

# Biostimulation of In-Situ Uranium Reduction at the NABIR Field Research Center Using a Nested Recirculation Scheme and Aboveground Groundwater Conditioning



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# Objectives

Primary Objective: To perform experiments to evaluate the rates and mechanisms of U(V) reduction in situ at FRC, subject to biostimulation. Secondary Objective: To develop an effective ex-situ treatment system to precondition the site and maintain an appropriate environment during the experiments.

# Major Engineering Challenges

Several factors complicate the stimulation of subsurface microbial uranium reduction.

- 1. High levels of nitrate (~8 g/L) inhibit microbial uranium reduction because denitrification intermediates reoxidize U(IV).
- The extremely low pH (~3.5) and the presence of volatile organic compounds (VOCs) are inhibitory to biological activity.
- As pH is increased to levels suitable for microbial activity, AI, Tc, Ca, Mg, and Mn precipitate. Precipitate formation in the subsurface could clog the aquifer.

# The FRC Site



# **Outline of Basic Strategy**

 Ex-situ:
 Eliminate clogging agents, precondition treatment zone

 remove aluminum and calcium through two precipitation steps

 remove volatile organic compounds through stripping

 remove nitrate in a denitrifying fluidized bed reactor

 neutralize acid

In-situ: - Biostimulation for denitrification of residual nitrate and U(VI) biomineralization, i.e., removal though reduction and precipitation.

# **Treatment Configuration**





Aboveground Groundwater Conditioning

### U(VI) Reduction in a Contaminated Soil Column



UPPER GRAPH: No significant microbial activity (or ethanol consumption) was observed within the first 30 days until FBR biomass was introduced to the soil column. After that point, acetate accumulated as ethanol was degraded. LOWER GRAPH: No U(VI) reduction was observed within the first 30 days. The U(VI) concentration in the effluent increased when FBR biomass was introduced, perhaps due to increased soil pH which resulted in increased desorption or dissolution of U(VI) from the soil. A significant delay (-50 days) occurred for the reduction of both U(VI) and sulfate, which may be due to the preferential reduction of Fe(III) and Mn(IV) minerals in the soil.

### **Geologic Media**



The geologic media at the site consists of saprolite, which has a highly interconnected fracture network with densities of 100-200 fractures/m. Fractures constitute < 5-10% of total porosity, yet are able to carry >85% groundwater flux (preferential flow). Belowground Experiment: Flow Configuration



Two recirculation loops establish a protected zone for uranium reduction. The outer loop captures contaminated site water for above-ground treatment and surrounds the inner uranium reduction zone with a layer of treated water.

In the inner loop, a high percentage of injected water is captured in the extraction well for recirculation. Ethanol as an electron donor is added to this water before it is reinjected, and its pH and TIC level is adjusted as necessary.

# Belowground Experiment: Tracer Recovery Test



The recovery behavior of dominant metals and ligands during the test is mainly due to the kinetic mass transfer between the immobile region and the mobile region. All metals analyzed showed a similar recovery pattern.



A two-region model was developed to simulate bromide and nitrate data of the tracer test and recovery. Results indicate that over 80% of nitrate is inside the immobile region or low-conductivity region, which implies a long clean-up time for nitrate. The mobile region responds well to advective removal, so nitrate concentration in this region can be maintained at a low level.

# **Belowground Experiment: Biostimulation**









Data shown is for sampling level 3 of well FW-102, days 160-200. **PHASE 1**: Flushing to remove AI, Ca, and most nitrate (days 1-69). **PHASE 2**: pH adjustment to -6 (days 69-136). pH was adjusted in order to reduce U(VI) mobility with sorption and achieve a pH favorable for denitrification.

PHASE 3: In-situ denitrification (days 137-180). pH was adjusted to -6.5 and ethanol was added in 4 separate runs to stimulate *in-situ* denitrification. Extracted water was passed through a vacuum stripper to remove dissolved nitrogen gas. Nitrate concentrations decreased during each run, but rebounded between runs due to diffusion of nitrate from the soil matrix.

#### PHASE 4: Biostimulation of U(VI) reduction (days 180-195). During run 5, more ethanol was provided than needed for only

During run 5, more etnanol was provided than needed for only denitrification, and pH was raised to -7. Nittate was removed, and when ethanol feed stopped, U(VI) increased despite a decrease in pH, suggesting U(VI) was attenuated during the run by microbial reduction.



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