Investigations of HRC®-Stimulated Bioreduction of Cr(VI) at Hanford 100H

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http://www-esd.lbl.gov/ERT/hanford100h/

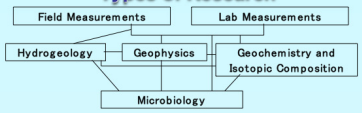
Hypothesis

Lactate (HRC) injection into chromium-contaminated groundwater through an injection well will cause bioreduction of chromate [Cr(VI)] and precipitation of insoluble species of [Cr(III)] on soil particles, probably catalyzed at oxide surfaces at the field scale.

Objective

To perform field investigations to assess the potential for immobilizing and detoxifying chromium contaminated soils and groundwater using bioremediation at the Hanford 100H site

Types of Research

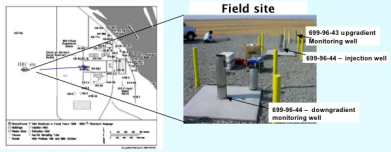


- Drilling, coring, and completion of two new boreholes a field site
- Development of a conceptual model of background conditions
- Microbial and lactate-induced treatability studies
- Geophysical characterization and monitoring
- Hydraulic measurements

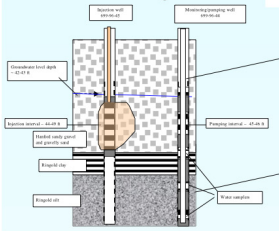
Cable tool drilling of Well 699-94-44 with continual split spoon sampling, May 2003

I. Background Geological, Hydrological, Geophysical, and Microbial Conditions at Hanford 100H

Chromium in groundwater at Hanford100D area is a source of contamination at Hanford 100H area



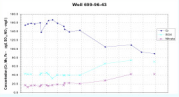
Well Design



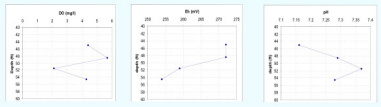
Photographs of cores (4 in diameter)

38.5 ft - Hanford gravelly sand

54 ft Ringold silt



Concentration Measurements (PNNL data)

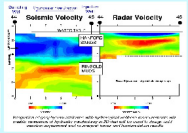


Changes with depth of DO, Eh and pH in Well 699-94-44, 2/26 2004

Geophysical Measurements

Surface GPR imaging allows:
- Mapping water table
- Assessing spatial variability
- Delineating hydrostratigraphy

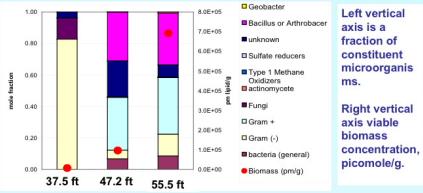
Seismic and radar tomographic velocity cross-sections between the injection and sampling wells



Microbial Analyses

- Phospholipid fatty acid analyses (PLFA)
- Terminal restriction fragment length polymorphism (T-RFLP) with primers for Fe and sulfate reducers, and nitrate dissimilatory reactions;
- Live/dead direct counts;
- TEA, ED, DOC, DIC, CO2, O2 Limiting nutrients, e.g., N, P, S, Fe;
- Nitrogen and oxygen isotope ratio; $^{53}Cr/^{52}Cr$ ratios
- Clone libraries
- 16S rDNA microarray analysis

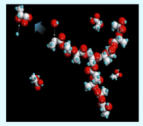
Sediment Microbial Community from the PLFA Analysis of R2A Enrichment of Sediment Samples

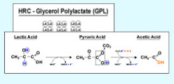


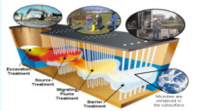
Left vertical axis is a fraction of constituent microorganisms.

Right vertical axis viable biomass concentration, picomole/g.

II. Lactate/Polylactate (HRC™) Properties





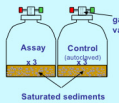


- HRC properties
  - a polymer of lactic acid (glycerol polylactate)
  - fermented by indigenous microorganisms to produce H_2, an electron donor
  - a field longevity of 12-18 months
  - in the subsurface, slowly releases lactic acid to stimulate anaerobic bacteria and ferment the lactic acid to gain carbon and energy
- HRC, when injected into chromium contaminated groundwater
  - generates electron donors (lactate and hydrogen) for microbial production of reducing conditions to stimulate precipitation of Cr(III) solids
  - stimulates microbial reduction and production of species that can chemically reduce Cr(VI) to Cr(III) like Fe(II) and hydrogen sulfide.
  - causes the microbial population to remove the oxygen, nitrate, sulfate and other competing electron acceptors, which, in turn, depresses the redox potential in the aquifer, affecting the transformation of Cr(VI) species to Cr(III) species, which are precipitated on soil particle surfaces.
- Factors affecting Cr(VI) biostimulation

  Aquifer geochemistry (inorganic common anions and cations, Eh, pH, temperature and DO), nitrate, oxidation conditions caused by recharge of infiltrating water or water from the river and the presence of manganese oxide.

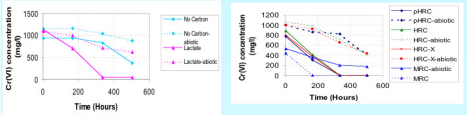
III. Microcosm Bench-Scale Study

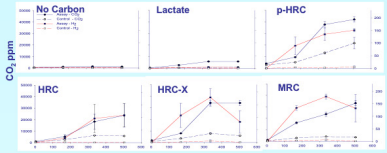
Test Schematic

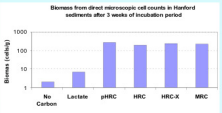


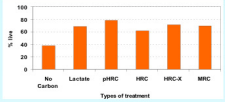
- 100 g Hanford sediment and 33 ml Hanford groundwater (from Well 699-96-43) amended with:
  - Cr(VI) to 1000 ppb
  - Carbon equivalent to 0.4g C kg^{-1} sediment (~ 1g HRC kg^{-1})
- Autoclaved controls

Decrease in Cr(VI), CO_2 and H_2 Concentration with Time as Affected by Different Treatment





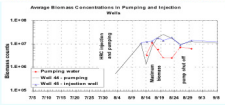


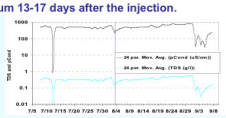


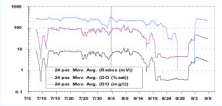
- All carbon applications stimulated Cr(VI) removal, mainly by biological activity
- Efficacy of Cr(VI) removal by MRC and HRC stimulation
  MRC > HRC = HRC-X = p-HRC
- Aqueous H_2 concentrations of 7-10 nM is associated with methanogenesis;
  1-1.5 nM with sulfate reduction;
  0.2 nM with Fe(III) reduction
  <0.05 nM with Mn(IV)/NO_3^-/Cr(VI) reduction

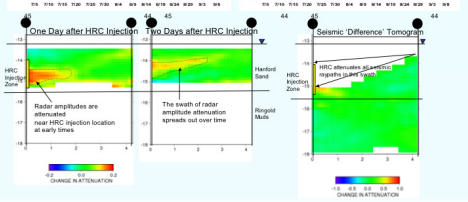
IV. Pilot Field Experiment of Groundwater Biostimulation Using HRC Injection

- 40 lbs of ^{13}C-labeled HRC were injected, followed by Br-tracer injection, over the depth interval of 44 ft to 50 ft in the Hanford formation in Well 699-44-45 on 8/3/2004.
- All in all 11 gal of water were used as a primer to fill the injection hose before the injection, dilute HRC, and as a chaser after the HRC injection.
- Pumping from the monitoring well 699-96-44 (15 ft from the injection well) started immediately after the injection and continued for 27 days (until August 30).
- Br breakthrough occurred 7 days after the injection, and the maximum was reached 11 days after the injection.
- Microbial cell counts reached the maximum 13-17 days after the injection.

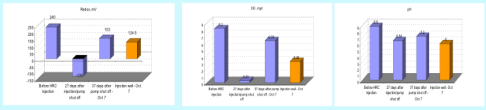




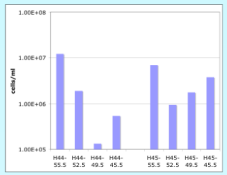




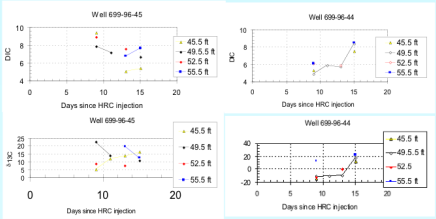
Redox Potential, DO, and pH in the Monitoring and Injection Wells



Well 699-96-44 (blue color). Data from August 30, 2004, when the pump was shut off, to October 7 are characterizing natural gradient flow



Desulfovibrio vulgaris DFA



V. Key Findings, Directions of Future Research, and Benefits

- Under background conditions, Hanford sediments contain
  - Microbial populations (<10^5 cells g^{-1}), which are probably too low for direct enzymatic Cr(VI) reduction, but biostimulation may increase biomass to >10^8 cells g^{-1}.
  - Several types of bacteria, including *Bacillus/Arthrobacter* and *Geobacter* species, which are known to:
    - Withstand high concentrations of heavy metals, metabolize recalcitrant chlorinated compounds, and reduce or sorb hexavalent chromium.
- Bench-scale treatability studies show
  - All HRC and MRC products tested stimulated bacterial biomass and activity, enhanced Cr(VI) removal from solution, and resulted in highly reducing conditions
  - 16S rDNA microarrays identify diverse bacterial communities after stimulation, and permit ~9,000 bacterial species to be monitored during remediation
- Field-scale HRC injection in the groundwater generated
  - An increase in the biomass up to 2×10^7 cells g^{-1}
  - Highly reducing conditions with DO of 0.35 mg/l, Redox Potential of -130 mV, and pH of 6.5.
- Geophysical measurements are capable of monitoring the distribution of the HRC plume in the subsurface
- Directions of future research:
  - Determine the critical biogeochemical parameters necessary to maximize the extent of Cr(VI) bioreduction and minimize Cr(III) reoxidation in ground water. In particular, evaluate if dissolved oxygen and manganese oxides could reoxidize Cr(III) to Cr(VI)
  - Develop a 3D reactive transport code, TOUGHREACT-BIO, to simulate coupled biological and geochemical processes
- Benefits:
  - In-situ bioreduction of Cr(VI) in groundwater is expected to be a rapid and cost-effective remediation action. Anticipated cost savings are approximately 30-80% over accepted cleanup methods such as pump-and-treat.

Publications:

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