LBNL Sustainable Systems SFA: Unraveling Biogeochemical Pathways Mediating Sustained Chromium Reduction - Reactive Transport Modeling of Microbially-Mediated Processes at the Hanford 100H Site

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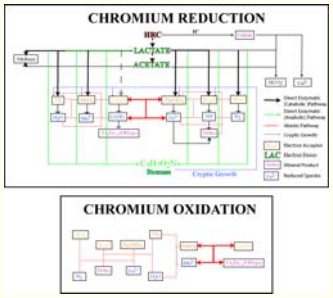
ABSTRACT

A reaction-transport model was developed to investigate the lactate- and acetate-induced bioreduction of Cr(VI) in the groundwater of the Hanford 100H aquifer. Bioreduction of Cr(VI) with these electron donors is captured using a mixed thermodynamic-kinetic approach, with the modified Gibbs free energies of the reactions based in part on Liu et al. (2002). These calculations also consider other organic acid metal aqueous complexes affecting the thermodynamic driving force. The principal kinetic reactions include HRC dissociation to lactate, direct reductive precipitation of $Cr(OH)_3$, bioreduction of goethite to produce Fe(II) leading to abiotic reduction of Cr(VI); calcite dissolution in the acidic plume and precipitation elsewhere, with accounting for the influence of bicarbonate concentrations on the extent of Cr(VI) reduction. A 3-D reaction-transport model of the 100H site was developed including discretized wells, a heterogeneous permeability field conditioned on geophysical data, and hydrological parameters and flow velocities tuned on multiple Br tracer tests. It was found that the time-dependent drop in total Cr concentrations observed in pumping wells could be captured quite closely, assuming that the viscous HRC plume was relatively immobile with its distribution indicated by geophysical imaging. The model was further extended to include the effects of Cr isotopic ($^{53}Cr/^{52}Cr$) fractionation by reduction, which has been shown in laboratory experiments to result in a shift in ^{53}Cr of ~3.5‰ (Ellis et al. 2002), compared to Cr(VI) sorption showing a small fractionation of ~0.04‰. Modeling results for 100H showed Cr fractionation of ~2-3‰ (heavier) in fluids during Cr reduction, consistent with measured data and providing an independent method for determining reaction pathways and their individual rates. The extent and rates of calcite dissolution/precipition are also captured by incorporation of $^{87}Sr/^{86}Sr$ systematics.

BACKGROUND, HYPOTHESIS & APPROACH

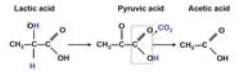
Biogeochemical Reaction Network

A simplified biogeochemical reaction network for Cr(VI) reduction is shown below, illustrating key pathways and feedback mechanisms. As discussed in the following section, several reactions involving C, S, Cr, Ca, and O can result in significant stable isotopic fractionation. The goal of the reaction-transport modeling is to interrogate this network, including various isotopic species and potential fractionation mechanisms (kinetic, equilibrium reaction, or transport-controlled), in the framework of well-constrained hydrological system.



HRC Characteristics

- HRC is a polylactate that:slowly releases lactic acid when mixed with water
- Lowers pH (will react with calcite coatings and caliche
- Provides carbon and energy source and stimulates microbial processes
- Hydrogen is a primary electron donor that can reduce oxygen, nitrate, iron, sulfate
- Chemical composition quite complex, adding uncertainty regarding effects on groundwater chemistry



Analytical data (raw) on HRC composition

Anions	mM	Cations	mg/L
Lactate	4000-5000	B	0.39
Acetate	na	Na	26.21
Propionate	nd	Mg	0.089
Pyruvate	0.002	Al	0.009
Chloride	0.400	Si	90.64
Nitrite	nd	K	2547
Nitrate	4.3	Ca	n/a
succinate	nd	Cr	0.055
phosphate	100	Mn	0.022
citrate	2	Fe	1.074
sulfate	nd	Cu	n/a
oxalate	nd	Zn	0.036
formate?	1	As	0.059
pH	2.3	Sr	0.015
		Mo	0.069
		Pb	0.002

BACKGROUND, HYPOTHESIS & APPROACH

Geochemical and Isotopic Constraints On Reaction Pathways and Rates

Reduction of CrO_4^{2-} with lactate as the electron donor (and acetate) is captured using a mixed thermodynamic-kinetic approach, with the modified Gibbs free energies of the reactions based in part on Liu et al. (2002). The principal kinetic reactions include HRC dissociation to lactate, direct reductive precipitation of $Cr(OH)_3$, bioreduction of goethite to produce Fe(II) leading to abiotic reduction of Cr(VI); calcite dissolution and precipitation. Multiple isotopic systems (e.g., $\delta^{53}Cr$, $\delta^{13}C$, $\delta^{18}O$, $\delta^{87}Sr$,) are also used to constrain reaction pathways, rates, transport rates and mechanisms, subsurface physical and geochemical heterogeneity, and abiotic versus biotic pathways.

The primary reactions controlling Cr(VI) reduction considered in the model are listed below. Specific isotopic systems that may yield constraints on these reactions are shown in the right hand column. Mineral-water systems are treated kinetically and aqueous species reactions are at local equilibrium.

Thermodynamic-Kinetic Model: — Isotopic Indicators

HRC --> $Lact^- + H^+$ (kinetic) — $\delta^{13}C$ tracer

Cr-VI to Cr-III:

$$CrO_4^{2-} + 0.75Lact^- + 12.5H^+ + 0.5H_2O = Cr(OH)_3(s) + 0.75Acet^- + 0.75HCO_3^- + 1.75H^+$$

$\delta^{53}Cr$, $\delta^{13}C$

Fe-III to Fe-II:

$$FeOOH(Goethite) + 0.25Lact^- + 1.75H^+ = Fe^{2+} + 0.25Acet^- + 0.25HCO_3^- + 1.5H_2O$$

$\delta^{56}Fe$, $\delta^{13}C$

$$CaCO_3(Calcite) + H^+ = Ca^+ + HCO_3^-$$

$$H^+ + HCO_3^- = CO_2(gas) + H_2O$$

$\delta^{87}Sr$, $\delta^{44}Ca$, $\delta^{13}C$, ^{14}C, $\delta^{18}O$-CO_2, $\delta^{13}C$

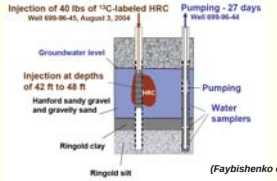
Abiotic and biotic sulfate reduction (various reactions) — $\delta^{34}S$, $\delta^{18}O$-SO_4

3-D Model Development

The 3-D model includes the following main components:

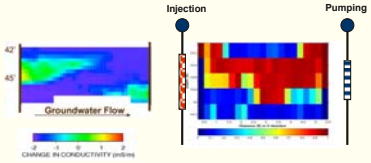
- 3-D permeability heterogeneity based on geophysical imaging
- Hydrological parameters conditioned on Br tracer tests
- Thermodynamic-kinetic model for HRC degradation, biogeochemical reactions, $Cr(OH)_3$ precipitation, Fe redox reactions
- Isotopic species to delineate reaction pathways: redox ($\delta^{53}Cr$), mineral-water-gas ($\delta^{13}C$, $\delta^{87}Sr$)
- HRC treated as an immobile phase which slowly breaks down to lactate and hydrogen ion in groundwater
- TOUGHREACT v2 (Xu et al., 2006) used for reaction-transport simulations

Schematic diagram showing 2004 HRC injection test



(Faybishenko et al., 2008)

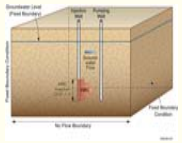
Geophysical Data & Permeability Heterogeneity



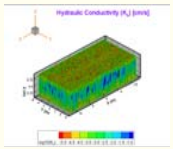
3-D Model Design, Boundary Conditions, and 3-D Permeability Field

The model domain is 24 m long (in the x direction), 6 m wide (in the y direction). and covers a depth of 1 m in the vertical direction, representing the thickness of the Hanford sediments. The grid is radial and refined near the injection (at x=0 m) and pumping wells (x=5.0 m). Farther away from the injection and pumping wells, the grid is rectangular and less refined. The model domain is assumed to be located entirely in the saturated zone. Permeability is heterogeneous, with the distribution obtained from conductivity measurements [Hubbard et al., 2006].

3-D Model Conceptualization



3-D Permeability Field

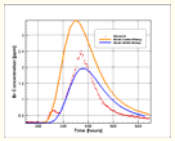


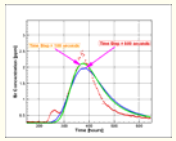
RESULTS

Br Tracer Test Data and Model

The hydrological model was first conditioned to data from Br tracer tests performed before and after HRC injection, with conditions listed below. Sensitivity studies were performed on the effects of time-stepping and gridding on arrival times.

- 149.5 gm Br injected at 11.5 gm/liter for 2 hours 46 minutes
- Pumping at 0.3-0.45 gallons per minute for 27 days





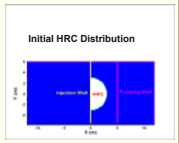
3-D Model Simulations of HRC Injection Test

For the 2004 HRC injection experiment, approximately 40 lbs (~18 kilograms) of HRC was mixed with 10 gallons (~ 37.8 liters) of water. This gave an initial lactic acid concentration of 1.5 mol/liter in the injection solution. The pH of the injected solution was approximately 3.0. The composition of the upstream groundwater is tabulated below. The initial HRC distribution was fixed as shown in the figure at right below. The fixed HRC distribution captures many aspects of the system over relatively short spatial and temporal scales, yet sinking and migration of the viscous dense mixture complicates the dispersal of lactate in the system.

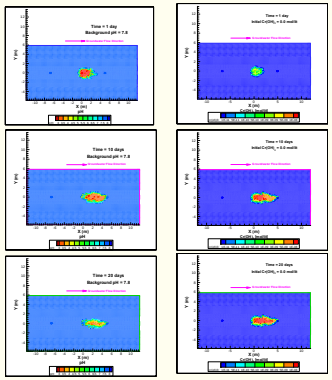
We compared simulated time-series of Cr(VI) in the dissolved phase with measured Cr(VI) field data (pH and $Cr(OH)_3$, shown below for several times. Modeling confirms that Fe(II) has a strong impact on the extent of Cr(VI) reduction. In addition, since it is assumed that the model domain is located in the saturated zone, no separate gas phase was present. Consequently, carbon dioxide produced during the reaction was accounted for as dissolved bicarbonate (HCO_3^-). This resulted in an oversaturation with HCO_3^- (as no carbon dioxide could leave the model domain), ultimately resulting in some suppression of Cr(VI) reduction. Alternatively, if the calcite dissolution rate is reduced (see bottom right figure) the extent of Cr reduction is greater.

Chemical composition of initial groundwater (Water collected from 699-96-43 on 1/4/2001)

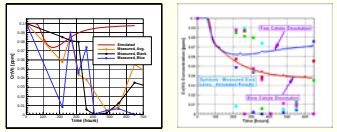
Component	Conc (mg/l)
Ca^{2+}	64
Na^+	22.7
K^+	7.58
Al^{3+}	0.186
Fe^{2+}	0.022
Cl^-	30.7
Br^-	Trace
NO_3^-	42.3
$HCO3^-$	77.6
SO_4^{2-}	74.2
SiO_2(aq.)	2.23
$Lact^-$	~0
CrO_4^{2-}	0.100



pH — Precipitated $Cr(OH)_3$



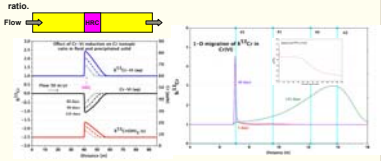
Pumping well measured vs. modeled Cr(VI)



RESULTS

Redox-Sensitive Cr Isotopic Fractionation

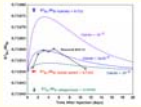
The model was extended to include the effects of Cr isotopic ($^{53}Cr/^{52}Cr$) fractionation by Cr(VI) reduction. Laboratory experiments have shown a shift in ^{53}Cr of ~3.5‰ (Ellis et al. 2002), compared to Cr-VI sorption showing a small fractionation of ~0.04‰. An idealized 1-D model is shown on the left illustrating the shifts in $\delta^{53}Cr$ via Cr(VI) reduction and $Cr(OH)_3$ precipitation. At right is a simplified 1-D model of the 100H site, with HRC as an immobile phase in the injection well. A constant flow rate from left to right of about 48 m/year captures the average transport velocity over the first month of the November 2008 HRC injection test. Note that the maximum shift is ~4.5‰ in the injection well, but the larger plume developed away from the well has a maximum increase of ~3‰, similar to measurements performed in earlier tests. This model did not consider the dissolution of previously reduced Cr from earlier HRC injections, which would likely give rise to strongly fractionated Cr(III) having a lower $^{53}Cr/^{52}Cr$ ratio.

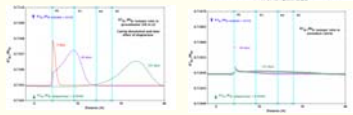


Sr Isotopic Shifts from Water-Rock Interaction

The pH of the HRC once dissolved is moderately acidic, with a pH of around 2.7. Injection of this acidic solution results in calcite dissolution and potentially some reactions with silicate minerals. Calcite dissolution/precipitation has an important influence on Cr(VI) reduction and potentially permeability. Maher et al. (2003) showed that there are large differences in the Sr isotopic ratios of minerals, pore waters, and leachates in the Hanford formation. Here, the $^{87}Sr/^{86}Sr$ ratio is tracked through all the aqueous species reactions, with dissolution/precipitation of Sr-bearing phases as solid solutions.

At the right is shown the measured $^{87}Sr/^{86}Sr$ ratio of water from the injection borehole. Three model simulations show the strong sensitivity to small amounts of calcite (or the rate) in the injection interval. Below are the curves of for Sr isotopic ratios in fluids (left) and in precipitated calcite (right) as a function of distance along the path of the wells.





SUMMARY

A 3-D reaction-transport model was developed to investigate the lactate- and acetate-induced bioreduction of Cr(VI) in the groundwater of the Hanford 100H aquifer. Bioreduction of Cr(VI) was captured using a mixed thermodynamic-kinetic approach, based in part on Liu et al (2002). The 3-D model includes highly discretized wells, a heterogeneous permeability field conditioned on geophysical data, and hydrological parameters and flow velocities tuned on multiple Br tracer tests. Although many complications arise owing to the high viscosity and density of HRC, its complex composition, and mineral-water reactions induced by the acidic plume, to first order the system is strongly driven to Cr reduction directly by lactate and then acetate. Increases in the Cr isotopic ratio of collected fluids suggests precipitation, possibly to a solid Cr-hydroxide or mixed Fe-Cr hydroxide phase, rather than sorption of Cr(VI). The thermodynamic-kinetic models have been extended to consider a range of isotopic species in the aqueous, solid, and gas-phase, including $^{53}Cr/^{52}Cr$, $^{87}Sr/^{86}Sr$, and $^{13}C/^{14}C$. These systems are used to distinguish and constrain reaction mechanisms, pathways, and rates. Simplified 1-D models of the 100H site have shown good agreement in the magnitudes and trends of $^{53}Cr/^{52}Cr$ and of $^{87}Sr/^{86}Sr$, especially with respect to the rates of HRC degradation and mixing, and of calcite dissolution. $^{13}C/^{12}C$ systematics are being incorporated both as a tracer for labeled lactate and as a sensitive indicator of mineral-water-gas-biological reactions. Once more complete data sets are available for recent and planned HRC injection tests, detailed comparison to 3-D modeling results including the specifics of the injection/production/monitoring procedures will be performed.

Acknowledgments

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