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Kinetics of Chromium (VI) Reduction by Ferrous Ion

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AMARILLO NATIONAL RESOURCE CENTER FOR PLUTONIUM/
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A Report on

Kinetics of Chromium (VI) Reduction by Ferrous Iron

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Abstract

Chromium is a primary inorganic contaminant of concern at the Pantex Plant. Chromium concentrations have been found to be two orders of magnitude higher than the drinking water standards, particularly in certain wells in the perched aquifer below Zone 12.

In situ reduction of a mobile form of chromium, Cr(VI) to an immobile form, Cr(III), was examined as a viable option to active soil restoration. Successfully immobilizing chromium in the vadose zone as Cr(III) will reduce the amount of chromium that reaches the groundwater table.

The results from the solution experiments indicated that chromium was rapidly and stoichiometrically reduced by Fe(II) in solution. Also, the slurry experiments showed that the aquifer solids removed Fe(II) from solution, but a portion of the iron removed remained available for reaction with Cr(VI), but at a slower rate.

A model to predict different amounts of iron pseudo-components was developed, which allowed prediction of iron amounts required to reduce chromium under in situ conditions.

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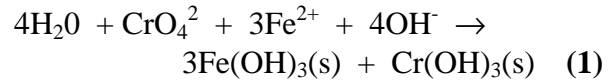
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1. INTRODUCTION

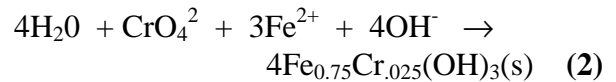
Chromium is a primary inorganic contaminant of concern at the Pantex Plant site. Chromium concentrations have been found to be two orders of magnitude higher than the drinking water standard, particularly in the some wells in the perched aquifer below Zone 12.

Oxidation states of chromium range from -2 to +6 (Fendorf and Zasoski, 1992), but only the +3 and +6 states are stable under most natural water environments. Cr(VI) is known to be more toxic to humans, animals, and plants, and is more mobile in the environment than Cr(III) (Moore and Ramamoorthy, 1984; Richard and Bourg, 1991). Conversely, Cr(III) is less toxic and readily precipitates as Cr(OH)₃ or as the solid solution Fe_xCr_{1-x}(OH)₃ under alkaline or even slightly acidic conditions (Rai et al., 1987). Therefore, reduction of Cr(VI) to Cr(III) is a viable option to remediate sites contaminated with Cr(VI). Fe(II) is a commonly used reductant for Cr(VI) in wastewater treatment. Cr(VI) reduction by Fe(II) is also of interest because Fe(II) is found in various types of soils and is a primary electron donor in subsurface environments. Fe(II) can be released from primary silicates and oxides, such as muscovite and biotite, and secondary layer silicates, such as vermiculite, illite, smectites, and chlorite (Eary and Rai, 1989). Cr(VI) reduction by Fe(II) near neutral pH to produce their separate hydroxide solids can be

described by the following stoichiometric reaction:



Cr(VI) reduction by Fe(II) is reported to be very rapid and stoichiometric in solution (Eary and Rai, 1988; Fendorf and Li, 1996). It is also reported to lead to the formation of a mixed iron/chromium solid solution of the form Fe_xCr_{1-x}(OH)₃ (Rai et al., 1987). When Fe(III) is produced solely from the stoichiometric reaction with chromate, the value of x is 0.75.



However, little is known about how Fe(II) reduces chromate in the presence of soils or other solid materials. Therefore, experimental studies were conducted to evaluate the ability of Fe(II) to reduce Cr(VI) under conditions found in the perched aquifer under the Pantex Plant. Kinetics of chromium reduction were investigated because we suspected that the reaction would be retarded in the presence of aquifer materials by adsorption, oxidation, or other surface reactions. Simultaneously, equilibrium aspects of the reaction were also examined to predict the amounts of Fe(II) required to effectively reduce Cr(VI). Finally, kinetic and equilibrium aspects of chromium reduction by Fe(II) were modeled to describe the chromium remediation process and provide a tool for designing remediation processes.

2. MATERIALS AND METHODS

2.1 Materials

The aquifer solids were collected from well PTX06-1012, which is located at the southern boundary of the Pantex Plant west of Zone 12. Elevated chromium concentrations have not been observed in the vicinity of this well. The aquifer solids were air-dried and screened to particle sizes below 0.25 mm. There were no efforts taken during collection, storage, drying or sieving of the aquifer solids to maintain the redox state they had when in-situ.

Measured amounts of $K_2CrO_4(s)$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O(s)$ were dissolved in deionized water and used as the sources of Cr(VI) and Fe(II), respectively. The water used for Fe(II) stock solution was deoxygenated with nitrogen gas. Artificial groundwater was used in all experiments to provide a condition similar to the perched aquifer. Major inorganic species were chosen from observations of well PM-20 data from 1985 through 1994. The composition of the artificial groundwater is described in Table 1.

2.2 Experimental Methods

All experiments were conducted in 1.0 liter glass filtering flasks. In the first solution experiment, artificial groundwater containing Cr(VI) was initially deoxygenated with

nitrogen gas and the pH of the solution was adjusted to pH 8.3 by adding 1N NaOH and 0.1 N NaOH. When the acidic Fe(II) stock solution was added, the pH moved to near pH 7.5. Samples of 20 mL were taken at times 10s, 2, 6.4, 11, 15, and 20 min after addition of the iron solution. The samples were filtered through 0.45 μ m nitrocellulose membrane filters, acidified, and analyzed for total chromium. It should be noted that siderite ($FeCO_3$) can precipitate in this system whenever the Fe(II) concentration is above 0.27 mg/l. This calculation assumes that the bicarbonate concentration is the same as the alkalinity and uses an equilibrium coefficient (K_s^*) of 1.995 (Stumm and Morgan, 1981) with the following stoichiometric equation:



A second solution experiment was conducted to ensure that the addition of a concentrated Fe(II) stock solution with low pH was not biasing reduction kinetics due to low pH values that occur in the vicinity of the Fe(II) solution before complete mixing. In this experiment, two 400 ml artificial groundwater solutions containing Fe(II) and

Table 1: Composition of the Artificial Groundwater Used in Reduction Experiments

Ion	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	Cl ⁻	HCO ₃ ⁻
Concentration (mg/l)	45.5	9.1	51.9	75.9 ^a	232.2 ^b	201.3 ^c

^aHigher than concentrations found in well PM-20 due to the contribution from alkalinity ($NaHCO_3$) addition.

^bHigher than concentrations found in well PM-20 because it was added as the anionic component of the cation reagents.

^cConcentration at pH 7.5. (165 mg/l as $CaCO_3$)

Cr(VI), respectively, were deoxygenated and the pH of Fe(II) solution was adjusted to 7.1 by adding 0.1 N NaOH and Cr(VI) to 7.8 by adding 1N and 0.1N H₂SO₄ solution. After the two solutions were mixed, samples of 20 ml were withdrawn at 1.5, 4.4, 10.6, 15, and 30 min and analyzed as described above. For both experiments, initial concentrations for Cr(VI) and Fe(II) were 2 mg/l and 9.66 mg/l (1.5 times the stoichiometric amount), respectively.

Two sets of experiments were carried out using aquifer solids in the slurry reactor. In these experiments, Fe(II) was first added and allowed to react with artificial groundwater containing aquifer solids for 24 hours and then the Cr(VI) stock solution was spiked to yield a final concentration of 2 mg/l. The mixing of the slurries was provided by magnetic stirrers with 3 inch stirring bars. In the first set of the experiments, aquifer solids were added to the artificial groundwater at a 1% solid/solution ratio. Fe(II) was added at concentrations equivalent to 0, 1.5, 2.5, and 3.5 times the stoichiometric amounts required to reduce all of the chromium that would be added. Fe(II) concentrations were measured after the equilibration period but before addition of chromium. Additional samples were taken at up to 43 days after addition of chromium. These samples were filtered through 0.45 μ nitrocellulose membrane, acidified, and analyzed for total chromium, Fe(II), and total Fe. The solutions were maintained anoxic throughout the experiments with a gas mixture of nitrogen and carbon dioxide. The gas mixture consisted of

99.38% nitrogen and 0.62% carbon dioxide, which maintained the pH of the slurries near pH 7.5. The gas mixture was passed through deionized water before being delivered to the reactors.

A second set of slurry experiments was conducted with solid/solution ratio of 10% and Fe(II) concentrations that were 0, 3, 9, and 15 times the stoichiometric amount (calculated for conditions after chromium injection). Samples were treated by the same procedure used in 1% slurry experiments. Iron concentrations were measured for samples taken immediately before and one day after chromium addition. Total chromium concentrations were measured up to 6 days after chromium addition.

2.3 Analytical Methods

Total dissolved chromium concentrations were measured by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). The instrument used was a Hewlett Packard ICP-MS 4500 equipped with a Cetac standard sample introduction system that used a Direct Injection Nebulizer. Chromium was monitored at the atomic masses of 50, 52, and 53. The method detection limit for total dissolved chromium was 0.50 ppb.

Fe(II) and total Fe was measured colorimetrically by the Ferrozine method. Fe(III) concentration was determined by the difference between total Fe and Fe(II) concentrations. The method detection limit for Fe(II) was 0.02 mg/l.

3. RESULTS AND DISCUSSIONS

3.1 Removal of Chromium (VI) by Ferrous Iron in Solution

The solution experiments showed rapid and complete removal of Cr(VI) from solution with solution pH of 7.6. It should be noted that the experimental protocol of analyzing filtered samples for total chromium does not directly measure reduction of Cr(VI) to Cr(III). However, removal of chromium is very good evidence for this reduction, because of the high solubility of Cr(VI) and the low solubility of Cr(III), especially in the presence of Fe(III) at neutral pH.

The results from the first solution experiment showed that total dissolved chromium concentration was less than 20 $\mu\text{g/l}$ for all samples analyzed, with the earliest sample taken 10 seconds after addition of Fe(II). Similar results were observed in the second solution experiment. Chromium concentrations were obtained over a 30 minute period and are shown in Figure 1. The rapid removal of chromium observed here near neutral pH agrees with the results reported by other researchers. Eary and Rai (1988) reported that chromium reduction was

completed within the first 1 to 2 minutes with an Fe(II) dose of 0.67 stoichiometric amount. A closer examination of chromium reduction kinetics was recently conducted by Fendorf and Li (1996). Their study confirms that Cr(VI) reduction by Fe(II) in solution can be completed in a matter of seconds.

The speed with which chromium is removed indicates that kinetics will not be important in systems that remove Cr(VI) by solution reactions. Removal will be sufficiently fast for almost all applications. Furthermore, doses of Fe(II) near stoichiometric should be sufficient to remove chromium to very low levels.

However, rapid kinetics and stoichiometric Fe(II) doses may not apply to chromium removal in the presence of aquifer solids. Reactions with the solids could reduce the rate at which Fe(II) reacts with chromium or convert it to forms that are ineffective as reductants. Adsorption on solid surfaces or redox reactions with other oxidants in the solids are two potential reactions that could affect chromium removal by Fe(II) in these ways. The following section discusses the results from slurry experiments used to evaluate these potential reactions of Fe(II).

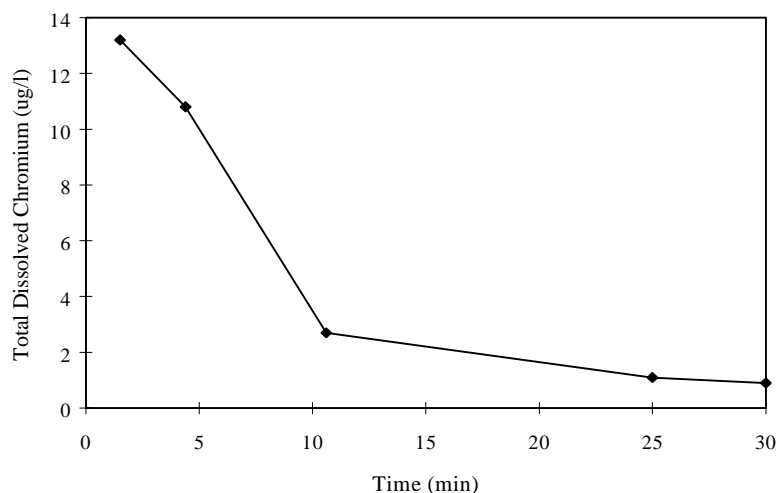


Figure 1: Total Dissolved Chromium Concentration After Fe(II) Addition in Second Solution Experiment (initial chromium concentration was 2000 $\mu\text{g/l}$, but is not shown on this figure)

3.2 Removal of Chromium (VI) by Ferrous Iron in the Presence of Aquifer Solids

The chromium data for slurry experiments with a 1% solid/solution ratio are tabulated in Table 4 in Appendix A and plotted in Figure 2. Fe(II) concentrations were below detection limits (0.02 mg/l) for all experiments shown in Figure 2 at 1% solid/solution ratio and sampling times less than 5 hours. Despite the low concentration of Fe(II) in solution, chromium was being removed. This indicates that although the aquifer solids remove Fe(II), at least a portion of it remains available for reaction, although at a much reduced rate compared to iron in solution. The removal of chromium appears rapid at first, but slows over time. Removal of iron from solution could be due to adsorption, oxidation or precipitation reactions.

Rainwater and Givens (1996) conducted experiments to determine the adsorption isotherms of Cr(VI) on aquifer solids taken from the same well as the solids used in this study. Linear partition coefficients of 0.40 and 0.36 l/kg for Cr(VI) were reported. Using the average value of the partition coefficient (0.38 l/kg), concentrations of chromium after 24 hours in reactors without added Fe(II) can be predicted to be 1.992 mg/l and 1.93 mg/l for the 1% and 10% slurry reactors, respectively.

These can be compared to the measured values of 1.986 mg/l and 1.717 mg/l. Therefore, similar results were obtained in both experiments, but the mechanism for removal have not been investigated. The extent to which removal of chromium in the absence of added Fe(II) is due to sorption, precipitation or redox reactions cannot be determined with current data.

The fact that complete removal of chromium was not obtained with iron doses well above stoichiometric indicates that a portion of the iron added to the reactors is not available for reaction with chromium.

For all three experiments with iron addition, some chromium was removed instantaneously, i.e. before the first sample was taken (1 minute). Subsequent removal was rapid, but slowed over time. However, when Fe(II) was not added, chromium was removed only by a slow reaction. The slow reaction with chromium indicates that aquifer solids have an intrinsic ability to remove Cr(VI). This may be due to formation of reactive sites on the solid by naturally occurring reductants such as Fe(II), organic matter, or sulfides (Bartlett, and Kimble, 1976; Boyko and Goodgame, 1986; Goodgame, Schroeder and Lee, 1975). It may also be due to sorption of Cr(VI) onto the surface without further reaction.

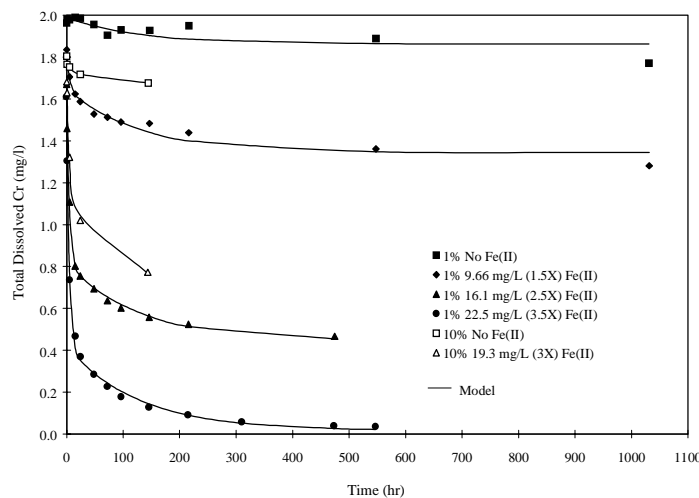


Figure 2: Changes in Chromium (VI) Concentration with Time in 1% Slurry Experiments

Figure 2 also shows the results from the slurry experiment conducted with 10% solid/solution ratio. The additional amounts of aquifer solids result in greater inhibition of chromium removal as indicated by the fact that the chromium concentrations in the reactor with iron doses 3 times stoichiometric and a 10% solid/solution ratio lie above those in the reactor with lower iron dose (2.5 times stoichiometric) and solid/solution ratio (1%). The higher solids concentration also resulted in higher amounts of chromium removed in the reactor which did not receive Fe(II), due to the intrinsic reduction capacity of the solids.

Additional experiments with a 10% solid/solution ratio were conducted with Fe(II) additions that were 9 and 15 times the stoichiometric amount, but they are not shown in Figure 2 because substantially all of the Cr(VI) was removed within 30 minutes. In these two reactors, dissolved iron was detected at two sampling times and the values are reported in Table 5 in Appendix A. The reactor with Fe(II) added at 15 times the stoichiometric amount had a concentration of Fe(II) of 3.37 mg/l after the equilibration period. This concentration is below the stoichiometric amount (6.44 mg/l) required to completely reduce a Cr(VI) concentration of 2.0 mg/l. A day after chromium addition, the concentration of Fe(II) was observed to be 0.44 mg/l, indicating that iron was being supplied to the solution in order to completely reduce the chromium and supply a residual concentration. Additional research is being planned to more fully understand the behavior of iron in this system.

3.3 Model for Kinetics of Chromium Removal

Experiments for chromium reduction by ferrous iron in the presence of aquifer solids show that removal kinetics are complex. Some chromium is removed before it is possible to sample the reactors. Removal

rates of chromium are gradually reduced over time. This may be due to the formation of different species of Fe(II) that react with chromium at different rates. The chemical form of these species is unknown, but they could be sorbed or precipitated. Regardless of their chemical form, the experimental results indicate that chromium is reacting with species at different rates. Therefore, a kinetic model was developed that describes removal of chromium by reaction with different types of iron at different first-order rates. The model contains four iron pseudo-components that are assumed to react with chromium instantaneously, rapidly, slowly, and not at all. Chromium removal can then be described by instantaneous, rapid, and slow reactions as shown by the following equation. The details of the model derivation are given in Appendix B.

$$C_{cr} = C_{cr,r}^0 \exp(-k_r t) + C_{cr,s}^0 \exp(-k_s t) + C_{cr,n}^0 \quad (4)$$

where:

C_{cr} = concentration of chromium in solution, (mg/l);

$C_{cr,r}^0, C_{cr,s}^0, C_{cr,n}^0$ = initial concentrations of chromium that reacts with the rapidly reacting iron pseudo-component and the concentration of chromium that reacts with the slowly-reacting pseudo-component, and the concentration of chromium that does not react, (mg/l);

k_r, k_s = first-order rate coefficients for rapid and slow reactions, (1/hr).

Non-linear regressions were conducted with the model and measured data to obtain values of the model coefficients. Values for k_r and k_s of 0.224 (1/hr) and 0.00783 (1/hr) were obtained. Values for initial concentrations of the types of chromium are given in Table 2.

The model predictions are shown in Figure 2 as lines with measured concentrations as symbols. Agreement of measurements with the model appears to be generally good. However, errors in the model predictions are not random but tend to follow the same pattern in each data set. The pattern indicates there are not just three different rates of chromium removal, but a spectrum of removal rates. However, modeling the distribution of rates by three distinct types is a reasonable balance between model complexity and accuracy. The concentrations of

chromium that react with the different iron species can be used to calculate the concentrations of the iron pseudo-components by using the reaction stoichiometry (Equation 1) which shows that 3.22 mg Fe(II) will reduce 1.0 mg Cr(VI). Therefore, if 1.0 mg/l of chromium is known to react rapidly ($C_{cr,r}^0 = 1.0$ mg/l) then the concentration of rapidly reacting iron ($C_{fe,r}$) is 3.22 mg/l. The details of these calculations are presented in Appendix B and the results are shown in Table 3.

Table 2: Concentration of Chromium Components Obtained from Nonlinear Regression

Exp.	Solid/Soln Ratio (%)	Iron Dose (mg/l)(stoich)	$C_{cr,r}^0$ (mg/l)	$C_{cr,s}^0$ (mg/l)	$C_{cr,n}^0$ (mg/l)	Error*
1	1	0 (0X)	0.000	0.127	1.863	0.0422
2	1	9.66 (1.5X)	0.182	0.305	1.344	0.0306
3	1	16.1 (2.5X)	0.806	0.369	0.445	0.0376
4	1	22.5 (3.5X)	1.105	0.400	0.017	0.0493
5	10	0 (0X)	0.058	0.083	1.649	0.0167
6	10	19.3 (3X)	0.559	0.542	0.592	0.0268

$$*\text{Standard estimate of the error} = \sqrt{\frac{\sum (C_{obs} - C_{model})^2}{N - 3}}$$

where:

C_{obs} = observed chromium concentration (mg/l)

C_{model} = chromium concentration predicted by the model (mg/l)

N = number of data for each experiment

Table 3: Concentration of Iron Components

Exp.	Solid/Soln Ratio (%)	Iron Dose (mg/l)(stoich.)	C _{fe,r} (mg/l)	C _{fe,s} (mg/l)	C _{fe,n} (mg/l)	C _{fe,i} (mg/l)
1	1	0 (0X)	0.000	0.408	0.000	0.035
2	1	9.66 (1.5X)	0.585	0.981	7.991	0.546
3	1	16.1 (2.5X)	2.596	1.188	11.537	1.222
4	1	22.5 (3.5X)	3.557	1.287	16.597	1.541
5	10	0 (0X)	0.188	0.267	0.000	0.675
6	10	19.3 (3X)	1.799	1.746	15.915	0.991

3.4 Prediction of Chromium Removal by Mixtures of Ferrous Iron and Aquifer Solids

A key part of developing a method for removing chromium by addition of Fe(II) is determining the amount of iron required. If the system does not contain appreciable solids, the amount required is near the stoichiometric amount (3.22 mg Fe/ mg Cr). However, if the system does contain aquifer solids, the required dose is above the stoichiometric amount and it appears to depend on both the amount of iron added and the amount of aquifer solids present. Application of iron reduction for in-situ remediation of a chromium-contaminated aquifer would be an application where the required iron dose would not be stoichiometric. A model has been developed that describes removal of chromium as occurring by reaction with different types of iron (instantaneously reacting, rapidly reacting, slowly reacting, and non-reacting).

This model could be used to calculate the amount of iron required to achieve any level of chromium removal if the concentrations of the iron species could be determined. Therefore, a model was developed that predicts the concentration of different iron pseudo-components as a function of the amount of solids present and the dose of Fe(II) added.

The model assumes that the concentration of each pseudo-component can be formed in two ways. One is similar to the formation of adsorbed phases. It depends both on the dose of Fe(II) and the amount of aquifer solids that are present. Another way pseudo-components are formed depends on the amount of aquifer solids that are present, but is independent of the iron dose. This mechanism describes the intrinsic capacity of aquifer solids to reduce chromium in the absence of external reductants. The model equations are shown below and the details of the model are described in Appendix B.

$$C_{fe,i} = K_{0,i}D + \frac{K_{p,i}DC_{fe}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D} \quad (5)$$

$$C_{fe,r} = K_{0,r}D + \frac{K_{p,r}DC_{fe}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D} \quad (6)$$

$$C_{fe,s} = K_{0,s}D + \frac{K_{p,s}DC_{fe}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D} \quad (7)$$

$$C_{fe,n} = K_{0,n}D + \frac{K_{p,n}DC_{fe}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D} \quad (8)$$

where:

$C_{fe,i}$, $C_{fe,r}$, $C_{fe,s}$, $C_{fe,n}$ = concentrations of iron pseudo-components that react instantaneously, rapidly, slowly, and not at all with Cr(VI), (mg/l);

$K_{0,i}$, $K_{0,r}$, $K_{0,s}$, $K_{0,n}$ = coefficients describing intrinsic pseudo-components that react instantaneously, rapidly, slowly, and not at all with Cr(VI), (mg/g);

$K_{p,i}$, $K_{p,r}$, $K_{p,s}$, $K_{p,n}$ = coefficients describing “sorption-like” mechanism forming pseudo-components that react instantaneously, rapidly, slowly, and not at all with Cr(VI), (l/g);

D = mass of solids in slurry per volume of solution, (g/l);

C_{fe}^0 = concentration of ferrous iron added to the solution, (mg/l).

The model coefficients ($K_{0,i}$, $K_{0,r}$, $K_{0,s}$, $K_{0,n}$, $K_{p,i}$, $K_{p,r}$, $K_{p,s}$, $K_{p,n}$) were obtained by least squares regression using calculated values of the concentrations of pseudo-components and are tabulated in Table 7 in

Appendix A. The regression was constrained to maintain all coefficients greater or equal to zero. This resulted in $K_{0,i}$ and $K_{0,r}$ being calculated as zero and $K_{0,n}$ calculated as a small value. To simplify the model, the value of $K_{0,n}$ was also set to zero.

The key use of the model is to predict the concentration of non-reacting iron, because this pseudo-component determines how much iron is required above the stoichiometric amount. Distribution of iron among the reactive pseudo-components will affect how fast reduction occurs, but not the final concentration of chromium.

Figure 3 shows the model predictions and the calculated values for the non-reactive iron component at various iron doses. Predictions for both 1% and 10% slurry experiments shown in Figure 3 are reasonable.

Calculation of iron doses required for chromium removal must also consider that aquifer materials can have an intrinsic ability to remove chromium in the absence of

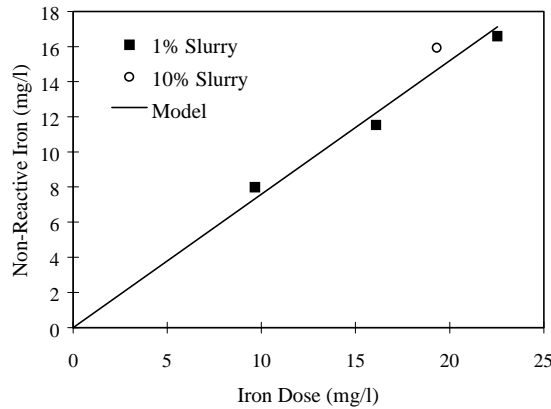


Figure 3: Model Prediction of Non-Reactive Iron Component

additions of Fe(II). The concentration of chromium that can be reduced is equal to the sum of the intrinsic reduction capacity of the solids plus the dose of Fe(II) minus the non-reactive iron formed in the system all divided by the stoichiometric ratio of Fe to Cr:

$$\text{Chromium Removal (mg/l)} = (C_{\text{fe,in}} + C_{\text{fe}}^0 - C_{\text{fe,n}}) / 3.22 \quad (9)$$

where:

$C_{\text{fe,in}}$ = intrinsic reduction capacity of the solids expressed in terms of the stoichiometrically equivalent concentration of Fe(II) (mg/l)

$C_{\text{fe,n}}$ = concentration of iron pseudo-component that does not react with Cr(VI), (mg/l).

Equation 9 was used to predict the amounts of chromium that would be reduced by different doses of Fe(II) using aquifer characteristics found at the well PTX06-1012. This is the source of the aquifer solids used in the slurry experiments. The mass of solids per volume of solution (D) can be calculated from the characteristics of the aquifer solids at

PTX06-1012 (dry density = 1.801 kg/l, porosity = 0.49). This results in $D = 3.69$ kg/l at in-situ conditions. Equations 8 and 9 can now be used to calculate the concentration of Cr(VI) that can be reduced for a given dose of Fe(II). The results are shown in Figure 4 and indicate that the aquifer solids have a substantial intrinsic reduction capacity. However, it should be noted that the intrinsic capacity of aquifer solids will have been consumed by Cr(VI) anywhere that significant concentrations of chromium are observed. Therefore, the intrinsic capacity of the solids cannot be expected to be important in typical cases of in-situ remediation. It should also be noted that the intrinsic capacity measured for the aquifer solids used in the slurry experiments may not be representative of the actual in-situ capacity. There was no attempt made to maintain the redox state of the aquifer solids during collection, storage or handling. It is possible that exposure of the solid to air may have resulted in some loss of the intrinsic reduction capacity of the material.

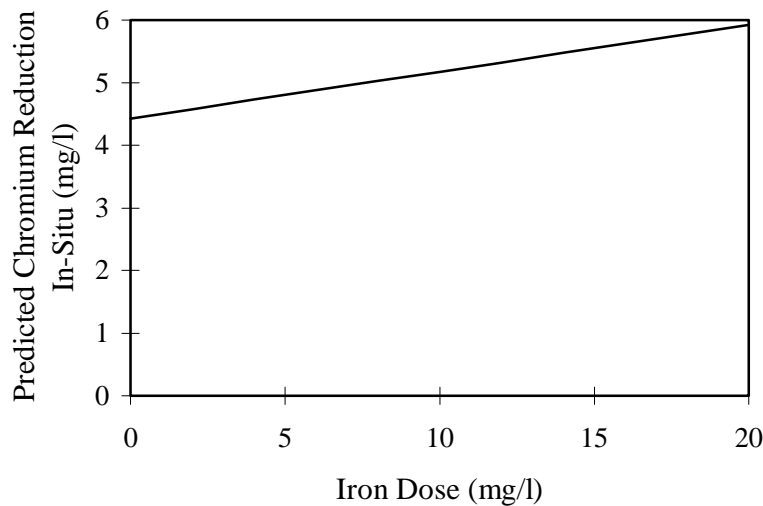


Figure 4: Prediction of Chromium Reduction by Fe(II) and Aquifer Solids at the Well PTX06-1012

4. SUMMARY AND CONCLUSIONS

The results from the solution experiments indicate that Cr(VI) is rapidly and stoichiometrically reduced by Fe(II) in solution. This means that application of iron reduction to chromium removal from groundwater or from ion exchange regenerant solutions will not be limited kinetically and only slightly more than stoichiometric amounts are necessary to achieve near complete removal.

The slurry experiments show that the aquifer solids remove Fe(II) from solution, but that a portion of the iron removed remains available for reaction with Cr(VI), although at a slower rate. The ability of the solids to develop a solid-phase reduction capacity from the Fe(II) added has implications for in-situ treatment of a contaminated aquifer. Fe(II) added to the aquifer will be removed, but will transfer a portion of its capacity to reduce Cr(VI) to the solids phase. Therefore, the solids will continue to reduce Cr(VI) even when groundwater flow carries additional Cr(VI) to the solids. The existence of subsurface zones of aquifer solids with the capacity to remove chromium will facilitate in-situ applications. Fe(II) could be injected down a well to produce a reactive zone and then the well could be used to extract the

groundwater. As the groundwater passes through the reactive zone, the chromium could be removed. Other methods could be developed to produce reactive zones as required by site conditions.

A pseudo-component model was developed to describe removal of chromium in systems with aquifer solids. The model describes chromium removal as occurring as the result of reaction of Cr(VI) with three types of iron – instantaneously reacting, rapidly reacting and slowly reacting. The model also describes the loss of reducing capacity of iron through production of non-reacting iron. The model generally is able to describe the removal of chromium in the slurry reactors well; however, the pattern of model errors indicates that mechanisms at work are more complex than those in the model.

A correlation model was also developed to predict the amount of different iron pseudo-components that will be produced by different doses of iron in the presence of different amounts of aquifer solids. This model allows prediction of the amount of Fe(II) required to reduce a given amount of chromium under in-situ conditions, if experiments are conducted on aquifer material that is representative of that found in the subsurface.

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Appendix A

Table 4: Changes in Chromium (VI) Concentration with Time in 1% Slurry Experiments

Time(hr)	Exp. 1 No Fe(II)	Time(hr)	Exp. 2 1.5X Fe(II)	Time(hr)	Exp. 3 2.5X Fe(II)	Time(hr)	Exp. 4 3.5X Fe(II)
0.02	1.963	0.02	1.836	0.02	1.670	0.02	1.612
0.5	1.982	0.5	1.800	0.5	1.459	0.5	1.304
5	1.978	5	1.705	5	1.108	5	0.737
15	1.989	15	1.624	15	0.802	15	0.465
24	1.986	24	1.588	24	0.755	24	0.368
48	1.956	48	1.528	48	0.694	48	0.284
72	1.905	72	1.513	72	0.637	72	0.227
96	1.930	96	1.490	96	0.602	96	0.177
146.7	1.928	146.5	1.483	145.9	0.558	145.8	0.127
216.3	1.950	216.1	1.439	215.8	0.524	215.6	0.091
547.6	1.889	547.3	1.362	474.4	0.467	310.2	0.058
1030.9	1.771	1031.25	1.281	-	-	474.0	0.0382
-	-	-	-	-	-	546.5	0.0355

Table 5: Dissolved Iron Concentration in 10% Slurry Experiments

Exp	After Fe(II) Equilibration with Aquifer Solids					1 Day After Chromium Injection				
	Iron Dose		Dissolved Iron (mg/l)			Iron Dose		Dissolved Iron (mg/l)		
	(Stoich.)	(mg/l)	Fe(II)	Fe(III)	Total	(Stoich.)	(mg/l)	Fe(II)	Fe(III)	Total
5	0.00	0.0	<D.L.*	<D.L.*	<D.L.*	0.0	0.0	<D.L.*	<D.L.*	<D.L.*
6	3.04	19.6	<D.L.*	<D.L.*	<D.L.*	3.0	19.3	<D.L.*	<D.L.*	<D.L.*
7	9.13	58.8	0.8	0.17	0.97	9.0	58.0	<D.L.	0.08	0.08
8	15.21	98.0	3.37	0.80	4.17	15.0	96.6	0.44	0.46	0.90

*Detection Limit (0.02 mg/l)

Table 6: Changes in Chromium (VI) Concentration with Time in 10% Slurry Experiments

Time(hr)	Exp. 5 No Fe(II)	Time(hr)	Exp. 6 3X Fe(II)	Time(hr)	Exp. 7 9X Fe(II)	Time(hr)	Exp. 8 15X Fe(II)
0.02	1.805	0.02	1.682	0.02	0.103	0.02	0.0054
0.50	1.766	0.50	1.630	0.52	0.014	0.50	0.0032
5.0	1.752	5.03	1.322	5.0	0.014	5.0	0.0030
24.0	1.717	24.0	1.020	24.0	0.013	24.0	0.0024
144.6	1.676	143.7	0.772				

Table 7: Coefficients for Chromium Reduction Model Obtained from Least Squares Regression

Ko,i (mg/g)	Ko,r (mg/g)	Ko,s (mg/g)	Ko,n (mg/g)	Kp,i (l/g)	Kp,r (l/g)	Kp,s (l/g)	Kp,n (l/g)
0.0	0.0	4.88E-3	0.0	1.23E+2	2.68E+2	1.24E+2	1.62E+3

Appendix B - Model Derivations

Model for Kinetics of Chromium Removal

Experiments for chromium reduction by ferrous iron in the presence of aquifer solids show that removal kinetics are complex. Chromium removal is rapid initially, and then gradually slows. It appears that a variety of iron species may be formed that react with chromium at different rates. Therefore, a kinetic model was developed that assumes that chromium is removed by reaction with a set of iron pseudo-components that react at different rates. Pseudo-components are assumed that react instantaneously, rapidly, slowly, and not at all. Chromium removal can then be described by an instantaneous, rapid, and slow reactions:

$$C_{cr} = C_{cr,r}^0 \exp(-k_r t) + C_{cr,s}^0 \exp(-k_s t) + C_{cr,n}^0$$

where:

C_{cr} = concentration of chromium in solution, (mg/l);

$C_{cr,r}^0, C_{cr,s}^0, C_{cr,n}^0$ = initial concentrations of chromium that reacts with the rapidly reacting iron pseudo-component and the concentration of chromium that reacts with the slowly-reacting pseudo-component, and the concentration of chromium that does not react, (mg/l);

k_r, k_s = first-order rate coefficients for rapid and slow reactions, (1/hr).

The measured chromium concentrations from each experiment were fitted to this model by non-linear regression to obtain values for $C_{cr,r}^0, C_{cr,s}^0, C_{cr,n}^0$ for each

experiment and set of values for k_r, k_s that apply to all experiments.

The concentrations of iron components were calculated from the results of the regressions for each experiment:

$$C_{fe,r} = 3.222 C_{cr,r}^0$$

$$C_{fe,s} = 3.222 C_{cr,s}^0$$

$$C_{fe,i} = 3.222(C_{cr}^0 - C_{cr,r}^0 - C_{cr,s}^0 - C_{cr,n}^0)$$

where:

$C_{fe,i}, C_{fe,r}, C_{fe,s}, C_{fe,n}$ = concentrations of iron pseudo-components that react with chromate instantaneously, rapidly, slowly, and not at all, (mg/l);

C_{cr}^0 = concentration of chromium added to the solution, (mg/l).

A material balance can be used to calculate the concentration of the iron pseudo-component that does not react with chromium, but the intrinsic reaction capacity of the solids before any iron is added must be considered. The intrinsic reduction capacity can be determined from experiments conducted without iron addition. The intrinsic reduction capacity is the sum of instantaneously, rapidly and slowly reacting iron in an experiment when no iron was added to the slurry:

$$C_{fe,n} = C_{fe}^0 + C_{fe,in} - (C_{fe,i} + C_{fe,r} + C_{fe,s})$$

$$C_{fe,in} = (C_{fe,i})_{zerodose} + (C_{fe,r})_{zerodose} + (C_{fe,s})_{zerodose}$$

Model for Chromium Removal By Mixtures of Ferrous Iron and Aquifer Solids

Experiments indicate that chromate is reduced by mixtures of iron and aquifer solids at different rates. Furthermore, not all of the ferrous iron added appears to retain its capacity to reduce chromate when mixed with solids. The fraction of iron added that can reduce chromate appears to depend on the dose of iron and the amount of solids present. Therefore, the results of the slurry experiments are not directly transferable to in-situ conditions. A pseudo-component speciation model was developed to provide a tool to make such predictions.

The model assumes that the concentration of each pseudo-component is composed of a term that is independent of the amount of iron present and a term that is proportional to the amount of iron present in solution. This is consistent with the assumption that there are components that have the ability to reduce chromate that are intrinsic to the aquifer solids (do not depend on addition of iron) and components produced by reactions with iron. The reaction mechanism is assumed to behave similarly to sorption. The intrinsic pseudo-components would exist at concentrations proportional to the amount of solids present (D) and independent of the dose of iron. The “sorption-like” mechanism would result in production of pseudo-components in proportion to the amount of solids present and the amount of soluble ferrous iron present (C_{fe}). The first term in each of the following equations represents the intrinsic pseudo-components and the second term represents the pseudo-components formed by the “sorption-like” mechanism. A linear sorption isotherm is assumed to describe the “sorption-like” mechanism.

$$C_{fe,i} = K_{0,i}D + K_{p,i}C_{Fe}D$$

$$C_{fe,r} = K_{0,r}D + K_{p,r}C_{Fe}D$$

$$C_{fe,s} = K_{0,s}D + K_{p,s}C_{Fe}D$$

$$C_{fe,n} = K_{0,n}D + K_{p,n}C_{Fe}D$$

where:

$C_{fe,i}$, $C_{fe,r}$, $C_{fe,s}$, $C_{fe,n}$ = concentrations of iron pseudo-components that react instantaneously, rapidly, slowly, and not at all with chromate, (mg/l);

$K_{0,i}$, $K_{0,r}$, $K_{0,s}$, $K_{0,n}$ = coefficients describing intrinsic pseudo-components that react instantaneously, rapidly, slowly, and not at all with chromate, (mg/g);

$K_{p,i}$, $K_{p,r}$, $K_{p,s}$, $K_{p,n}$ = coefficients describing “sorption-like” mechanism for forming pseudo-components that react instantaneously, rapidly, slowly, and not at all with chromate, (l/g);

D = mass of solids in slurry per volume of solution, (g/l);

C_{fe} = concentration of ferrous iron in solution, (mg/l).

A material balance on iron added can be made by assuming that all of the iron added forms a pseudo-component by the “sorption-like” mechanism or remains in solution as ferrous iron:

$$C_{fe}^0 = K_{p,i}C_{fe}D + K_{p,r}C_{fe}D + K_{p,s}C_{fe}DK_{p,n}C_{fe}D + C_{fe}$$

where:

C_{fe}^0 = dose of ferrous iron added to system, (mg/l).

This result can be rearranged to provide an equation for the concentration of ferrous iron in solution, which can be substituted into the defining relations for each pseudo-component to show how their formation depends on iron dose.

$$C_{fe,i} = K_{0,i}D + \frac{K_{p,i}DC_{fe}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D}$$

$$C_{fe,r} = K_{0,r}D + \frac{K_{p,r}DC_{fe}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D}$$

$$C_{fe,s} = K_{0,s}D + \frac{K_{p,s}DC_{fe}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D}$$

$$C_{fe,n} = K_{0,n}D + \frac{K_{p,n}DC_{fe}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D}$$

The coefficients ($K_{0,r}$, $K_{0,s}$, $K_{0,n}$, $K_{p,r}$, $K_{p,s}$, $K_{p,n}$) can be obtained by least squares regression using calculated values of the concentrations of pseudo-components.