

Redox Kinetics of Chromium(VI) in the Presence of Aquifer Materials Amended with Ferrous Iron

Inseong Hwang* · Bill Batchelor**

*En3 Co., Ltd., Seoul, Korea (ihwang@en3kr.com),

**Civil Engineering Department, Texas A&M University, College Station, Texas, USA
(bill-batchelor@tamu.edu)

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 one year.

Key words: Chromium(VI); Ferrous Iron; Redox Kinetics; Aquifer Solids; Remediation

1. INTRODUCTION

Chromium is a common metal found at contaminated sites. 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). Previous studies report that Fe(II) can reduce Cr(VI) in contaminated soils or aquifer solids to precipitate Fe-Cr hydroxide.^{(1),(2)} 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, Texas.

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 above reaction to determine the amounts of Fe(II) required to effectively reduce Cr(VI), and (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).

2. MATERIALS AND METHODS

The aquifer solids were air-dried and screened to particle sizes below 0.25 mm. Artificial groundwater (AGW) was used in all experiments to provide a condition similar

to the perched aquifer found beneath the Pantex Plant.

All experiments were conducted in 1.0 liter glass filtering flasks at room temperature. First, kinetics of Cr(VI) reduction by Fe(II) was characterized in AGW solutions. 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 0.1 N NaOH solution, and the pH of the Cr(VI) solution was adjusted to 7.8 by adding 1 N and 0.1 N H₂SO₄ solutions. After the two solutions were mixed, samples of 20 mL were withdrawn at 1.5, 4.4, 10.6, 25, and 30 min. The samples were filtered through 0.45- μ m nitrocellulose membrane filters, acidified, and analyzed for total dissolved chromium (TDCr).

Two sets of experiments were carried out using aquifer solids in the slurry reactor. In the first set of the experiments, aquifer solids were added to the AGW at a solid/solution ratio of 1%. 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. Samples were taken up to 72 days after addition of 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. 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. TDCr concentrations were measured up to 52 days after chromium addition.

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. Initially, molecular oxygen was supplied to the reactors by aeration until the slurries were saturated with oxygen. Then the reactors were capped with cotton plugs to allow the slurries to equilibrate with the atmospheric oxygen. TDCr concentrations of the solutions were measured before starting aeration and at appropriate intervals for about 10 months.

3. RESULTS AND DISCUSSION

3.1 Chromium Reduction Experiments

The solution experiments showed rapid and complete removal of Cr(VI) from solutions with a pH value of about 7.5. In the solution experiment, the TDCr concentration decreased over two orders of magnitude (i.e. from 2.0 mg/L to below 20 g/l) within 10 seconds after addition of Fe(II).

TDCr concentrations observed in the slurry experiments are shown in Fig. 1. Dissolved Fe(II) concentrations were below detection limits (0.03 mg/l) for all results shown in Fig. 1. Figure 1 shows that the rate of Cr(VI) reduction in the slurries is much slower than that observed for the reaction with iron in solution. In systems containing Fe(II), the rate of Cr(VI) removal is initially rapid and becomes much slower with time. However, when Fe(II) was not added, chromium was removed only by a slow reaction. Fig. 1 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 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. 1, because substantially all of the Cr(VI) was removed within 30 minutes.

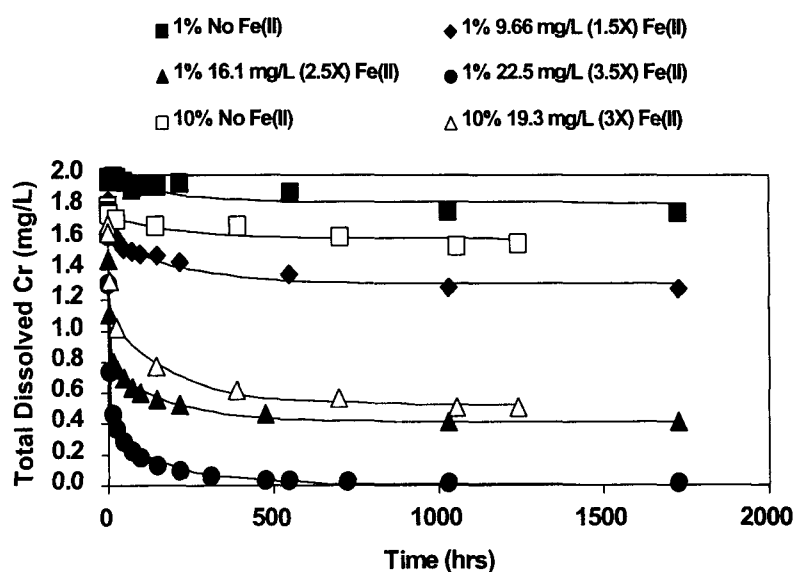


Fig. 1. Changes in Cr(VI) concentrations after addition of Fe(II) in the presence of aquifer materials.

3.2 Reoxidation Potential of Reduced Chromium in the Presence of Aquifer Solids

Fig. 2 shows that Cr(III) was generally stable in the presence of oxygen for a period of almost one year. Linear regressions were conducted on the data and the hypothesis was tested that the slopes were zero. Table 1 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 zero cannot be rejected for the first three experiments listed in Table 1. The hypothesis that the slope is zero 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 zero can be rejected at the 5% significance level for the experiment 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 (~ 0.004 mg/l-yr) 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.

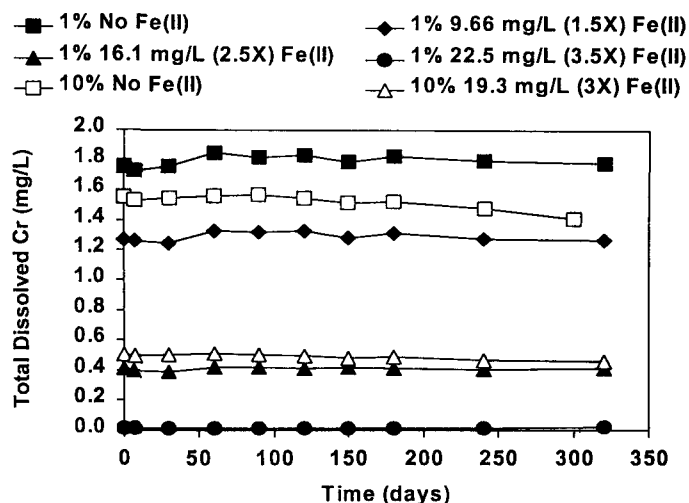


Fig. 2. Changes in Cr(VI) concentration with time in aerobic conditions.

Table 1. Summary of statistical analysis of chromium concentrations over time

Soil content(%)	Fe(II) dose (mg/l, stoichiometric amount)	Regression slope (mg/l)	t-statistic	P-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

4. 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. 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.

5. REFERENCES

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