The five aqueous reagents selected for testing are consistent with U.S. Environmental Protection Agency (USEPA) recommendations (USEPA, 2000).

Calcium polysulfide (CaS_5 or CaS_x) is a NSF International approved reagent for drinking water treatment. It is a nontoxic reagent that oxidizes under aerobic conditions to form calcium, SO_4^{2-} and elemental sulfur. Calcium polysulfide has been recently used more frequently as a reducing agent for Cr(VI) owing to its ability to reduce Cr(VI) to Cr(III) without the need for acidification. Sulfur atoms have the ability to catenate into linear chains of sulfur atoms to create a polysulfide salt when reacted with a metal. When sulfur is reacted with calcium metal, a calcium polysulfide salt is formed that contains anywhere from 2 (CaS_2) to 7 (CaS_7) sulfur atoms per calcium atom. The average amount of sulfur is 4 to 5 sulfur atoms per calcium atom. When the polysulfide anion reacts with Cr(VI) in the groundwater, the sulfide is converted from a –2 oxidation state to zero oxidation state, thus releasing two moles of electrons for each mole of polysulfide anion reacted. The calcium polysulfide reduction reaction with CrO_4^{2-} is shown below, assuming that the average polysulfide salt contains 5 sulfur atoms per each calcium atom. The polysulfide anion has a stoichiometric requirement with Cr(VI) of 3 to 2, polysulfide to Cr(VI). Polysulfide reacts with Cr(VI) and does not form significant precipitate. However, there may be concern in specific cases because of the low mass yield of precipitate after reaction that the total chromium concentration may not be effectively treated with polysulfide. Total chromium concentrations after treatment were evaluated in this study to determine if this was a significant issue.

The redox reaction shows that three moles of calcium polysulfide are required to reduce two moles of Cr(VI). This is equivalent to 5.77 mg/l calcium polysulfide to reduce each 1 mg/l of Cr(VI) dissolved in the groundwater. The reaction for calcium polysulfide with CrO_4^{2-} is as follows:

$$\textit{Reduction}: \quad 10H^+ + 2CrO_4^{2-} + 6e^- \rightarrow 2Cr(OH)_3 + 2H_2O \tag{9.2.1}$$

$$\textit{Oxidation}: \quad 3CaS_5 \rightarrow 3Ca^{2+} + 15S + 6e^- \tag{9.2.2}$$

$$10H^+ + 2CrO_4^{2-} + 3CaS_5 \rightarrow 2Cr(OH)_3 + 3Ca^{2+} + 2H_2O + 15S \tag{9.2.3}$$

Sodium dithionite is an effective reagent for *in-situ* treatment of Cr(VI). It has been tested extensively by the Department of Energy's (DOE) Pacific Northwest National Laboratory (PNNL), because it decomposes into naturally occurring nontoxic byproducts that stimulate the reduction of Cr(VI) and do not destroy water quality down gradient. The $S_2O_4^{2-}$ reacts with metal species such as Fe(III) and Mn(IV) in a typical soil reducing them to Fe(II) and Mn(II). The reduced Fe formed in solution and within the solid matrix of the soil. The reduced species in the solid matrix of the soil form a reservoir that can continue to reduce influent Cr(VI) from Cr(VI) to Cr(III), which is insoluble at ambient pH and has a lower toxicity than Cr(VI). The Fe will

precipitate with the Cr(III) forming a solid that is insoluble even at low pH (<2). One of the problems associated with $Na_2S_2O_4$ is that the reaction of the $S_2O_4^{2-}$ decreases the pH, consuming the buffering capacity of the soil. At low pH $S_2O_4^{2-}$ decomposes and its reactivity decreases. The stoichiometric requirement of $S_2O_4^{2-}$ for CrO_4^{2-} is 3 to 2, but reaction kinetics and side reactions can significantly alter the reaction.

$$\textit{Reduction}: \quad 16H^+ + 2CrO_4^{2-} + 6e^- \rightarrow 2Cr^{3+} + 8H_2O \tag{9.2.4}$$

$$\textit{Oxidation}: \quad 3S_2O_4^{2-} + 6H_2O \rightarrow 12H^+ + 6SO_3^{2-} + 6e^- \tag{9.2.5}$$

$$4H^+ + 2CrO_4^{2-} + 3S_2O_4^{2-} \rightarrow 2Cr^{3+} + 6SO_3^{2-} + 2H_2O \tag{9.2.6}$$

Sodium thiosulfate ($Na_2S_2O_3$) is another common NSF approved water treatment chemical that is used to reduce Cr(VI) to Cr(III). In the thiosulfate ($S_2O_3^{2-}$) reaction, the sulfur atom is converted from a +2 oxidation state to a $+2\frac{1}{2}$ oxidation state when $S_2O_3^{2-}$ reacts to form the tetrathionate anion ($S_4O_6^{2-}$). One mole of electrons are released for each mole of $S_2O_3^{2-}$ that is consumed during the reaction.

The redox reaction shows that three moles of $Na_2S_2O_3$ are required to reduce one mole of Cr(VI). This is equivalent to 9.12 mg/l $Na_2S_2O_3$ to reduce 1 mg/l of Cr(VI) dissolved in the groundwater. The reaction of $Na_2S_2O_3$ with CrO_4^{2-} proceeds similar to $Cr_2O_7^{2-}$:

$$\textit{Reduction}: \quad 8H^+ + CrO_4^{2-} + 3e^- \rightarrow Cr^{3+} + 4H_2O \tag{9.2.7}$$

$$\textit{Oxidation}: \quad 3S_2O_3^{2-} \rightarrow 1.5S_4O_6^{2-} + 3e^- \tag{9.2.8}$$

$$8H^+ + CrO_4^{2-} + 3S_2O_3^{2-} \rightarrow Cr^{3+} + 1.5S_4O_6^{2-} + 4H_2O \tag{9.2.9}$$

Sodium hydrogen sulfite ($NaHSO_3$) is also an NSF approved reagent and the most commonly used treatment chemical for Cr(VI) in industrial water treatment applications. In the hydrogen sulfite (HSO_3^-) reaction, the sulfur atom is converted from a +4 oxidation state to a +6 oxidation state, thus releasing 2 electrons for the redox reaction.

The redox reaction shows that three moles of $NaHSO_3$ are required to reduce two moles of Cr(VI). This is equivalent to a 3 mg/l $NaHSO_3$ demand for 1 mg/l of Cr(VI) dissolved in the groundwater. The reaction of $NaHSO_3$ with the CrO_4^{2-} ion proceeds in a similar manner:

$$\textit{Reduction}: \quad 16H^+ + 2CrO_4^{2-} + 6e^- \rightarrow 2Cr^{3+} + 8H_2O \tag{9.2.10}$$

$$\textit{Oxidation}: \quad 3HSO_3^- + 3H_2O \rightarrow 9H^+ + 3SO_4^{2-} + 6e^- \tag{9.2.11}$$

$$7H^+ + CrO_4^{2-} + HSO_3^- \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O \tag{9.2.12}$$

Iron(II) sulfate ($FeSO_4$) is also a NSF International approved reagent for drinking water treatment. It is a nontoxic reagent that forms iron(III) sulfate ($Fe_2(SO_4)_3$) after upon oxidation. All of the Fe(III) precipitates with Cr(III). One drawback of the reagent is that the high stoichiometric requirement for treatment of Cr(VI) of 3 to 1 (Fe(II) to Cr(VI)) also increases the yield of precipitate. The fast reaction and precipitation of Fe(II) and chromium reaction byproducts effectively transform Cr(VI) and remove total chromium from solution. The kinetics of $FeSO_4$ treatment of CrO_4^{2-} have been evaluated extensively by Fendorf and Li (1996), and observed that the rate is highest at pH 8, and above that oxygen competition for CrO_4^{2-} reduces the observed rate. The anticipated limitation of Fe(II) is that it forms excessive amounts of precipitate that limit its applicability in groundwater treatment because of the problems with waste generation. Iron(III) hydroxides generated from the treatment have been shown to have toxicity characteristic leaching procedure (TCLP) concentrations of approximately 60 mg/l in some treatment system, which will classify the waste as hazardous. Further stabilization can limit this problem. The reaction of CrO_4^{2-} with Fe(II) is as follows:

$$\textit{Reduction}: \quad 8H^+ + CrO_4^{2-} + 3e^- \rightarrow Cr^{3+} + 4H_2O \tag{9.2.13}$$

$$\textit{Oxidation}: \quad 3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^- \tag{9.2.14}$$

$$8H^+ + 3Fe^{2+} + CrO_4^{2-} \rightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O \tag{9.2.15}$$

$$\rightarrow \text{or } (Cr_xFe_{1-x})(OH)_3(s)$$

where $0 \leq x \geq 1$

9.2.4 Solid Treatment Reagent

One solid reagent, Fe impregnated silica (SiO_2) sand, was tested for its effectiveness as a permeable reactive barrier. The material is intended as a substitute for elemental Fe in reactive barriers. It is an Fe-impregnated SiO_2 sand created by placing SiO_2 sand in contact with molten ductile Fe, allowing the Fe to cool, and then removing the sand from the Fe. This process creates a SiO_2 sand containing approximately 2% Fe by mass with a sponge-type surface when viewed under an electron microscope. The Fe contains around 3% silicon (Si), which helps it to resist atmospheric corrosion. Column studies flushing 1000 pore volumes of groundwater containing 400 mg/l $CaCO_3$ hardness through the material revealed that the material did not loose its reactivity. The main benefit of the material is the cost since the material costs only 25% as much as elemental Fe.

The reaction for the SiO_2 sand Fe is the same as that for elemental Fe, in which the chromium reacts with Fe(II) generated on the Fe-SiO_2 surface, forming the same products as described in the above referenced $FeSO_4$

reaction. In traditional elemental Fe barriers, the Fe surface can become fouled by iron(III) hydroxides formed on the Fe surface, limiting its effectiveness for treatment. The sponge-type surface of the Fe has a much higher area, reducing the impact of fouling and creating more reactive sites. The Si limits the access to individual reactive sites, but limited reaction prevents the Fe from reacting rapidly and depleting the reducing capacity of the reactive barrier prematurely.

9.2.5 Reductant Stoichiometry and Reaction Kinetics

The reaction stoichiometry and kinetics were tested using increasing concentrations of the reducing agents and set reaction periods. Bench-scale reactions were conducted using four 29.6 ml, glass sample containers. Subsets of each reagent were prepared by adding two and three times the reductant stoichiometric requirement. Control samples were prepared by adding site groundwater to a clean container in order to account for changes in Cr(VI) concentration over time.

All of the sample sets were allowed to react for one hour, while being mixed in a tumbler rotating at a speed of 18 revolutions per minute. After one hour, one sample was removed from each of the 10 test groups and 1% mass/volume NaOH was added by micropipette to raise the pH to 10.5. The samples were then stirred and allowed to sit for 15 min. Following this neutralization period, samples were passed through a 0.45 μm filter and the liquid placed into a 120 ml sample container with nitric acid (HNO_3) preservation.

Each sample was shipped to Merit Laboratory, Inc. in East Lansing, Michigan for total chromium analysis by USEPA Methods 3015A (sample digestion) and 200.8 (analysis). The total chromium analysis results represent the amount of Cr(VI) in solution after reaction, since the insoluble, Cr(III) is removed by the filtration step, assuming no other Cr oxidation state is present.

The remaining samples were left in the tumbler for continued testing activities. The sample collection procedures detailed above were repeated following reaction time frames of 2 and 3 h.

Based on the results of the preliminary testing, the best performing treatment reagent was selected for further verification testing of the reaction kinetics. Test samples of the composite groundwater were prepared and over-dosed with reductant to ensure complete reduction of Cr(VI). The information gained by this testing was combined with the previous results to identify an optimal reagent concentration that provided sufficient reduction of Cr(VI) in solution and a representative reaction time frame for kinetics confirmation.

Testing was conducted using 120 ml samples of the composite groundwater and the previously identified volume of treatment reagent. Samples were sent to Merit Laboratories, Inc. for off-site analysis of Cr(VI) following reaction

periods of 1.0, 1.5, 2.0, and 2.5 h. Sample collection at each time interval followed earlier procedures, with the representative sample adjusted to pH 10.5 using 1% mass/volume NaOH to stop the chemical reaction.

9.2.6 Reductant Treatment and Solids Generation

Bench-scale testing activities were focused on the evaluation of the reducing agents $NaHSO_3$, $Na_2S_2O_4$, $Na_2S_2O_3$, $FeSO_4$, and CaS_5. These compounds were selected owing to the theoretical reaction kinetics and the minimal colloidal-range solids generated as by-products (with the exception of $FeSO_4$) of the reduction process. The first phase of testing was designed to verify the reaction kinetics and identify the optimal reactant under the given site-specific conditions. Once the best treatment chemical was determined, the second phase of testing was used to evaluate solids production and potential concerns for pore-space fouling during *in-situ* applications.

Testing was conducted by preparing three samples that were subsequently sent to Particle Technology Labs, Ltd. in Downers Grove, Illinois for Elzone particle size analysis. The test was conducted by filling three beakers with 1000 ml of a composite groundwater sample. The three samples were treated as follows:

1. An untreated groundwater sample containing 4.3 mg/l Cr(VI)
2. A groundwater sample treated with 43 mg/l CaS_5
3. A groundwater sample treated with 43 mg/l CaS_5 and pH adjusted to 6.5 after treatment

Following preparation of the three tests, the samples were allowed to react over a 24 h period prior to shipment for particle size analyses.

Total precipitate generation per treatment reagent was conducted for $FeSO_4$ and CaS_5. Precipitate mass was measured on 2-l samples of groundwater treated with three times the CaS_5 and $FeSO_4$ stoichiometric requirement respectively for a 0.30 mg/l Cr(VI) concentration.

9.2.7 Soil Reductant Demand

Once the appropriate reducing agent was identified and optimal reaction kinetics determined for the Cr(VI) impacted groundwater, site-specific characteristics and parameters were evaluated. Since the process was also considered for application to the subsurface, the potential physical and geochemical limitations of a successful remedial program were evaluated.

Examination of the soil samples collected from a test boring identified subsurface zones of relatively higher permeability at depths of 13.1 and 24.8 m below ground surface. The samples were characteristic of silty sand and fell within the identified upper and lower aquifer units where the groundwater

samples used in the test were collected. Representative samples of these two soil intervals were used during the third phase of bench-scale testing, designed to determine the soil reductant demand of the proposed treatment reagent.

The two test samples were prepared by combining 80 g of soil with 80 ml of distilled water in a 500 ml sample container equipped with a screw-top lid. The optimal dose of reducing agent identified in the previous phases was applied to the soil/water mixtures. Each sample was shaken for 5 min to ensure proper mixing and then the oxidation-reduction potential (ORP) of the test samples was monitored. For purposes of determining when the reducing agent was no longer reacting with the soil, a negative ORP measurement was considered indicative of the presence of excess treatment chemical. The validity of this method was confirmed by iodine titration prior to testing.

Following the initial ORP monitoring, the sample containers were placed in a tumbler rotating at a speed of 18 revolutions per minute. After 3 h of mixing the samples were removed and the ORP recorded. If the measurement was positive, the batch addition of reducing agent was repeated and the samples were placed back into the tumbler. If the results were negative, the sample mixing continued without further chemical addition. This procedure was repeated until the ORP measurements remained negative for a period of 24 h. The total volume of reductive chemical required to achieve and maintain the negative ORP reading was recorded and the total mass added to the soil/water matrix calculated.

When ORP readings confirmed that the soil reductant demand was exceeded, 10 ml of water were collected from each test sample and titrated using a 0.01% mass/volume solution of iodine to determine the concentration of unspent reducing agent present in the water. The mass of unspent reductant was subtracted from the total mass added to the soil/water matrix to provide the soil demand for the 80 g sample. Values were calculated for both subsurface intervals and expressed in terms of milligrams reducing agent/kilogram soil.

Once the reductant soil demand was determined, the soil/water sample matrices were spiked with a known volume of 5% mass/volume potassium chromate (K_2CrO_4) solution. The samples were then placed in the tumbler and mixed at a speed of 18 revolutions per minute for a 24 h period. Following the mixing period, the soil was allowed to settle and the water was then passed through a 0.45 μm filter. The filtrate was placed in a container and shipped to Merit Laboratories, Inc. for Cr(VI) analysis using EPA Method 218.4. The results of these sample analyses were used to evaluate the ability of the residual reducing agent to address continued chromium impacts.

9.2.8 Test Results

The results of the 3 h reaction test are presented in Table 9.2.1 and Table 9.2.2 for only CaS_5 and $FeSO_4$. The 3 h reaction test showed that $NaHSO_3$ and

TABLE 9.2.1

Calcium Polysulfide and Ferrous Sulfate Treatment Effectiveness

	Total Chromium			
	Calcium Polysulfide		Iron(II) Sulfate	
Dosing level	Initial mg/l	Final mg/l	Initial mg/l	Final mg/l
1 × Stoichiometric	0.39	0.026	0.39	0.018
2 × Stoichiometric	0.39	<0.010	0.39	<0.010
3 × Stoichiometric	0.39	<0.010	0.39	<0.010

$Na_2S_2O_3$ provided no reduction of Cr(VI) at neutral pH values, despite increasing reagent dosages. CaS_5 reduced Cr(VI) with an efficiency ranging from 11.6 to 100% reduction at dosages ranging from 1 to 3 times the stoichiometric requirement. The data also indicated that reductive reactions with calcium polysulfide appear complete after 2 h of reaction, since no further reduction was observed in the samples at 3 h. $FeSO_4$ reaction is complete within 1 h for Cr(VI) reduction, but the settling kinetics for total chromium removal require longer settling times. $NaHSO_3$ and $S_2O_3^{2-}$ did not react effectively even at much higher treatment concentrations at neutral pH. $Na_2S_2O_4$ was observed to be effective at 80 times the stoichiometric concentration with reaction within 24 h.

The testing confirmed that 100% reduction of Cr(VI) can be achieved at a dosage ratio of 9 mg/l of calcium polysulfide to 1 mg/l of Cr(VI) dissolved in the groundwater, which is 1.56 times the stoichiometric requirement. The reaction kinetics for the 9 to 1 ratio sample is presented in Table 9.2.3.

9.2.8.1 Analysis of Particles (Results)

The geometric mean particle size on a population basis for the untreated water was determined to be 0.694 μm with a standard deviation of 1.326 μm. On a mass basis, the geometric mean was 1.089 μm with a standard deviation of 2.019 μm. The total mass of suspended solids in the water was 22 mg/l. Suspended particles in this size range are very difficult to remove from water by gravity separation and filtration methods.

TABLE 9.2.2

Calcium Polysulfide Treatment Concentrations

Calcium Polysulfide Concentration (mg/l)	Chromium Reduction(%)	Ratio of CaS_s/Cr(VI)
42	100	9.0
63	100	13.5
83	100	18.0

TABLE 9.2.3

Cr(VI) Kinetic Testing Results

Reaction 1.1.1.1 Time (hours)	Calcium Polysulfide Concentration (mg/l)	Post-Treatment Chromium (mg/l)	Chromium Reduction (%)
0	0	4.3	0
1	43	0.516	88
1.5	43	0.215	95
2	43	0.095	97.8
2.5	43	0.093[a]	97.8
2.5	43	0.332[b]	92.3

[a] Filtered at 0.45 microns

[b] Decant water only, no filtering

The addition of calcium polysulfide to the water produced a coagulation effect that increased the geometric mean particle size on a population basis to 1.823 μm with a standard deviation of 1.388 μm. On a mass basis, the geometric mean increased to 2.645 μm with a standard deviation of 1.488 μm. This shows that the particle size of the suspended solids was substantially increased, thus facilitating suspended solids removal. The total mass of suspended solids in the treated water was 48 mg/l after the CaS_5 reaction. Additional testing showed that the suspended solids concentration increased to 200 mg/l when the pH was adjusted to 10.5 using 170 mg/l NaOH. This sample was not analyzed for mean particle size. Rapid settling and good clarification was observed in the water sample that was pH adjusted to 10.5. The decant water of this sample contained 20 mg/l suspended solids.

Calcium carbonate makes up a significant portion of the solids that precipitate during CaS_5 treatment. This is owing to a disruption in the CO_3^{2-} equilibrium caused by increased pH in the water. To test the effect of $CaCO_3$ on the coagulation, one of the groundwater samples was pH adjusted to 6.5 following CaS_5 treatment to evaluate whether lower pH would reduce the concentration of colloidal $CaCO_3$ particles. The pH adjustment resulted in a geometric mean particle size based on a population basis of 1.904 μm with a standard deviation of 1.623 μm. However, on a mass basis the geometric mean was 5.088 μm with a standard deviation of 1.662 μm. The total mass of suspended solids in the treated water was 28 mg/l after pH adjustment. The quantity of sulfuric acid required to reduce the pH to 6.5 was 215 mg/l. This high acid demand indicates that pH adjustment is not a feasible remedial approach.

In less alkaline water from a second site, calcium polysulfide treatment resulted in precipitate formation at a concentration of less than 2.5 mg/l with a Cr(VI) concentration of 0.39 mg/l and a dosing concentration of 2 times the stoichiometric requirement. $FeSO_4$ treatment by comparison resulted in the formation of 3.7 times the amount of solid, or 9.25 mg/l at a dosing of 2 times the stoichiometric requirement for a 0.39 mg/l Cr(VI) solution versus 1 mg/l in the original precipitation study described above.

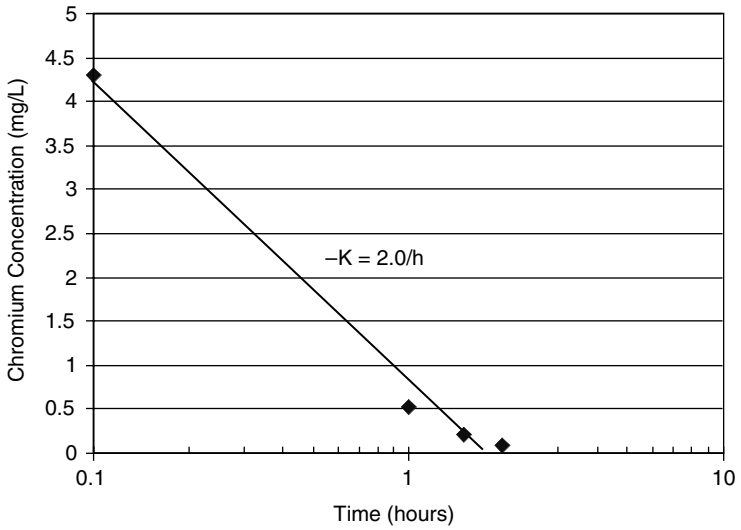

FIGURE 9.2.1
Pseudo-first order reaction for calcium polysulfide.

Although the decreasing dosage requirement of calcium polysulfide as a function of concentration indicates second-order kinetics, the data showed a poor correlation to second-order kinetics when evaluated graphically. Instead, a pseudo-first-order reaction was found to provide the best correlation with the data, showing that reduction occurred at a pseudo-first-order reaction rate constant of 2.0 h^{-1}. The trend line does not conform to a linear regression, but it provides a good approximation of the rate constant as shown in Figure 9.2.1.

9.2.8.2 Soil Reductant Demand Results

Permeable sand samples were evaluated to determine the amount of reducing agent the soils would consume if chromium reduction were performed *in situ*. Titrations were performed on the soil samples over a period of 10 days to monitor both long-term and short-term geochemical reactions.

During the titrations, the 80 g shallow soil sample consumed 145 ml of 0.01 M CaS_5 solution before an ORP less than –100 mV was sustained for 24 h. The remaining water in the sample was then back-titrated with a 0.01% iodine solution to determine the amount of reductant in the water not consumed by the soil. The soil reductant demand was calculated by subtracting the unconsumed reactant from the total reductant added to the sample. The results showed that the shallow soil had a reductant demand of 3440 mg of CaS_5 per kg of soil.

The same tests were repeated on the deep soil sample. 128 ml of 0.01 M CaS_5 solution was added to an 80 g soil sample in order to sustain an ORP

TABLE 9.2.4

Secondary Cr(VI) Reduction Results

Sample I.D.	Theoretical Cr(VI) Concentration (mg/l)	Actual Cr(VI) Concentration (mg/l)	Relative Percent Difference (%)
43	101	114	12
81.5	91.4	102	11

less than –100 mV. The remaining water was back-titrated with a 0.01% iodine solution to determine the fraction of reductant not consumed by the soils. The soil reductant demand for the deep soil calculated to be 2780 mg of CaS_5 per kg of soil.

Although the soils consumed between 2780 to 3440 mg of CaS_5 per kg of soil, some of the reductant demand may be useful in treating Cr(VI). Fe and other minerals in the soil may be reduced by the CaS_5, and these reduced minerals can later serve as reductants to reduce Cr(VI) to the trivalent state. Therefore, 1.87 ml of 5% were added to the soil sample collected from 13.1 m, and 1.65 ml of 5% K_2CrO_4 were added to the soil sample collected from 24.8 m. The soil samples were placed into a tumbler for a period of 3 days so CrO_4^{2-} could react with the treated soils. Following the reaction period, water from each sample was removed, filtered, and sent to Merit Laboratories for Cr(VI) analysis. The results showed no decrease in Cr(VI) concentrations that could be attributed to the secondary reducing reactions (see Table 9.2.4).

9.2.8.3 Reactive Permeable Barrier

The batch test results indicate that the Fe-impregnated SiO_2 sand was effective at reducing 100% of the reacted Cr(VI) in less than 24 h. The data, shown below in Figure 9.2.2, were linear on a semilog plot correlating to a regression line with an R-squared of 0.952. The pseudo-first-order reaction rate constant was not modeled, but would be anticipated to fall in the K = 0.2 h^- to 0.3 h^{-1} range.

9.2.9 Conclusions

The following conclusions were derived from the treatability study:

- $NaHSO_3$ and $Na_2S_2O_3$ did not reduce Cr(VI) at neutral pH at the concentrations tested in this study
- $Na_2S_2O_4$ reduced Cr(VI) at neutral pH, but at 40 to 80 times the stoichiometric requirement
- $FeSO_4$ reduced Cr(VI) at 2 and 3 times the stoichiometric requirement at the fastest rate tested, but generated 3.7 times the mass of precipitate generated by CaS_5

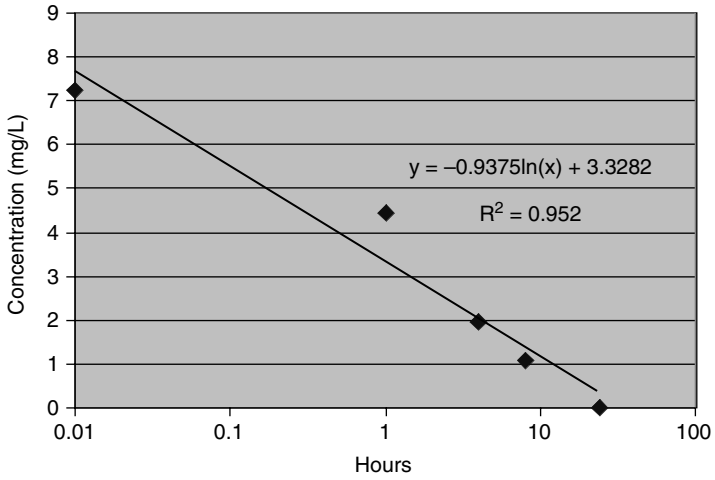

FIGURE 9.2.2
Reaction kinetics for iron impregnated silica sand batch experiments.

- Calcium polysulfide reduced Cr(VI) at 1.56 the stoichiometric demand or from 7 to 9 mg/l of CaS_5 per each mg/l of Cr(VI)
- The reduction rate for Cr(VI) by calcium polysulfide is best modeled using a pseudo-first-order reaction rate constant of 2.0 h^{-1} although the fit is based on a linear approximation of a nonlinear function
- Calcium polysulfide treatment coagulated suspended solids, and precipitated them from solution effectively. Rapid settling times with good clarification was observed at a pH of 10.5, although raising the pH was not required to get effective precipitation. The NaOH demand to increase the pH to 10.5 was 170 mg/l
- Reducing the pH of the water after calcium polysulfide treatment increased the particle size and also improved settling of solids. However, small traces of H_2S gas were noted during pH adjustment. The sulfuric acid (H_2SO_4) demand to lower the treatment water pH to 6.5 was 215 mg/l
- The site-specific soil reducing demand ranged from 2780 to 3440 mg of CaS_5 per kg of soil. Therefore, approximately 98% of the injected CaS_5 in an *in-situ* application would be used to create a reductive environment in the soils, and the remaining 2% would be used to reduce Cr(VI) in the groundwater
- Fe impregnated SiO_2 sand reduced Cr(VI) effectively within 24 h, and the SiO_2-impregnated Fe was stable during column studies after 1000 pore volumes indicating that the Fe will not undergo rapid auto-oxidation

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Au: please provide publisher name

9.3 Assessing the Potential for Biological Cr(VI) Reduction in an Aquifer Contaminated with Mixed Wastes

Sarah Middleton Williams, Craig S. Criddle, and Michael J. Dybas

9.3.1 Introduction

Owing to its widespread industrial use, Cr(VI) is often found in contaminated groundwater. In order to achieve concentrations of Cr less than the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for total soluble Cr (100 μg/l), remediation strategies focus on the reduction of Cr(VI) to insoluble Cr(III) forms, which are relatively stable and nontoxic. The only compounds able to oxidize Cr(III) at any appreciable rate are Mn oxides (Eary and Rai, 1987). Bioremediation may be effective for the removal of Cr(VI) from groundwater, as many aerobic and anaerobic microorganisms reduce Cr(VI) to Cr(III) while utilizing a wide range of electron donors (Bopp and Ehrlich, 1988; Ishibashi et al., 1990; Shen and Wang, 1993; Rege et al., 1997; Tebo and Obraztsova, 1998; Francis et al., 2000; Myers et al., 2000). The potential for a bioremediation scheme to remove Cr(VI) was investigated for an aquifer contaminated with mixed wastes in Schoolcraft, MI. In addition to high concentrations of NO_3^-, SO_4^{2-}, and chlorinated solvents, Plume G contains Cr(VI) contamination from a wood finishing operation in the range of 0.5 to 2.5 mg/l.

There are both abiological and biological mechanisms for Cr(VI) reduction in a subsurface environment. Naturally occurring abiologic reductants of Cr(VI) include Fe(II) compounds, sulfur(II) compounds, and organic matter and reduction can occur with or without a surface-catalyst. Microorganisms can reduce Cr(VI) directly, via a respiratory or cometablic pathway, indirectly, via production of Fe(II) or sulfide by Fe and SO_4^{2-}-reducing bacteria (DIRB or SRB (spell out acronym here), respectively).

Understanding the mechanism of Cr(VI) reduction in an aquifer will determine which metabolic group of organisms to stimulate. In a mixed waste setting, the success of bioremediation may also hinge upon understanding

the sequence in which electron acceptors are reduced. Bacteria often preferentially utilize more energetically-favorable electron acceptors. For example, in the presence of NO_3^-, reduction of Mn(IV), $S_2O_3^{2-}$, and Fe(III) in *Shewanella putrefaciens* 200 was inhibited, indicating that NO_3^- was the preferred electron acceptor for anaerobic respiration (DiChristina, 1992).

Nitrate could pose a potential problem in Cr(VI) remediation in two ways. If indirect reduction of Cr(VI) (by DIRB or SRB) were to be the dominant mechanism of Cr(VI) reduction, then these bacteria should be stimulated. NO_3^- often inhibits DIRB or SRB, thus a 2-step process treatment scheme may be needed, where NO_3^- is removed first. If direct reduction of Cr(VI) were to dominate, then NO_3^- could potentially inhibit Cr(VI) reduction since Cr(VI) and NO_3^- have similar redox potentials. Viamajala et al., (2002a) recently reported Cr(VI) reduction during denitrification in **MR-1?**. However, they found that NO_3^- and nitrite (NO_2^-) inhibited specific rates of Cr(VI) reduction in stationary phase cells (Viamajala et al., 2002b). This work examines whether indigenous microorganisms in Plume G aquifer material can reduce Cr(VI) and whether NO_3^- and Cr(VI) reduction simultaneously occur.

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Successful removal of Cr(VI) hinges upon the formation and stability of Cr(III) precipitates. The USEPA MCL for Cr is measured in terms of *total* soluble Cr, including both soluble Cr(VI) and insoluble Cr(III). At the pH of most groundwater, Cr(III) formed from Cr(VI) reduction will precipitate as insoluble Cr(III) hydroxides (Jardine et al., 1999). However, Cr(III) is known to complex with organic ligands (Nieboer and Jusys, 1988). In this work, we also determine whether various electron donors, which could serve as potential ligands, influence Cr(III) solubility.

9.3.2 Materials and Methods

9.3.2.1 Microcosms

Microcosms consisted of sediment from Plume G and anaerobic Schoolcraft groundwater amended with NH_4Cl, KH_2PO_4, trace metals, and vitamins in 250 ml serum bottles. Lactate was employed as the carbon and energy source and added to 0.01 mol/l from an autoclaved 1 mol/l sodium lactate stock. Microcosms were assembled in a Coy anaerobic chamber under an atmosphere of 10% hydrogen/balance nitrogen, sealed with butyl rubber stoppers and crimped. CrO_4^{2-} was added as electron acceptor in the form of K_2CrO_4 (99.9%, Sigma) from an anaerobic 500 mg/l stock solution. Samples were withdrawn in the anaerobic chamber, filtered with a 0.2 μm filter and stored at –20°C until analysis. All stock solutions were stored in serum bottles with a nitrogen headspace and kept in an anaerobic chamber.

9.3.2.2 Enrichment Culture

An enrichment culture was started using Plume G sediment and an anaerobic synthetic Schoolcraft groundwater medium. Lactate was employed as the carbon and energy source and added to 0.01 mol/l from an autoclaved

1 mol/l anaerobic sodium lactate stock. NO_3^- was added to approximately 0.005 mol/l from a 2 mol/l anaerobic stock solution. SO_4^{2-} and other electron acceptors (other than Cr(VI)) were excluded from the medium. The culture was successively transferred to new medium approximately every 3 weeks over a 9 month period prior to these experiments. For the experiments described here, 1 ml of the enrichment culture was used to inoculate 20 ml of anaerobic synthetic groundwater medium (described above) in 25-ml serum test tubes prepared in an anaerobic chamber. Samples were periodically removed and analyzed for soluble Cr(VI), NO_3^-, and NO_2^-.

9.3.2.3 Analytical Methods

Soluble Cr(VI) was determined colorimetrically using 1,5-diphenyl-carbazide in a sulfuric acid solution (pH 2) (Sandell, 1959). Samples were filtered with 0.2 μm filters prior to analysis. Absorbance was measured at 540 nm using a Uvikon XL Spectrophotometer (Bio-Tek Instruments). Total soluble Cr was measured using a TJA IRIS Advantage/1000 Radial ICAP Spectrometer with a solid state CID Detector. NO_3^- and NO_2^- were measured using ion chromatography with a LC 20 ion chromatograph (Dionex, Sunnyvale) equipped with CD 25 detector and an IonPac AS11-HC (4 mm) column (Dionex) using a NaOH buffer (0.025 mol/l NaOH) at a flow rate of 1.5 ml/min.

9.3.3 Results and Discussion

9.3.3.1 Simultaneous Cr(VI) and NO_3^- Reduction in Schoolcraft Microcosms

The first question we explored was whether biological Cr(VI) reduction would occur in Schoolcraft aquifer material using the native microflora. If indigenous microorganisms capable of reducing Cr(VI) were not present, then other remediation approaches would have to be considered, such as bioaugmentation with a known Cr(VI)-reducer. As shown in Figure 9.3.1a, 0.0001 mol/l Cr(VI) (6 mg/l) was completely reduced in microcosms containing Schoolcraft aquifer material and groundwater within 5 days. At the end of the experiment, total soluble Cr hovered just above the USEPA MCL of 0.000002 mol/l (100 μg/l), indicating that a small amount of the Cr(III) did not precipitate as the insoluble hydroxide, but remained in a soluble form. This will be discussed in a subsequent section. No Cr(VI) reduction occurred in heat-killed (pasteurized) controls, indicating that the mechanism of reduction was biological.

Figure 9.3.1b shows that NO_3^- and Cr(VI) were simultaneously reduced and that little SO_4^{2-} reduction occurred over the course of the experiment. These findings have several implications for the bioremediation of Plume G. First, it is clear that simple biostimulation can achieve the desired outcome. If NO_3^- had an inhibitory effect on Cr(VI) reduction, NO_3^- reduction/removal would have to precede Cr(VI) reduction, or organisms capable of

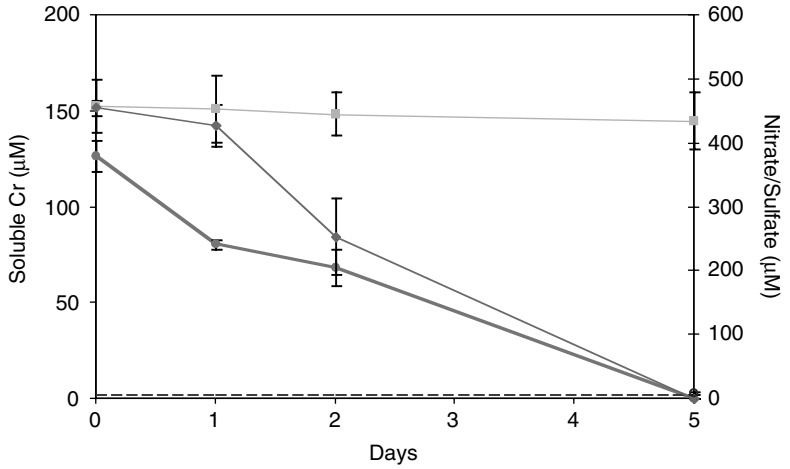

FIGURE 9.3.1A
Microcosms with schoolcraft aquifer material and groundwater simultaneously reduced Cr(VI) and nitrate.

simultaneous NO_3^- and Cr(VI) reduction would have to be added. Second, Cr(VI) reduction was not dependent upon SO_4^{2-}-reduction. This is also advantageous, as SO_4^{2-} reduction is often inhibited by NO_3^-.

One hypothesis is that NO_3^--reducing organisms in the aquifer material were able to reduce Cr(VI) cometabolically. As described below, enrichment experiments supported this hypothesis. However, it is also possible that indigenous Fe-reducing bacteria reduced Fe(III) to Fe(II), which in turn reduced Cr(VI).

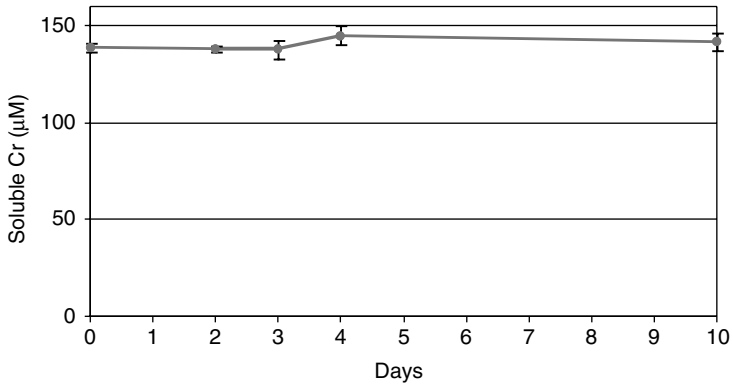

FIGURE 9.3.1B
Pasteurized microcosms did not show any Cr(VI) reduction, indicating that biological mechanisms are responsible for Cr(VI) reduction. Values are the average of duplicates and error bars represent the range. (Σ), soluble Cr(VI); (®), nitrate; (_), sulfate; (o), total soluble Cr; (---), EPA maximum contaminant level (MCL).

9.3.3.2 Cr(VI) Reduction During Denitrification in Schoolcraft Enrichments

To determine whether NO_3^--reducing bacteria could reduce Cr(VI), batch studies were performed in synthetic groundwater using enrichment cultures. The enrichments were inoculated with Schoolcraft sediment, grown on lactate and NO_3^-, and successively transferred into fresh media over a 9-month period. The enrichment culture was used to inoculate test tubes with anaerobic synthetic groundwater spiked with 0.01 mol/l lactate, 0.005 mol/l NO_3^-, and approximately 2.5 mg/l (0.00005 mol/l) or 10 mg/l (0.0002 mol/l) of Cr(VI). As shown in Figure 9.3.2a and Figure 9.3.2b, Cr(VI) and NO_3^- were simultaneously reduced at both low and high concentrations of Cr(VI). In enrichment cultures that were cultivated with Cr(VI) as the only electron acceptor, the Cr(VI) reduction rate was very slow and sometimes negligible (data not shown). In abiotic and autoclaved controls, minimal Cr(VI) reduction occurred (data not shown). The enrichment culture experiments showed that there are in fact indigenous microorganisms in Plume G that are capable of simultaneously reducing NO_3^- and Cr(VI). This supports the conclusion that cometabolic transformation by NO_3^--reducing organisms plays a significant role in the reduction of Cr(VI) in the Plume G aquifer material.

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9.3.3.3 Cr(III) Solubilization

Total soluble chromium was measured at the end of microcosm experiments in order to probe for the presence of soluble Cr(III). Soluble Cr(III) is commonly computed as the difference between total soluble Cr and total soluble Cr(VI).

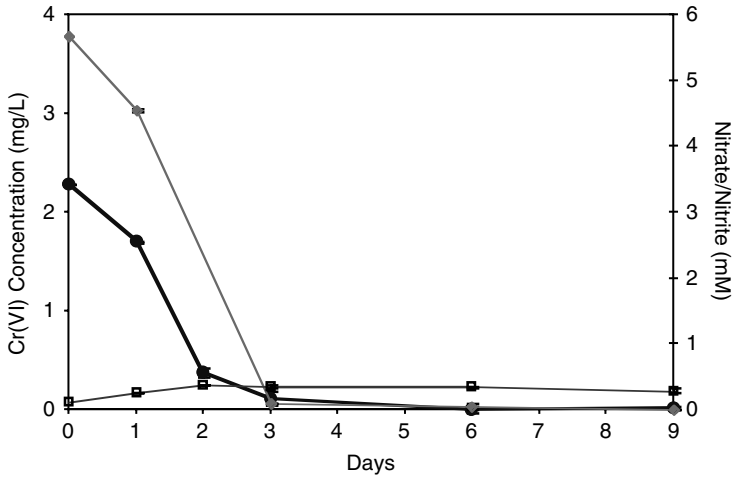

FIGURE 9.3.2A
Schoolcraft enrichment cultures simultaneously reduced Cr(VI) and nitrate at initial Cr(VI) concentrations of 11 mg/L (9.3.2A) and 2 mg/L.

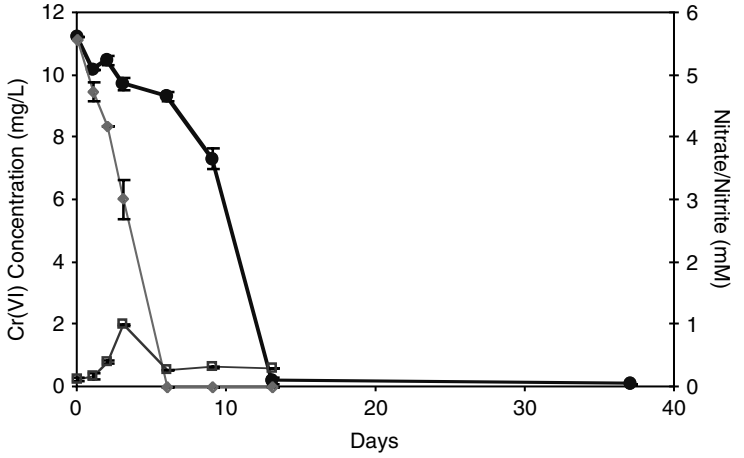

FIGURE 9.3.2B
Autoclaved and no-cell controls showed little Cr(VI) disappearance (2C). Values are the average of duplicates and error bars represent the range. (Σ), soluble Cr(VI); (®), nitrate; (_), nitrite.

As shown in Figure 9.3.3a, the total soluble Cr at the end of the experiment was slightly above the MCL. This finding motivated another set of experiments where electron donors were varied. When lactate was used as electron donor at 0.001 mol/l, both Cr(VI) and total soluble Cr approached zero by the end of the experiment, indicating minimal soluble Cr(III) (Figure 9.3.3a). Through the

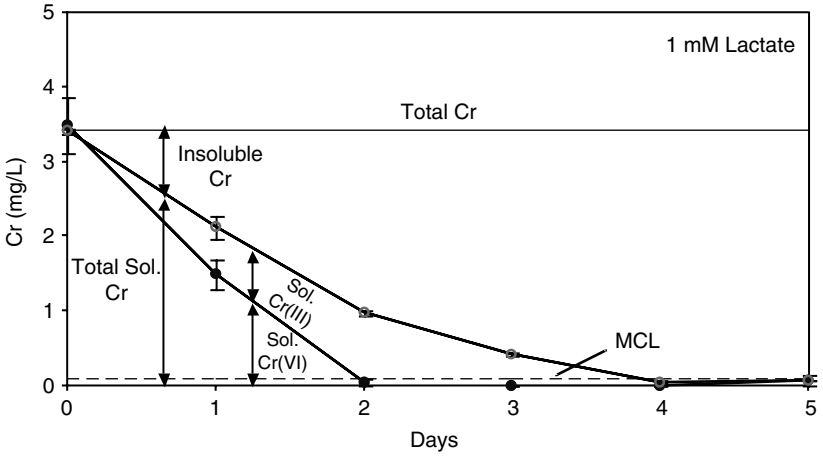

FIGURE 9.3.3A
Electron donor impacts the amount of Cr(III) that remains soluble following reduction of Cr(VI) to Cr(III) in microcosms containing Schoolcraft aquifer material. Soluble Cr(III) is the difference between total soluble Cr and soluble Cr(VI). Microcosms with lactate at 1 mM showed little Cr(III) left in soluble form.

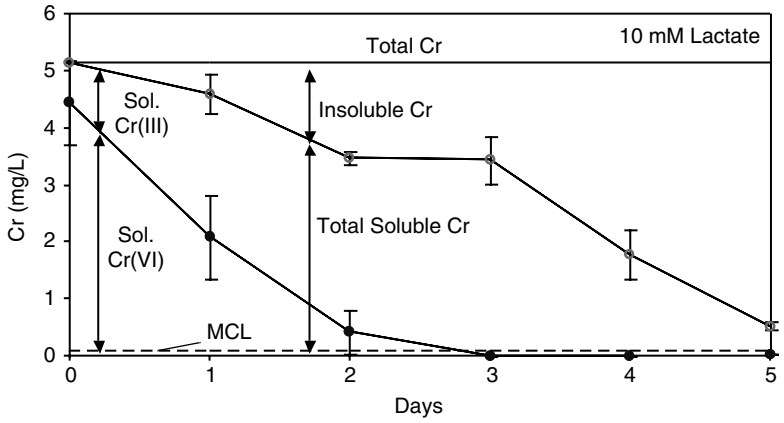

FIGURE 9.3.3B
Microcosms with lactate at 10 mM showed the final soluble [Cr(III)] to be above the MCL for total soluble Cr of 100 μg/L.

course of the experiment, some soluble Cr(III) seemed to be formed but precipitated out by day 4. However, when 0.01 mol/l lactate was used, the final soluble Cr concentration was 530 μg/l, well above the MCL (Figure 9.3.3b). Some Cr(III) remained soluble, presumably as a complex to lactate. As expected, this trend was most obvious when citrate was used as electron donor (Figure 9.3.3c), as it is known that citrate forms a complex with Cr(III). In the case of citrate, the

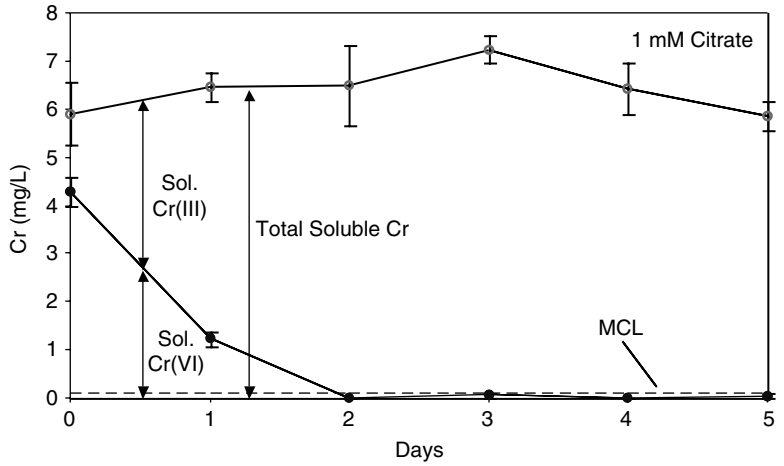

FIGURE 9.3.3C
Citrate caused the majority of Cr(III) to remain in soluble form throughout the experiment (9.3.3C). Values are the average of duplicates and error bars represent the range. (Σ), soluble Cr(VI); (o), total soluble Cr; (__), total Cr; (---), MCL.

total soluble Cr levels were well above the amount of Cr(VI) that was added to the microcosm. This is presumably owing to chromium in the sediment. Acetate at 0.001 and 0.01 mol/l, as well as palmitic acid beads (a source of slow release hydrogen) showed little soluble Cr(III) formation throughout the duration of the experiment (data not shown). These observations are important for bioremediation of Cr(VI) because the USEPA MCL is measured in terms of *total* soluble Cr, including both soluble Cr(VI) and Cr(III). In addition, it should be noted that bioremediation strategies based on the addition of large amount of fermentable organic carbon, such as molasses or vegetable oil, are likely to produce organic acids such as lactate that can potentially chelate and solubilize Cr(III).

9.3.4 Conclusions

Many electron acceptors are present in contaminated systems and often vary spatially and with time. Although NO_3^- has a half-reaction reduction potential that is comparable to Cr(VI), Schoolcraft organisms are able to reduce Cr(VI) while reducing NO_3^-. That native microflora from Plume G can reduce Cr(VI) in environments containing NO_3^- bodes well for bioremediation of Cr(VI) at the site. A pilot scale bioremediation scheme is currently operating at the Schoolcraft site to remove both chlorinated solvents and Cr(VI) using a biocurtain. Because neither NO_3^- nor chlorinated solvents (data not discussed here) prevented Cr(VI) reduction, the bioremediation scheme can operate as a one-step process. Lactate, used as carbon and energy source, is kept at a low enough concentration that Cr(III) does not appear to remain soluble following reduction of Cr(VI) to Cr(III).

Acknowledgments

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