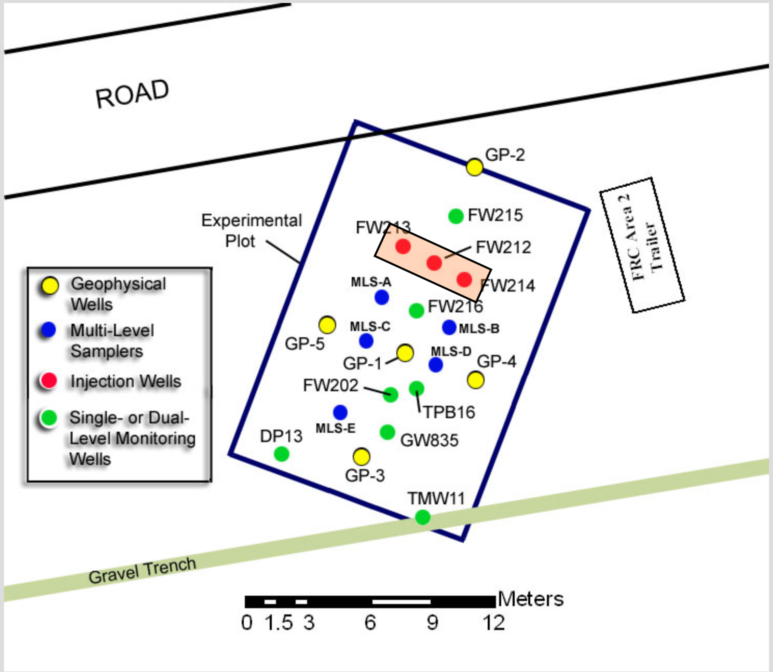
  $\alpha_T = 0.1$ m





Multicomponent Reactive Transport

- Conceptual model and hydrologic parameters from tracer test analysis
- 3 Injection Wells
  FW213, FW212, FW21
- 94 Species
- 135 Reactions(58 fast, 77 slow)
- 37 Terminal Electron Accepting Processes (TEAPs)
- 8 Biomass Populations



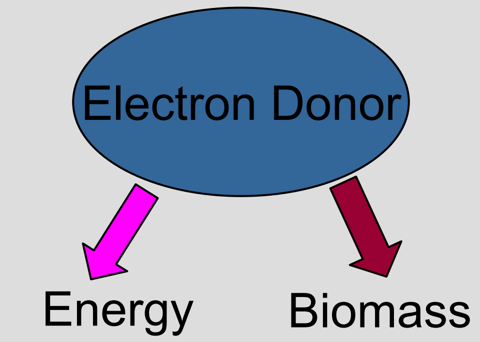
TEAP Reactions

Reaction	Catalyzed By
CH3CH2OH + 3O2 → 2HCO3- + H2O + 2H+	AM, DM
CH3CH2OH + 2.4NO3- + 0.4H+ → 2HCO3- + 1.2N2 + 2.2H2O	DM
CH3CH2OH + 0.5NO3- → CH3COO- + 0.5NH4+ + 0.5H2O	DRM1, DRM2, DRM3
CH3CH2OH + 2MnO2 + 3H+ → CH3COO- + 2Mn2+ + 3H2O	DRM2, DRM3
CH3CH2OH + 4FeOOH + 7H+ → CH3COO- + 4Fe2+ + 7H2O	DRM2, DRM3
CH3CH2OH + 0.5SO42- → CH3COO- + 0.5HS- + 0.5H+ + H2O	DRM3, SO4RM
CH3CH2OH + 2S0 + H2O → CH3COO- + 2HS- + 3H+	DMR3, S0RM
CH3CH2OH + 0.5HCO3- → CH3COO- + 0.5CH4 + 0.5H+ + 0.5H2O	MGM
CH3CH2OH + 2UO2(CO3)22- + H2O → CH3COO- + 4HCO3- + 2UO2(s) + H+	DRM2, DRM3, SO4RM, S0RM
CH3COO- + 2O2 → 2HCO3- + H+	AM, DM
CH3COO- + 1.6NO3- + 0.6H+ → 2HCO3- + 0.8N2 + 0.8H2O	DM
CH3COO- + NO3- + H2O + H+ → 2HCO3- + NH4+	DRM2, DRM3
CH3COO- + 4MnO2 + 7H+ → 2HCO3- + 4Mn2+ + 4H2O	DRM2, DRM3
CH3COO- + 8FeOOH + 15H+ → 2HCO3- + 8Fe2+ + 12H2O	DRM2, DRM3
CH3COO- + SO42- → 2HCO3- + HS-	DRM3, SO4RM
CH3COO- + 4S0 + 4H2O → 2HCO3- + 4HS- + 5H+	DRM3, S0RM
CH3COO- + H2O → HCO3- + CH4	MGM
CH3COO- + 4UO2(CO3)22- + 4H2O → 10HCO3- + 4UO2(s) + H+	DRM2, DRM3, SO4RM, S0RM

Complete oxidation **Incomplete oxidation**

TEAP Reactions

- **Overall balanced reaction for biological growth derived from bioenergetics-based approach in which the partitioning of electron flow between energy generation and biomass production is dependent on the free energy of the corresponding TEAP**



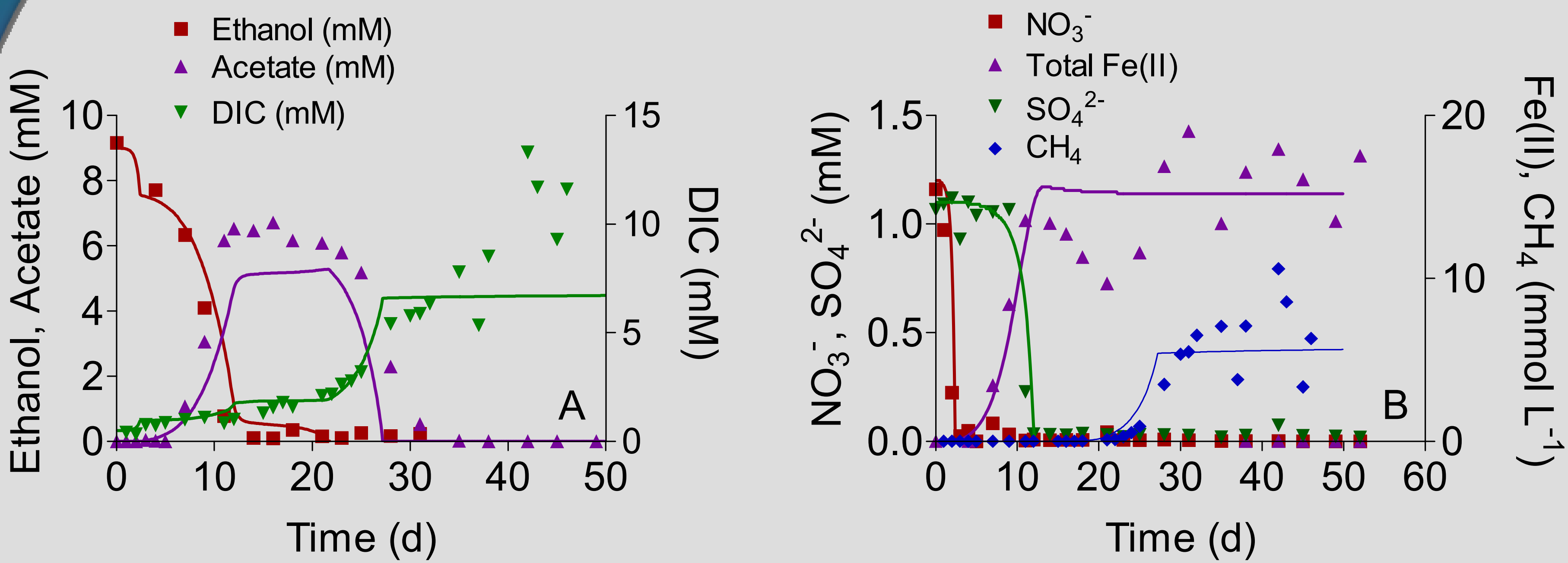
0.2500CH3CH2OH + 0.8256FeOOH(s) + 1.4391H+ + 0.0378HCO3- + 0.0038N2 = 0.2500CH3COO- + 0.0076DRM2_cell + 0.8256Fe++ + 1.4998H2O

- **Rate laws consider thermodynamic constraints**

$$R_{Fe(III)} = V\max_{Surf} \frac{[Cells]}{Km_{Cells} + [Cells]} [Fe(III)Surf_{Free}]\, f(\Delta G_{rxn})$$

$$f(\Delta G_{rxn}) = 1 - exp((\Delta G_{rxn} - \Delta G_{min})/RT)$$

ΔG_{min} = minimum free energy change required to drive cellular energy metabolism (-20 kJ/mol) (Schink, 1997)



Only adjustable parameter values: 1. Fe(III) oxide reduction rate law
2. Initial biomass values

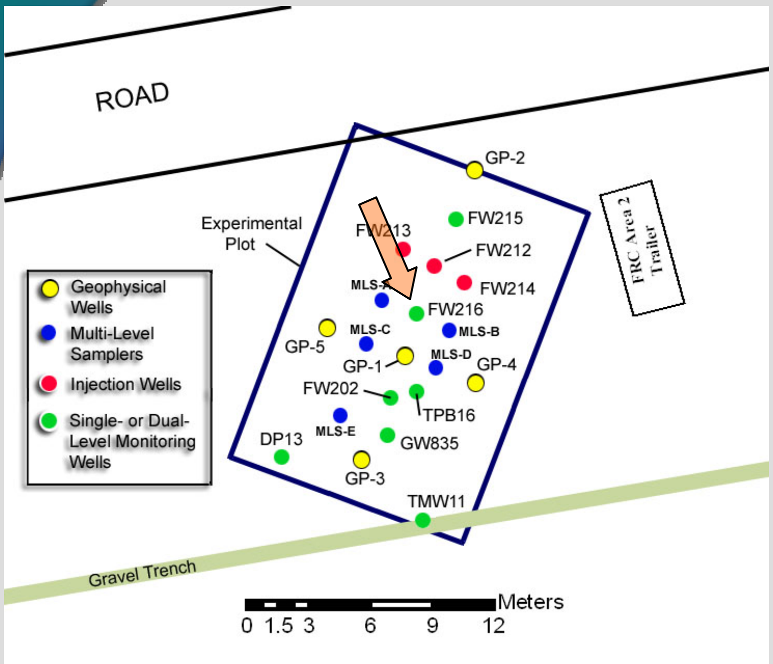
Simulation Conditions

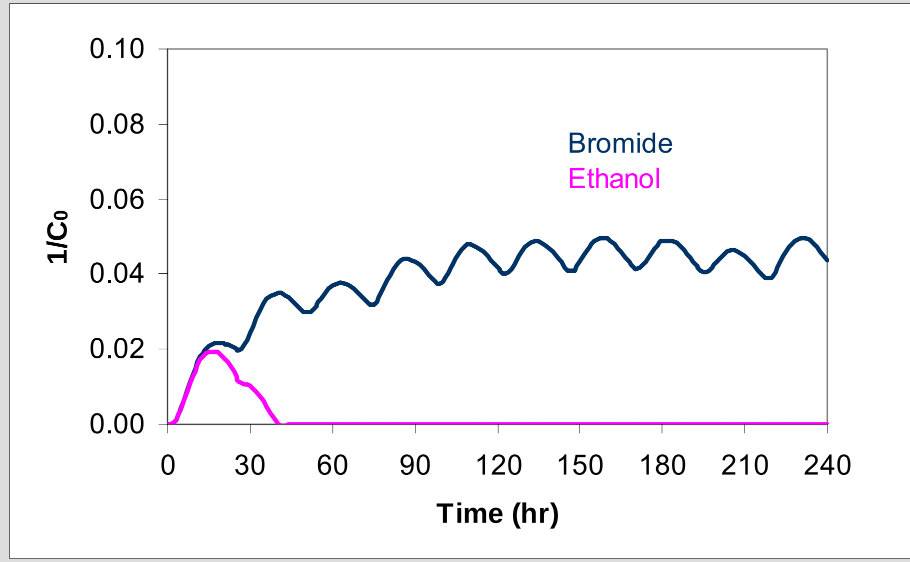
- Initial concentration of extractable Fe(III) = 0.225 M in disturbed and 0.15 M in intact saprolite, zero in the gravel zone
- Initial and upstream boundary concentration of nitrate = 0.5 mM
- Initial and upstream boundary concentration of dissolved sulfate = 8.85 mM
- Initial and upstream boundary concentration of U(VI) = 1 uM

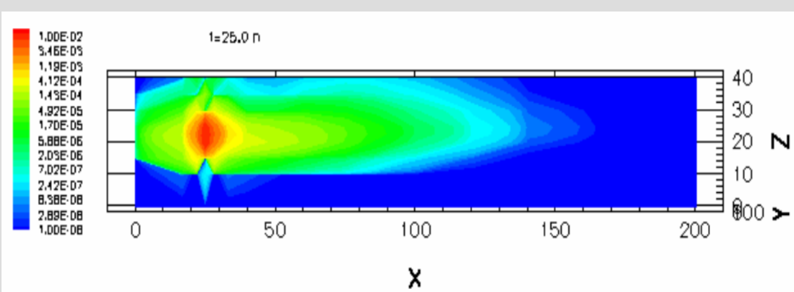
Simulation Conditions

- **Tracer and Ethanol Injection Scenarios**
  Injection of one hour every 24 hours at rate 3.0L/min.
  Injected tracer concentration = 500 mg/L
  Injected ethanol concentration = 10 mM
- **Simulation Period: 10 days**
- **Initial Δt = 0.01 hr, Δt_{max} = 0.5 hr**

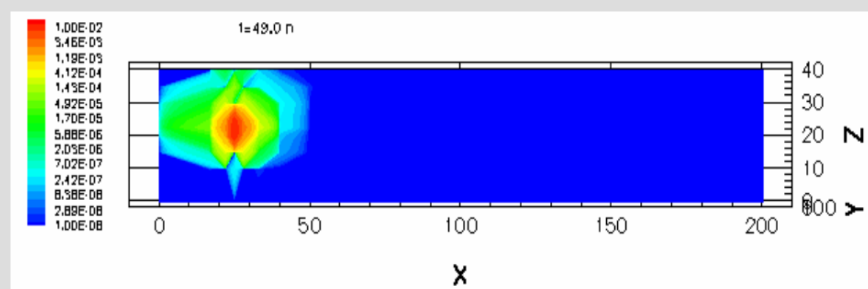
Ethanol, Bromide





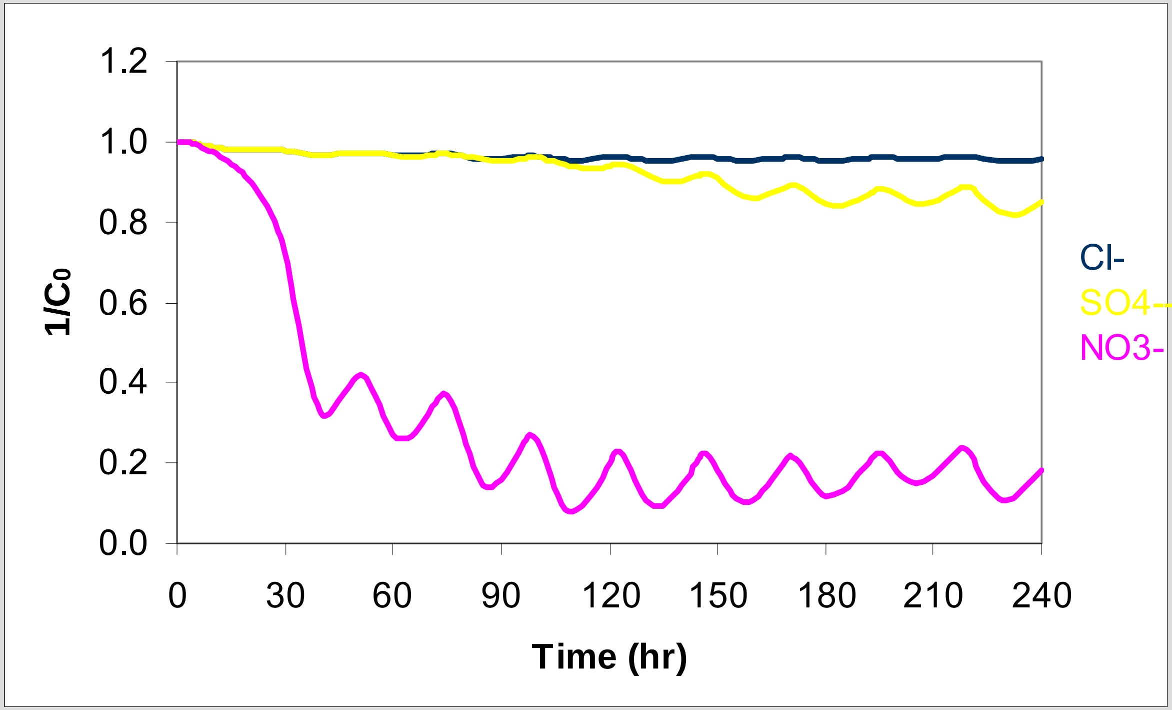


25 hours



49 hours

Nitrate and Sulfate Reduction



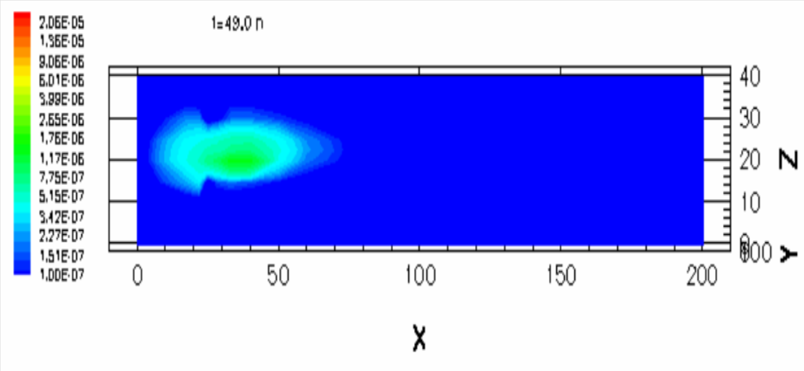
- Almost no flushing effect on Cl-
- Sulfate reduction starts after the 4th injection pulse
- 80 to 90 percent of nitrate reduction

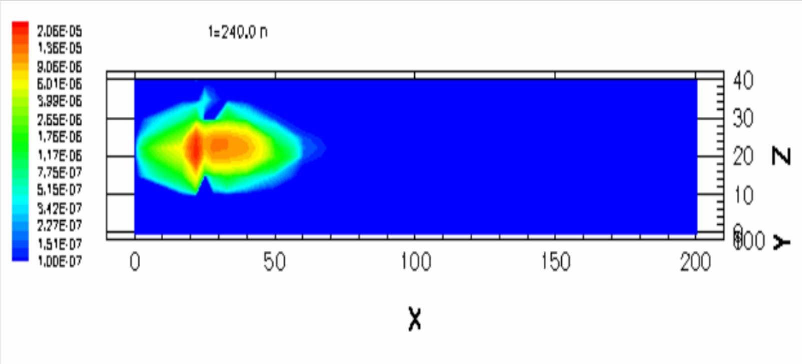
Iron and Uranium Reduction

49 hours

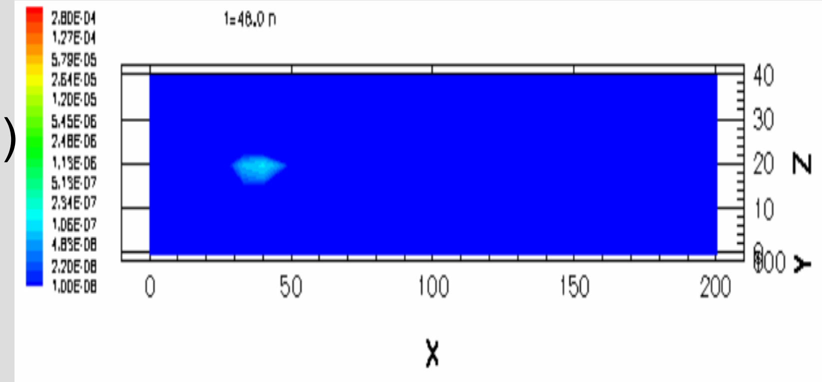
240 hours

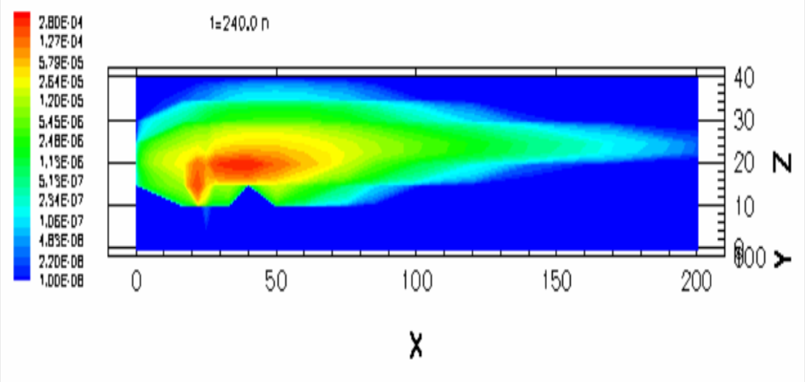
U(IV)



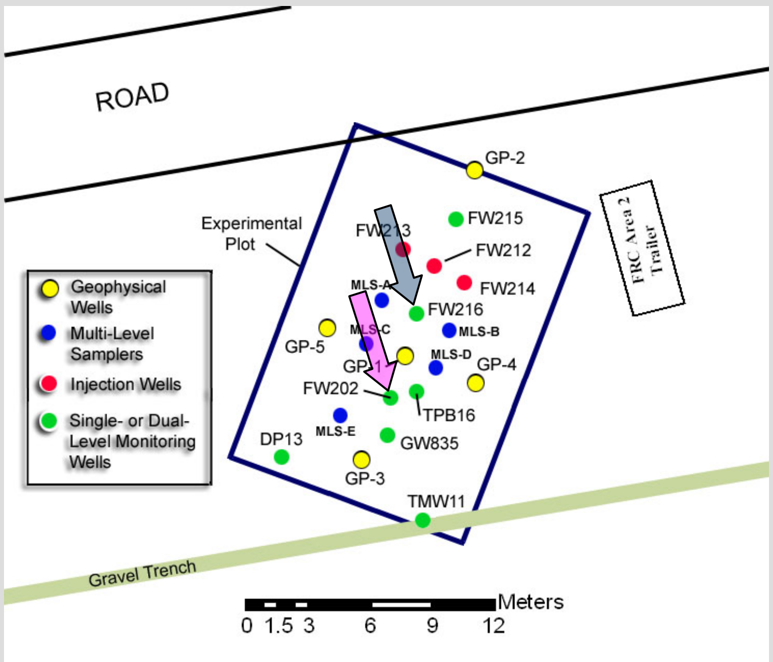


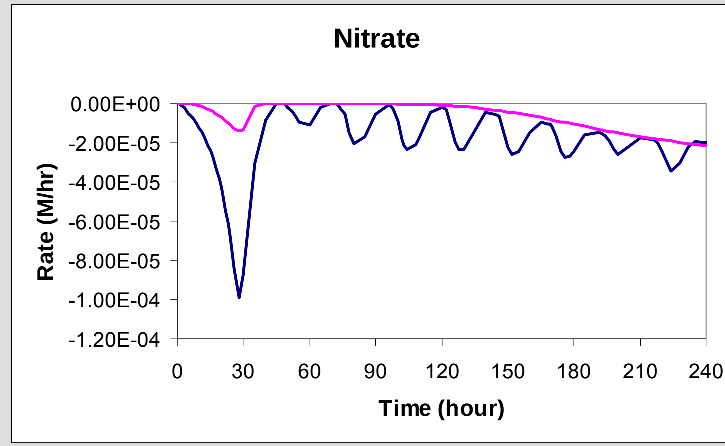
Fe(II)

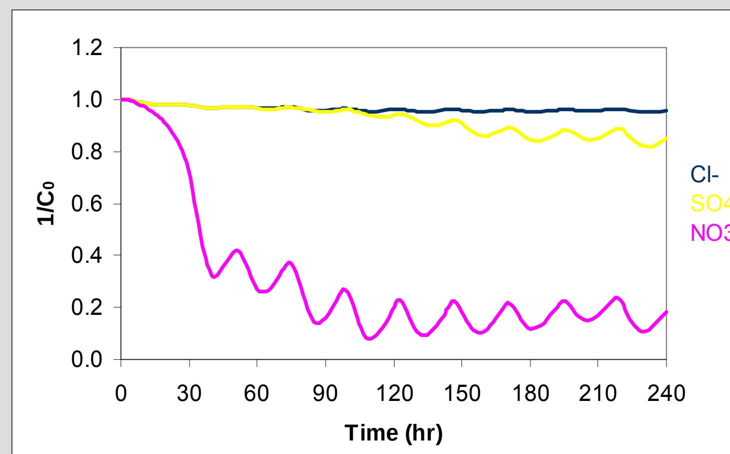




Influence Area of Injection







$FeS + 1.6NO_3^- + 1.6H^+ \rightarrow Fe^{2+} + SO_4^{2-} + 0.8N_2 + 0.8H_2O$

$Fe^{2+} + HS^- \leftrightarrow FeS + H^+$

$\equiv Fe^+ + HS^- \leftrightarrow \equiv FeS$

Field Scale Biostimulation

28 days.