



## Effects of ferrous iron and molecular oxygen on chromium(VI) redox kinetics in the presence of aquifer solids

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### Abstract

The kinetics and stoichiometry of the reduction of hexavalent chromium (Cr(VI)) with ferrous iron (Fe(II)) were examined in systems with and without aquifer solids. Cr(VI) reduction was rapid in the absence of solids, but demonstrated slower and more complex kinetics in the presence of aquifer solids. The aquifer solids removed Fe(II) from solution and a portion of the reducing capacity of Fe(II) was transferred to the aquifer solids. The solid phases were then able to continue to remove Cr(VI). This suggests in situ treatment of Cr(VI) by Fe(II) injection would be feasible in the aquifer environment. In general, re-oxidation of reduced chromium by molecular oxygen was not observed in our systems over time periods of nearly 1 year, suggesting that the potential for chromium solubilization under these oxidizing conditions will be low. An empirical model was developed to describe the reduction kinetics of Cr(VI) in the presence of solids. The model assumes that the reaction is brought about by pseudo-species of iron that react instantaneously, rapidly and slowly with Cr(VI). A fourth pseudo-species is assumed to be non-reactive. Model coefficients were determined by non-linear regression. The model was able to describe observed concentrations of chromium well, but analysis of model errors indicated the potential existence of a distribution of species with different reaction rates rather than just three distinct species. Another model was developed to predict concentrations of different pseudo-species depending on the total amount of Fe(II) added and the amount of aquifer solids present. This model assumed that pseudo-species

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could result from intrinsic characteristics of the aquifer solids as well as being formed by addition of Fe(II), which could sorb to the aquifer solids. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Chromium is a common metal found at contaminated sites. It is a contaminant of concern in groundwater at over 70% of US Department of Energy (DOE) facilities [1] and over 27 superfund sites for which Records of Decision were published before 1987 [2]. Oxidation states of chromium range from  $-2$  to  $+6$  [3], but only the  $+3$  and  $+6$  states are stable under most natural water environments [4,5]. Hexavalent chromium (Cr(VI)) is known to be more toxic to humans, animals, and plants, and is more mobile in the environment than trivalent chromium (Cr(III)) [4,5]. Conversely, Cr(III) is less toxic and readily precipitates as  $\text{Cr}(\text{OH})_3$  or as the solid solution  $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$  under alkaline or even slightly acidic conditions [6]. Therefore, reduction of Cr(VI) to Cr(III) is an option to remediate sites contaminated with Cr(VI).

One remediation method for chromium in groundwater involves injecting reducing agents into an aquifer to produce a reactive zone in which mobile Cr(VI) would be reduced to relatively immobile Cr(III). This remedial approach has been called In situ Redox Manipulation and has been evaluated at the laboratory, intermediate and field scales [7–10].

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 found in silicates and oxides, such as muscovite and biotite, and in secondary layer silicates, such as vermiculite, illite, smectites, and chlorite [11]. Cr(VI) reduction by Fe(II) in solution is reported to be very rapid, to be stoichiometric [12,13] and to lead to the formation of a mixed iron/chromium solid solution of the form  $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$  [5,6,12–14 (and references therein)]. When Fe(III) is produced solely from the stoichiometric reaction with chromate, the value of  $x$  is 0.75:



Previous studies report that Fe(II) can reduce Cr(VI) in contaminated soils or aquifer solids to precipitate Fe–Cr hydroxide [15,16]. In the present study, the Fe(II)-based remediation technology was tested using aquifer solids collected from the perched aquifer below the DOE Pantex Plant near Amarillo, TX. This plant covers over 16,000 acres and is the only facility in US for assembly and disassembly of nuclear weapons. Over the years, a number of activities at the plant have resulted in some contamination of the surface and subsurface environments. For example chromium has been identified as an inorganic contaminant of concern in the perched aquifer underneath the Pantex Plant Site [17]. The kinetics of chromium reduction were investigated because of the possibility that the reaction would be retarded in the presence of aquifer materials by adsorption, oxidation, or other surface reactions. Simultaneously, the stoichiometry of the reaction was also examined to predict the amounts of Fe(II) required to effectively reduce Cr(VI). In addition, although the present study demonstrates that Fe(II) can effectively reduce Cr(VI) under conditions found in the perched aquifer of

the Pantex Plant, any in situ remediation technique for Cr(VI) must consider the potential for subsequent re-oxidation of precipitated Cr(III), which could lead to mobilization of chromium as soluble Cr(VI). The most common naturally occurring oxidants of Cr(III) in soil–water systems are dissolved oxygen (DO) and manganese oxides. In subsurface environments, manganese oxides seem to be responsible for most oxidation of Cr(III), whereas the oxidation by dissolved oxygen is reported to be slow and limited [2,3,18,19].

Objectives of the present study were to: (1) investigate the kinetics of Cr(VI) reduction by Fe(II) in the presence of Pantex aquifer materials, (2) examine the stoichiometry of the aforementioned reaction to determine the amounts of Fe(II) required to effectively reduce Cr(VI), (3) examine the potential for Cr(III) re-oxidation by molecular oxygen in the presence of Pantex aquifer slurries in which Cr(VI) had been previously reduced by Fe(II), and (4) model the kinetic and equilibrium aspects of Cr(VI) reduction by Fe(II) to provide a tool for designing remediation processes.

## 2. Experimental

### 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 [17]. Elevated chromium concentrations in the perched aquifer 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 their original redox state. However, the perched aquifer is generally oxic, so major changes in redox state should not have occurred. Pertinent characteristics of the perched aquifer solids are listed in Table 1 [20].

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 sources of Cr(VI) and Fe(II), respectively. The water used for Fe(II) stock solution was deoxygenated with nitrogen gas (>99.99%). Artificial groundwater (AGW) was used in all experiments to provide a condition similar to the perched aquifer found beneath the Pantex Plant. The composition of AGW is described in Table 2.

### 2.2. Experimental methods

#### 2.2.1. Chromium reduction experiments

All experiments were conducted in 1.01 glass filtering flasks at room temperature ( $22 \pm 2$  °C). First, kinetics of Cr(VI) reduction by Fe(II) was characterized in AGW solutions.

Table 1  
Characteristics of the aquifer solids

Clay (%)	Silt (%)	Sand (%)	USCS classification	Void ratio	Bulk dry density (kg/l)	Cation exchange capacity (meq./g)	Organic carbon (mg/kg)
3.8	1.0	95.2	SM	0.49	1.81	0.034	6560

Table 2  
Composition of the artificial groundwater used in reduction experiments

Ion	Concentration (mg/l)
Ca <sup>2+</sup>	45.5
K <sup>+</sup>	9.1
Mg <sup>2+</sup>	51.9
Na <sup>+</sup>	75.9
SO <sub>4</sub> <sup>2-</sup>	11.2
Cl <sup>-</sup>	232
HCO <sub>3</sub> <sup>-</sup>	201

In the first solution experiment, AGW containing Cr(VI) was initially deoxygenated with nitrogen gas and the pH of the solution was adjusted to 8.3 by adding aliquots of 1.0 and 0.1N NaOH solutions. When the acidic Fe(II) stock solution was added, the pH decreased to about pH 7.5 and the final solution volume was 800 ml. Samples of 20 ml volume were taken at times 10 s, 2, 6.4, 11, 15, and 20 min after addition of the iron solution. The samples were filtered through 0.45  $\mu$ m nitrocellulose membrane filters, acidified, and analyzed for total dissolved chromium (TDCr). It should be noted that siderite (FeCO<sub>3</sub>) could precipitate in this system whenever the Fe(II) concentration is above 0.27 mg/l, assuming an equilibrium coefficient ( $C^*K_s$ ) of 1.995 mol/l [21] and that the bicarbonate concentration is the same as the alkalinity:



However, no precipitate was observed, presumably because the siderite precipitation reaction was much slower than the Cr(VI)–Fe(II) redox reaction and subsequent Cr(III)–Fe(III) precipitation.

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 high Fe(II) concentrations and/or low pH values that would occur in microenvironments in the vicinity of the spiked Fe(II) solution before complete mixing. In this second experiment, two 400 ml AGW solutions containing Fe(II) and Cr(VI), respectively, were deoxygenated and the pH of the Fe(II) solution was adjusted to 7.1 by adding 0.1N NaOH solution, and the pH of the Cr(VI) solution was adjusted to 7.8 by adding 1 and 0.1N H<sub>2</sub>SO<sub>4</sub> solutions. After the two solutions were mixed, samples of 20 ml were withdrawn at 1.5, 4.4, 10.6, 25, and 30 min and treated as was done in the first solution experiment. For both experiments, initial concentrations for Cr(VI) and Fe(II) were 2 and 9.66 mg/l (1.5 times the stoichiometric amount), respectively. The initial Cr(VI) concentration was chosen to be representative of the most contaminated groundwaters at the Pantex Plant.

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 AGW containing aquifer solids for 24 h before the Cr(VI) stock solution was spiked at a dose of 2 mg/l. The mixing of the slurries was provided by magnetic stirrers with 3 in. stirring bars. In the first set of the experiments, aquifer solids were added to the AGW at a solid/solution ratio of 1%. The final volume of the solution was 900 ml. Fe(II) was added at concentrations equivalent to 0, 1.5,

2.5, and 3.5 times the stoichiometric amounts (calculated for conditions after chromium injection) required to reduce all of the chromium that would be added. These doses were chosen to cover the range expected to be effective in removing Cr. Dissolved Fe(II) concentrations were measured after the equilibration period but before addition of chromium. Additional samples were taken up to 72 days after addition of chromium. These samples were treated as described in the solution experiments and analyzed for total chromium. The solutions were maintained anoxic throughout the experiments with a gas mixture of nitrogen (99.38%) and carbon dioxide (0.62%), 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 a solid/solution ratio of 10% and Fe(II) concentrations that were 0, 3, 9, and 15 times the stoichiometric amounts. These doses were chosen to cover the range expected to result in effective removal of Cr. Samples were treated by the same procedure used in the 1% slurry experiments. Dissolved Fe(II) concentrations were measured for samples taken immediately before and 1 day after chromium addition. TDCr concentrations were measured up to 52 days after chromium addition.

### 2.2.2. Chromium re-oxidation experiments

Cr(III) re-oxidation experiments were carried out at the room temperature using the same slurries used in the reduction experiments contained in the same reactors. Re-oxidation was initiated when substantial changes in TDCr concentrations were no longer observed in the reduction experiments. The re-oxidation experiments for 10% slurries with 0 and 3 times the stoichiometric Fe(II) were started 52 days after chromium addition in the reduction experiments; re-oxidation experiments for the other slurries were started 72 days after addition of chromium.

Initially, molecular oxygen was supplied to the reactors by aeration until the slurries were saturated with oxygen, which resulted in DO concentrations ranging from 8.6 to 8.8 mg/l. Then the reactors were capped with cotton plugs to allow the slurries to equilibrate with the atmospheric oxygen. DO concentrations of the slurries were maintained above 4.8 mg/l throughout the experiments. The pH values of the slurries were adjusted to 7.5 and did not vary more than  $\pm 0.25$  pH unit. The amount of water lost to evaporation was measured gravimetrically, and deionized water was added to make up for the loss before sampling. Mixing of the slurries initially was provided by magnetic stirrers with 3 in. stirring bars. The mixing intensity was set to keep all the solids suspended for an hour a day. Reactions were found to be very slow after 30 days, so the slurries were shaken intermittently by hand for 10 s after this initial period. TDCr concentrations of the solutions were measured before starting aeration and at appropriate intervals for about 10 months. Samples were treated by the same procedure used in the reduction experiments.

### 2.3. Analytical methods

TDCr concentrations were measured by inductively coupled plasma-mass spectroscopy (ICP-MS). The instrument used was a Hewlett-Packard ICP-MS 4500 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 TDCr was 0.50  $\mu\text{g/l}$ .

Samples were acidified to  $\text{pH} < 2$  and stored at  $4^\circ\text{C}$  before analysis.  $\text{Fe(II)}$  and total Fe were measured colorimetrically by the Ferrozine method as described previously [22,23]. The method detection limit for  $\text{Fe(II)}$  was  $0.03 \text{ mg/l}$ .

### 3. Results and discussion

#### 3.1. Removal of chromium(VI) by ferrous iron in solution

The solution experiments showed rapid and complete removal of  $\text{Cr(VI)}$  from solutions with a  $\text{pH}$  value of about 7.5. It should be noted that the experimental protocol of analyzing filtered samples for total chromium does not directly measure reduction of  $\text{Cr(VI)}$  to  $\text{Cr(III)}$ . However, decreasing TDCr concentration is very good evidence for this reduction, because of the high solubility of  $\text{Cr(VI)}$  and the low solubility of  $\text{Cr(III)}$ , particularly in the presence of  $\text{Fe(III)}$ , at neutral  $\text{pH}$  [6,12]. In the first solution experiment, the TDCr concentration decreased over two orders of magnitude (i.e. from  $2.0 \text{ mg/l}$  to below  $20 \mu\text{g/l}$ ) within 10 s after addition of  $\text{Fe(II)}$  (data not shown). Similar behavior was observed in the second solution experiment, suggesting that low  $\text{pH}$  values and high  $\text{Fe(II)}$  concentrations that occur in the vicinity of the spiked  $\text{Fe(II)}$  solution did not bias the reduction kinetics in the first solution experiment. Fig. 1 shows the log of TDCr concentrations in the second solution experiment as a function of time.

The rapid removal of chromium observed here near neutral  $\text{pH}$  agrees well with the results reported by other researchers [3,12–14 (and references therein)]. These experimental results indicate that kinetics will not be limiting in systems near  $\text{pH} 7$  that contain only soluble  $\text{Cr(VI)}$  and  $\text{Fe(II)}$ . Furthermore, doses of  $\text{Fe(II)}$  near stoichiometric should be sufficient to reduce chromium to very low levels. However, rapid kinetics and stoichiometric  $\text{Fe(II)}$  doses

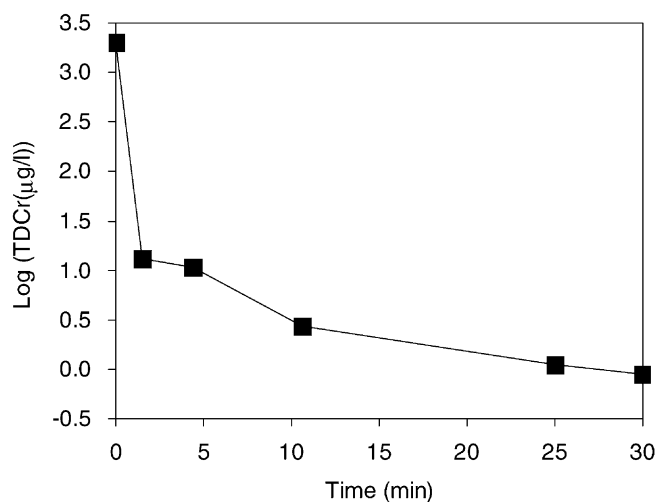


Fig. 1. Changes in  $\text{Cr(VI)}$  concentration after  $\text{Fe(II)}$  addition in the second solution experiment.

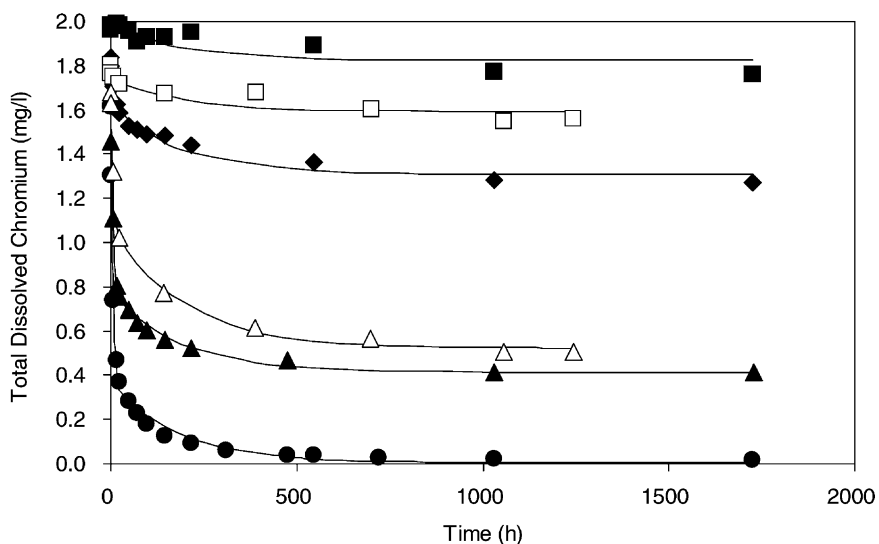


Fig. 2. Changes in Cr(VI) concentrations after addition of Fe(II) in the presence of aquifer materials: (■) 1% no Fe(II); (▲) 1% 16.1 mg/l (2.5×) Fe(II); (□) 10% no Fe(II); (◆) 1% 9.66 mg/l (1.5×) Fe(II); (●) 1% 22.5 mg/l (3.5×) Fe(II); (△) 10% 19.3 mg/l (3×) Fe(II); lines, predictions by the kinetic model.

may not apply to chromium removal in the presence of soils or aquifer solids. Reactions between Fe(II) and the solids could reduce the rate at which it reacts with chromium or they could 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 the slurry experiments used to evaluate these potential reactions of Fe(II).

### 3.2. Removal of chromium(VI) by ferrous iron in the presence of aquifer solids

TDCr concentrations observed in the slurry experiments are shown in Fig. 2. Dissolved Fe(II) concentrations were below detection limits (0.03 mg/l) for all results shown in Fig. 2. Despite the low concentration of Fe(II) in the solution, chromium was being removed, which indicates that some iron remains available for reaction, even though it has been removed from solution by the aquifer solids. However, Fig. 2 also shows that the rate of Cr(VI) reduction in the slurries is much slower than that observed for the reaction with iron in solution. Although the rate of Cr(VI) removal is initially rapid, it becomes much slower with time.

Rainwater and Givens [24] conducted experiments that measured removal of Cr(VI) from solutions in contact with the Pantex aquifer solids that were taken from the same well as the solids used in this study. They assumed that Cr(VI) removal was due to adsorption and used their results to calculate linear partition coefficients of 0.40 and 0.36 l/kg. Using the average value of these coefficients (0.38 l/kg), TDCr concentrations can be predicted to be 1.99 and 1.93 mg/l for the 1 and 10% slurry reactors without addition of Fe(II), respectively.

These predictions compare well with the values of 1.99 and 1.72 mg/l that were measured in the respective systems after 24 h. Note that although Cr(VI) removals were similar, the true mechanism(s) for Cr(VI) removal in our slurry systems without added Fe(II) cannot be determined merely by monitoring decreasing Cr(VI) solution concentrations. For example by extracting Cr(VI) from aquifer solids, Lee et al. [23] showed that 24 h was long enough for a small amount of Cr(VI) to be reduced by the material's intrinsic reduction capacity.

In the three 1% slurry experiments with iron addition, some chromium was removed nearly instantaneously, i.e. before the first sample was taken (1 min). 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 the formation of reactive sites on the solid by naturally occurring reductants, such as Fe(II), organic matter, or sulfides [18,25–27]. It may also reflect slow Cr(VI) sorption to the solids without subsequent chemical reaction.

Fig. 2 shows that additional amounts of aquifer solids result in greater inhibition of chromium removal by Fe(II). For example TDCr concentrations for a Fe(II) dose of 3 times the stoichiometric amount and a solid/solution ratio of 10% are higher than those for a solid/solution ratio of 1% and a Fe(II) dose 2.5 times the stoichiometric amount. Results of the 10% slurry experiments conducted with Fe(II) doses that were 9 and 15 times the stoichiometric amount are not shown in Fig. 2, because substantially all of the Cr(VI) was removed within 30 min. In these two experiments, dissolved Fe(II) was detected at two sampling times. For example the reactor with Fe(II) added at 15 times the stoichiometric amount had a Fe(II) concentration of 3.37 mg/l after equilibration with the aquifer solids, but before Cr(VI) was added. 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 0.44 mg/l, indicating that sufficient iron had been supplied to the solution to completely reduce the chromium and still provide a residual concentration in solution.

### 3.3. Re-oxidation potential of reduced chromium in the presence of aquifer solids

Fig. 3 shows TDCr concentrations for the Cr(III) re-oxidation experiments. Chromium concentrations for the 10% slurry experiments with Fe(II) doses at 9 and 15 times the stoichiometric amounts were all below the detection limit so they are not presented. Fig. 3 shows that Cr(III) was generally stable in the presence of oxygen for a period of almost 1 year.

Linear regressions were conducted on the data and the hypothesis was tested that the slopes were 0. Table 3 shows the results of the analysis. For the hypothesis to be rejected at the 5% significance level, the “*P*-value” would need to be less than or equal to 0.05. The hypothesis that the slope is 0 cannot be rejected for the first three experiments listed in Table 3. The hypothesis that the slope is 0 can be rejected for the experiments with 10% slurries, but the slopes are negative which means that there is a slight trend toward decreasing chromium concentrations. This is inconsistent with chromium re-oxidation, so these experiments also support the observation that slower oxidation is not occurring. The hypothesis that the slope is 0 can be rejected at the 5% significance level for the experiment



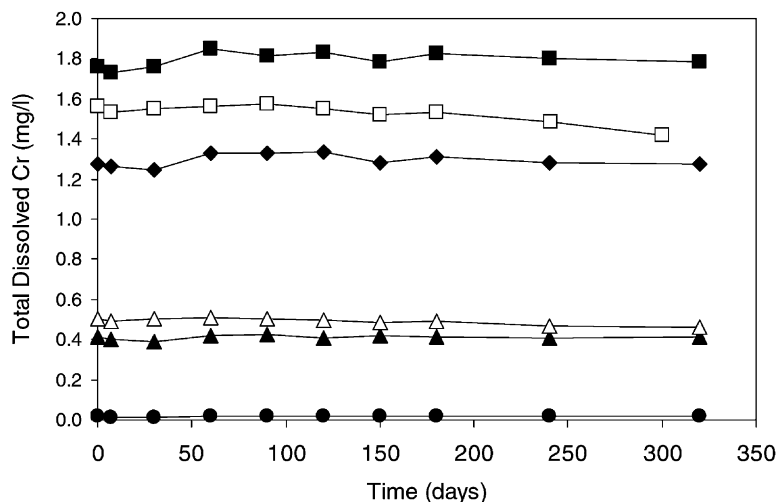


Fig. 3. Changes in Cr(VI) concentration with time in aerobic conditions: (■) 1% no Fe(II); (▲) 1% 16.1 mg/l (2.5×) Fe(II); (□) 10% no Fe(II); (◆) 1% 9.66 mg/l (1.5×) Fe(II); (●) 1% 22.5 mg/l (3.5×) Fe(II); (△) 10% 19.3 mg/l (3×) Fe(II).

with the 1% slurry and a Fe(II) dose 3.5 times the stoichiometric amount. However, even for this experiment the amount of Cr(III) being oxidized is very small ( $\sim 0.004$  mg/l year) and will likely not be significant in remediation applications. Our re-oxidation results generally support the idea that reducing Cr(VI) with Fe(II) in situ will immobilize it in subsurface systems even when more oxidizing conditions occur due to the input of atmospheric oxygen.

It has been reported that when Cr(III) is added to soils as  $\text{Cr}(\text{OH})_3$  that had been aged for 2 months, a very small amount of Cr(III) was oxidized [28]. This may help explain the behavior in the re-oxidation experiments, which began with relatively aged Cr(III) precipitates. However, the precipitates in our system were mixed chromium/iron hydroxides, rather than just chromium hydroxide. This also has implications for in situ reduction of chromium because the time needed for Cr(VI) reduction would generally be several months, during which time most of the precipitated chromium would become aged. However, it should be noted that manganese oxides in the aquifer materials might have been reduced

Table 3  
Summary of statistical analysis of chromium concentrations over time

Soil content (%)	Fe(II) dose (mg/l, stoichiometric amount)	Regression slope (mg/l/year)	<i>t</i> -Statistic	<i>P</i> -value
1	0	0.037	0.83	0.43
1	1.5	0.0083	0.21	0.84
1	2.5	0.0090	0.81	0.44
1	3.5	0.0043	4.90	0.0012
10	0	-0.14	-4.33	0.0025
10	3	-0.051	-4.78	0.0014

before the initiation of reduction experiments because no attempt had been made to maintain the redox state of the aquifer solids during collection, storage or handling. According to Bartlett and James [19,29], manganese oxides in fresh and moist soils maintain their capacity to oxidize Cr(III), whereas those in dried soils may lose their ability to oxidize Cr(III) because they are reduced in the drying procedure.

### 3.4. Model for kinetics of chromium(VI) removal

Experiments for Cr(VI) reduction by Fe(II) in the presence of aquifer solids show that removal kinetics are complex. Initial chromium reduction can be considered to be nearly instantaneous, because substantial removal occurs before it is possible to sample the reactors. After the initial sampling period, the rate of removal gradually slows with time. This may be due to the formation of different species of Fe(II) that react with chromium at different rates. The chemical forms of these species are unknown, but they could be sorbed or precipitated Fe(II) species. They may also be Fe(II) held in layered silicates [11,30]. Regardless of the chemical form of these species, the experimental results indicate that chromium is reacting with some reductants at different rates. Therefore, a kinetic model was developed that describes removal of chromium by reaction with different types of iron that react at different rates.

The model uses three iron pseudo-species that are assumed to react with chromium with rates that can be described as occurring instantaneously, rapidly, and slowly. The rapidly reacting and slowly reacting species are assumed to reduce Cr(VI) by first-order reactions. A fourth pseudo-species represents iron that does not react to reduce Cr(VI). This could represent Fe(II) that has reacted with oxidants such as molecular oxygen that could enter the experimental system though plastic tubing used to supply the purging gas.

The model calculates the total amount of chromium removed as the sum of the amounts removed by reaction with each pseudo-species:

$$C_{Cr} = C_{Cr,r}^0 \exp(-k_r t) + C_{Cr,s}^0 \exp(-k_s t) + C_{Cr,n}^0 \quad (3)$$

where  $C_{Cr}$  is the concentration of chromium in solution (mg/l) at sampling times greater than 0, i.e. after the instantaneous reaction occurs,  $C_{Cr,r}^0$  the initial concentration of chromium that will react with the rapidly reacting iron pseudo-species over the course of the experiment (mg/l),  $C_{Cr,s}^0$  the initial concentration of chromium that will react with the slowly reacting iron pseudo-species over the course of the experiment (mg/l),  $C_{Cr,n}^0$  the initial concentration of chromium that does not react (mg/l), and  $k_r$  and  $k_s$  are the first-order rate coefficients for rapid and slow reactions, respectively (1/h).

Non-linear least squares regressions were conducted using this model with the measured data to obtain values for model parameters ( $C_{Cr,r}^0$ ,  $C_{Cr,s}^0$ ,  $C_{Cr,n}^0$ ,  $k_r$ ,  $k_s$ ). Data presented in Fig. 2 were used in these regressions which were conducted using the “Solver” feature of an Excel spreadsheet. The values obtained for  $k_r$  and  $k_s$  were 0.20 (1/h) and 0.0054 (1/h), respectively. Values for initial concentrations of chromium reacting with the different iron pseudo-species are given in Table 4. The model predictions are shown in Fig. 2 as lines and measured concentrations are shown as symbols. Agreement of measurements with the model appears to be generally good. However, errors in the model predictions are not

Table 4  
Concentration of chromium species obtained from non-linear regression

Experiment	Solid/solution ratio (%)	Iron dose (mg/l, stoichiometric)	$C_{Cr,i}^0$ (mg/l) <sup>a</sup>	$C_{Cr,r}^0$ (mg/l)	$C_{Cr,s}^0$ (mg/l)	$C_{Cr,n}^0$ (mg/l)	Error <sup>b</sup>
1	1	0 (0×)	0.00850	0.000	0.168	1.82	0.0486
2	1	9.66 (1.5×)	0.169	0.201	0.323	1.31	0.0289
3	1	16.1 (2.5×)	0.383	0.839	0.365	0.413	0.0401
4	1	22.5 (3.5×)	0.485	1.15	0.362	0.00338	0.0553
5	10	0 (0×)	0.212	0.0410	0.155	1.59	0.0462
6	10	19.3 (3×)	0.309	0.592	0.575	0.524	0.0278

<sup>a</sup> Instantaneously reacting initial chromium concentration determined by difference.

<sup>b</sup> Standard estimate of the error =  $\sqrt{\frac{\sum(C_{obs}-C_{model})^2}{N-5}}$  where  $C_{obs}$  is the observed chromium concentration (mg/l),  $C_{model}$  the chromium concentration predicted by the model (mg/l), and  $N$  the number of data for each experiment.

random but tend to follow the same pattern in each data set. Measured concentrations tend to be below predictions at early times and greater than predictions at later times. This indicates that the model predicts rates that are too slow initially and too fast later. At very long times, the model again tends to over predict the measured concentrations, particularly at high solids concentrations. The model predicts that the concentrations should approach a constant value at very long times, but very slow reactions associated with aquifer solids may continue to remove chromium. This pattern indicates there may not be three discrete rates of chromium removal, but a continuum of removal rates. However, modeling the distribution of rates by three distinct types is a reasonable balance between model complexity and accuracy.

The change in concentrations of chromium that reacted with the different iron pseudo-species can be used to calculate the concentrations of the iron pseudo-species. This calculation uses the reaction stoichiometry given in Eq. (1). This equation predicts 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 ( $C_{Fe,r}$ ) that causes the reduction is 3.22 mg/l:

$$C_{Fe,r} = 3.22C_{Cr,r}^0 \quad (4)$$

$$C_{Fe,s} = 3.22C_{Cr,s}^0 \quad (5)$$

$$C_{Fe,i} = 3.22C_{Cr,i}^0 = 3.22(C_{Cr}^0 - C_{Cr,r}^0 - C_{Cr,n}^0) \quad (6)$$

where  $C_{Fe,i}$ ,  $C_{Fe,r}$ ,  $C_{Fe,s}$ , and  $C_{Fe,n}$  are the concentrations of iron pseudo-species that react with Cr(VI) instantaneously, rapidly, slowly and not at all, respectively (mg/l), and  $C_{Cr}^0$  is the concentration of chromium added to the solution (2 mg/l for the present study).

A material balance can be used to calculate the concentration of the iron pseudo-species that does not react with chromium ( $C_{Fe,n}$ ). However, first the long-term intrinsic capacity of the aquifer material to reduce or sorb chromium without addition of Fe(II) should be considered. The amount of iron pseudo-species associated with the long-term intrinsic removal capacity ( $C_{Fe,in}$ ) can be determined from experiments conducted without iron

Table 5  
Concentration of iron species<sup>a</sup>

Experiment	Solid/solution ratio (%)	Iron dose (mg/l, stoichiometric)	$C_{\text{Fe},i}$ (mg/l)	$C_{\text{Fe},r}$ (mg/l)	$C_{\text{Fe},s}$ (mg/l)	$C_{\text{Fe},n}$ (mg/l)
1	1	0 (0×)	0.0274	0.00	0.541	0.00
2	1	9.66 (1.5×)	0.544	0.647	1.04	8.00
3	1	16.1 (2.5×)	1.23	2.70	1.17	11.6
4	1	22.5 (3.5×)	1.56	3.70	1.17	16.7
5	10	0 (0×)	0.684	0.132	0.498	0.00
6	10	19.3 (3×)	0.996	1.91	1.85	15.9

<sup>a</sup>  $C_{\text{Fe},in}$  for 1 and 10% slurry experiments are 0.568 and 1.31 mg/l, respectively.

addition as the sum of instantaneously, rapidly and slowly reacting iron:

$$C_{\text{Fe},n} = C_{\text{Fe}}^0 + C_{\text{Fe},in} - (C_{\text{Fe},i} + C_{\text{Fe},r} + C_{\text{Fe},s}) \quad (7)$$

$$C_{\text{Fe},in} = (C_{\text{Fe},i})_{\text{zero dose}} + (C_{\text{Fe},r})_{\text{zero dose}} + (C_{\text{Fe},s})_{\text{zero dose}} \quad (8)$$

In Eq. (7),  $C_{\text{Fe}}^0$  is the dose of iron added to the reactor (mg/l).

The results of calculating the concentrations of iron pseudo-species are shown in Table 5. Table 5 shows that a significant fraction of iron added became non-reactive. This is believed mainly due to scavenging of Fe(II) by atmospheric oxygen that diffused into the system through plastic tubing. As such, it represents a characteristic of the experimental system used in the laboratory, not a characteristic of the aquifer material. Therefore, applications of Fe(II) reduction at larger scales should not observe such losses of reactive iron.

### 3.5. Prediction of chromium(VI) removal by mixtures of ferrous iron and aquifer solids

A key part of developing a method for removing chromium by addition of Fe(II) to contaminated soils and aquifers is determining the amount of iron required. In the absence of soil and oxidants other than Cr(VI), the amount required would be slightly larger than 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 appears to depend on both the amount of iron added and the solid/solution ratio. 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). In theory, 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 pseudo-species could be determined. Therefore, a model was developed that predicts the concentration of different iron pseudo-species 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-species 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 the ability of the solid

phase to reduce chromium is due in part to components of the aquifer material that have an intrinsic ability to reduce Cr(VI) (ability does not depend on addition of iron) and in part to production of components with the ability to reduce Cr(VI) (ability depends on addition of iron). The intrinsic pseudo-species are assumed to exist at concentrations proportional to the amount of solids present ( $D$ ) and to be independent of the dose of iron. The reaction that forms species with the ability to reduce Cr(VI) is assumed to behave similarly to sorption of Fe(II) onto aquifer solids. Therefore, “sorption-like” pseudo-species are assumed to be formed in proportion to the amount of solids present and the amount of soluble Fe(II) present ( $C_{\text{Fe}}$ ).

The first term in each of the following equations represents the intrinsic pseudo-species and the second term represents the pseudo-species formed by the “sorption-like” mechanism, which is assumed to be described by a linear sorption isotherm:

$$C_{\text{Fe},i} = K_{0,i}D + K_{p,i}C_{\text{Fe}}D \quad (9)$$

$$C_{\text{Fe},r} = K_{0,r}D + K_{p,r}C_{\text{Fe}}D \quad (10)$$

$$C_{\text{Fe},s} = K_{0,s}D + K_{p,s}C_{\text{Fe}}D \quad (11)$$

$$C_{\text{Fe},n} = K_{0,n}D + K_{p,n}C_{\text{Fe}}D \quad (12)$$

where  $K_{0,i}$ ,  $K_{0,r}$ ,  $K_{0,s}$ , and  $K_{0,n}$  are the coefficients describing intrinsic pseudo-species that react instantaneously, rapidly, slowly and not at all with Cr(VI), respectively (mg/g),  $K_{p,i}$ ,  $K_{p,r}$ ,  $K_{p,s}$ , and  $K_{p,n}$  the coefficients describing “sorption-like” mechanism for forming pseudo-species that react instantaneously, rapidly, slowly and not at all with Cr(VI), respectively (l/g),  $D$  the ratio of mass of solids in slurry to volume of solution (g/l), and  $C_{\text{Fe}}$  is the concentration of Fe(II) in solution (mg/l).

A material balance on iron added can be made by assuming that all of the iron added forms one of the pseudo-species by the “sorption-like” mechanism or remains in solution as Fe(II):

$$C_{\text{Fe}}^0 = K_{p,i}C_{\text{Fe}}D + K_{p,r}C_{\text{Fe}}D + K_{p,s}C_{\text{Fe}}D + K_{p,n}C_{\text{Fe}}D + C_{\text{Fe}} \quad (13)$$

where  $C_{\text{Fe}}^0$  is the dose of Fe(II) added to system (mg/l). This result can be rearranged to provide an equation for the concentration of Fe(II) in solution, which can be substituted into the defining relations for each pseudo-species to show how their formation depends on iron dose:

$$C_{\text{Fe},i} = K_{0,i}D + \frac{K_{p,i}DC_{\text{Fe}}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D} \quad (14)$$

$$C_{\text{Fe},r} = K_{0,r}D + \frac{K_{p,r}DC_{\text{Fe}}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D} \quad (15)$$

$$C_{\text{Fe},s} = K_{0,s}D + \frac{K_{p,s}DC_{\text{Fe}}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D} \quad (16)$$

$$C_{\text{Fe},n} = K_{0,n}D + \frac{K_{p,n}DC_{\text{Fe}}^0}{1 + K_{p,i}D + K_{p,r}D + K_{p,s}D + K_{p,n}D} \quad (17)$$

Table 6  
Coefficients for chromium reduction model obtained from least squares regression

$K_{0,i}$ (mg/g)	$K_{0,r}$ (mg/g)	$K_{0,s}$ (mg/g)	$K_{0,n}$ (mg/g)	$K_{p,i}$ (mg/g)	$K_{p,r}$ (mg/g)	$K_{p,s}$ (mg/g)	$K_{p,n}$ (mg/g)
0.0	0.0	7.58E-3	0.0	1.23E+2	2.80E+2	1.12E+2	1.62E+3

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-species and are shown in Table 6. The regression was constrained to maintain all coefficients greater or equal to 0. This resulted in  $K_{0,i}$  and  $K_{0,r}$  being calculated as 0 and  $K_{0,n}$  calculated as a small value. To simplify the model, the value of  $K_{0,n}$  was also set to 0.

The primary use of this model is to predict the concentration of non-reacting iron, because this pseudo-species determines how much iron is required above the stoichiometric amount in the experimental system studied. Distribution of iron among the reactive pseudo-species will affect how fast reduction occurs, but will not affect the final concentration of chromium. Fig. 4 shows the model predictions and the calculated values for the non-reactive iron species at various iron doses. The large measured and predicted values of non-reactive iron are believed to be due to loss of iron by reaction with atmospheric oxygen during the experiments. However, the good fit shown in Fig. 4 indicates that the modeling approach is able to predict the effects of iron dose and solids concentration on the concentration of non-reactive iron, even when it is higher than would be expected in larger-scale experiments where oxygen entry is reduced.

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 additions of

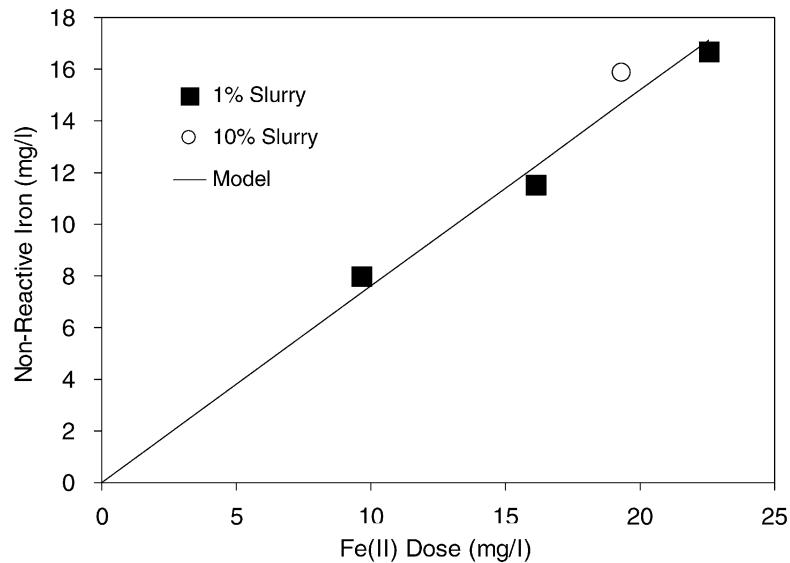


Fig. 4. Model prediction of non-reactive iron pseudo-species.

Fe(II). The maximum 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(II) to Cr(VI):

$$\text{chromium removal (mg/l)} = (C_{\text{Fe,in}} + C_{\text{Fe}}^0 - C_{\text{Fe,n}})/3.22 \quad (18)$$

where  $C_{\text{Fe,in}}$  is the intrinsic reduction capacity of the solids expressed in terms of the stoichiometrically equivalent concentration of Fe(II) (mg/l), and  $C_{\text{Fe,n}}$  is the concentration of iron pseudo-species that does not react with Cr(VI) (mg/l).

Eq. (18) was used to predict the amounts of chromium that would be reduced by different doses of Fe(II). These calculations used values for bulk dry density and void ratio reported for samples taken near where the aquifer materials used in these experiments were obtained (Table 1). This results in the calculation of the mass of solids per volume water ( $D$ ) of 3.69 kg/l at conditions in the aquifer. Eqs. (17) and (18) 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 Fig. 5 and they 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 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.

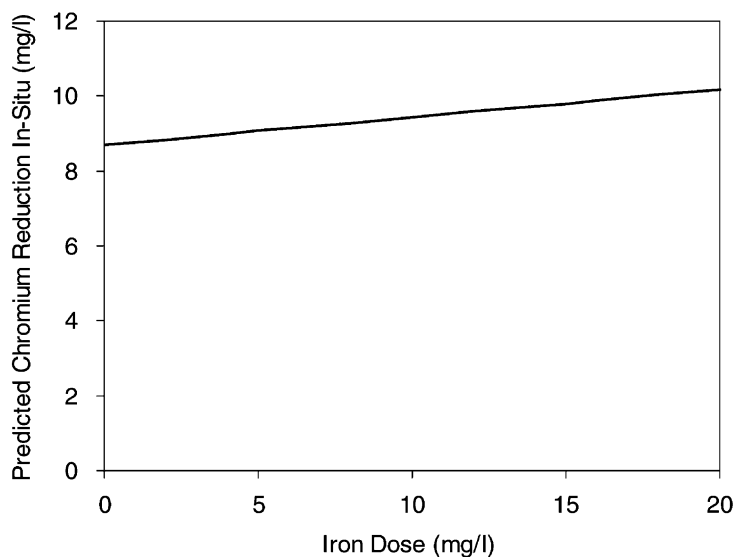


Fig. 5. Prediction of chromium reduction by Fe(II) under in situ conditions.

#### **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 wastewaters will not be limited kinetically and only slightly more than stoichiometric amounts are necessary to achieve near complete removal.

The slurry reduction experiments show that the aquifer solids remove Fe(II) from solution, but that only a portion of the iron removed remains available for reaction with Cr(VI) and that this reaction is much slower than observed for the reaction with iron in solution. The ability of the solids to develop the capacity for Cr(VI) reduction from the Fe(II) that was added has implications for in situ treatment of a contaminated aquifer. Fe(II) added to the aquifer will be removed, but it will transfer a portion of its capacity to reduce Cr(VI) to the solid 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. Reduction of soils by dithionite has been shown to increase reductive capacity of the soils for Cr(VI) [9,10,23].

Re-oxidation experiments suggest that once chromium is reduced in the perched aquifer, it will not be significantly solubilized under oxidizing conditions that would be caused by input of atmospheric oxygen. In fact, some evidence was observed for decreases in chromium concentration that could be caused by reduction of Cr(VI), even after oxidizing conditions were imposed. However, this conclusion is limited by the potential loss of oxidizing capacity of manganese oxides during soil storage prior to the experiments.

A pseudo-species 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 describes 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 assumed in the model.

A correlation model was also developed to predict the amount of different iron pseudo-species 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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