Micron-Size Zero-Valent Iron Emplacement in Porous Media Using Polymer Additives: Column and Flow Cell Experiments

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Abstract. At the Hanford Site, an extensive In Situ Redox Manipulation (ISRM) permeable reactive barrier was installed to prevent chromate from reaching the Columbia River. However, chromium has been detected in several wells, indicating a premature loss of the reductive capacity in the aquifer. Laboratory experiments have been conducted to investigate whether barrier reductive capacity can be enhanced by adding micron-scale zero-valent iron to the high-permeability zones within the aquifer using shear-thinning fluids containing polymers. Porous media were packed in a wedge-shaped flow cell to create either a heterogeneous layered system with a high-permeability zone between two low-permeability zones or a high-permeability channel surrounded by low-permeability materials. The injection flow rate, polymer type, polymer concentration, and injected pore volumes were determined based on preliminary short- and long-column experiments. The flow cell experiments indicated that iron concentration enhancements of at least 0.6% (w/w) could be obtained using moderate flow rates and injection of 30 pore volumes. The 0.6% amended Fe^0 concentration would provide approximately 20 times the average reductive capacity that is provided by the dithionite-reduced iron in the ISRM barrier. Calculations show that a 1-m-long Fe^0 amended zone with an average concentration of 0.6% w/w iron subject to a groundwater velocity of 1 m/day will have an estimated longevity of 7.2 years.

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1. Introduction

At the Hanford Site, chromate-rich water leaked into the soil and contaminated the groundwater. In 1995, a plume of dissolved hexavalent chromium [Cr(VI)] was discovered along the Columbia River shoreline and in the 100-D Area. Between 1999 and 2003, an In Situ Redox Manipulation (ISRM) barrier was installed to prevent chromate from reaching the Columbia River. The ISRM technology involves creation of a treatment zone within an aquifer by injection of chemicals to alter the redox potential. The Hanford Site barrier consists of 65 injection wells spaced across a 680-m section near the Columbia River. The reduction of ferric iron to ferrous [Fe(II)] iron provides the primary capacity to remove Cr(VI) from the groundwater as it flows through the treatment zone under natural flow conditions. Treatment of chromium contaminated groundwater occurs through reduction of chrome from the mobile hexavalent state to relatively immobile and less toxic trivalent state.

Initial field and laboratory tests indicated that the Hanford ISRM barrier should have maintained its reductive capacity for approximately 20 years in the presence of < 2 mg/L chromate and dissolved oxygen in the groundwater. Szecsody et al. (2005) showed that the presence of a widespread 60 mg/L nitrate plumed reduces the barrier longevity to about 7 to 10 years. However, less than three years after sodium dithionite injection, chromium concentrations in some of the wells increased, indicating that the treated aquifer has been losing its reductive capacity. In 2002, some barrier wells were re-injected with sodium dithionite to re-establish reductive capacity in the aquifer at these locations. Since then, however, chromium has been detected in several more wells, again indicating premature loss of reductive capacity in the aquifer. Possible causes for premature chromate breakthrough are associated with the presence of high-permeability zones in the aquifer. In these zones, groundwater moves relatively fast and is able to oxidize Fe(II) more rapidly.

One way enhancement of the current barrier reductive capacity can be achieved is by the addition of micron-scale zero-valent iron. This type of iron has been evaluated as a material to remediate a wide range of groundwater contaminants (Gillham and O'Hannisin 1994) because of it is an extremely strong chemical reductant. A particularly attractive feature of zero-valent iron is the potential to produce three electrons for Cr(VI) reduction compared to just one electron for Fe(II) reduction. Kaplan et al. (1994, 1996) showed the potential of injecting colloidal size Fe^0 (1–3 micron diameter) as a suspension into porous media.

Cantrell et al. (1997a, b) conducted column studies with several shear-thinning fluids to enhance Fe^0 colloid emplacement. The viscosity of these fluids decreases with increasing shear rate, resulting in a relatively high solution viscosity near the iron particles where the shear stress is low, relative to locations near the surfaces of porous media, where the shear stress is relatively high. Cantrell et al. (1997a, b) used three nontoxic polymers at different concentrations in 1-m-long columns containing laboratory sands. They showed

that the use of shear-thinning fluids greatly improved the injectability and mobility of the iron suspensions in porous media.

Previous iron emplacement studies with polymer additions have only been conducted with homogeneous porous media in one-dimensional columns. Detailed experiments in heterogeneous systems using multidimensional flow cells have not been performed. The objective of this study was, therefore, to investigate in a three-dimensional wedge-shaped flow cell the potential emplacement of zero-valent iron into high-permeable Hanford Site sediments (Ringold Unit E gravels) using shear-thinning fluids containing polymers. The injection flow rate, polymer type, polymer concentration, and injected pore volumes were determined based on preliminary short- and long-column experiments.

2. Materials and Methods

The laboratory experiments consisted of iron emplacement studies in water-saturated 20-cm-long columns, 1-m-long columns, and an intermediate-scale wedge-shaped flow cell. The primary purpose of the column experiments was to determine the most promising treatment to be used in the intermediate-scale flow cell. The 20-cm column experiments were used for preliminary displacement tests using two porous media, two zero-valent iron types, two polymer types, two polymer concentrations, three pore-volumes, and three different injection velocities, for a total of 44 experiments. Due to the limited availability of Ringold E sediment, 32 experiments were conducted with 12/20 Accusand (Unimin Corporation, Le Sueur, MN). From these experiments, eight treatments were repeated in the short columns using the permeable Ringold E sediment. Of these eight treatments applied to the Ringold E sediment, the two best treatments were used in 1-m-long columns for both porous media types. Results from these experiments were then used to select one treatment for investigation using the wedge-shaped flow cell. The performance criteria used were magnitude and uniformity of the amended zero-valent concentration in the columns.

The high permeability Ringold Unit E sediments used in this study were obtained from boreholes within the ISRM barrier. For this study, Ringold sediments with diameters between 0.1 and 1.0 cm were obtained from the available borehole materials and thoroughly mixed. The saturated hydraulic conductivity, obtained using a constant head method for five different packings, was 0.42 ± 0.12 cm/s. Because only a limited amount of Ringold sediment was available to be used for these experiments, the initial series of 20-cm column experiments was conducted with 12/20 Accusand (Unimin Corporation, La Sueur, MN). This laboratory sand has a hydraulic conductivity of 0.5 cm/s (Schroth et al. 1996), which is comparable to hydraulic conductivity value of high-permeability Ringold porous media (Szecsody et al. 2005).

The two micrometer-scale iron particles used in the experiments were S-3700 Fe^0 colloids with a diameter of 2 ± 1 μm (International Specialty Products, Wayne, NJ) and H-200 Special Zerovalent Iron with a diameter of 43 ± 5 μm (ARS Technologies, New Brunswick, NJ). All experiments were con-

ducted with 1% (w/w) iron concentration colloid suspension, and each colloid suspension contained 0.001% aerosol (Sigma Chemical, St. Louis, MO).

Two polymer compounds were used for testing the enhancement of zero-valent iron colloid emplacement: Slurry Pro CDP (K.B. Technology, Chattanooga, TN) and sodium-2-acrylamido-2-methylpropane sulfonate (Sigma Chemical Co.). In this paper, the Slurry Pro and sulfonate polymers are denoted as SP and AMPS, respectively. The selected SP concentrations were 0.01 and 0.02 % w/w, while the used AMPS concentrations were 0.25 and 0.5% w/w.

The 20-cm acrylic columns had a diameter of 10 cm and consisted of two stackable 10-cm sections. The 1-m-long column was similar to the smaller column except that ten stackable 10-cm compartments were used. After each experiment, the contents in each section were mixed and three 20-g samples obtained for the iron analyses. To be consistent with the iron enhancement studies by Kaplan et al. (1996) and Cantrell et al. (1997a, b), the number of pore volumes injected into the columns was 3, 10, and 30. The flow rates used in the 20-cm column studies were 0.01, 0.02, and 0.05 cm/s.

The wedge-shaped flow cell was made out of ⅜-inch polyethylene with a ¾-inch acrylic lid. Fig. 1 is a top view of the flow cell with the horizontal dimensions and sample locations. The flow cell, representing an 18° wedge, is 20 cm deep. The total volume of the flow cell is 59 L (15.6 gal). The porous media were packed into the flow cell to create either a high-permeability channel surrounded by low-permeability materials (Experiment 1) or a heterogeneous layered system with a high-permeability zone between two low-permeability zones (Experiment 2). The low-permeability material used in the two flow cell experiments was 70-mesh Accusand. The channel volume in Experiment 1 was 21.9 L. The Ringold layer in Experiment 2 had a volume of 29 L and a total of 57.8 kg Ringold material was used. Both experiments were sampled at five levels. The level locations are at 2.5 cm (Level 1), 7.5 cm (Level 2), 10 cm (Level 3), 12.5 cm (Level 4), and 17.5 cm (Level 5) from the bottom. Sixty-four samples were taken at each level.
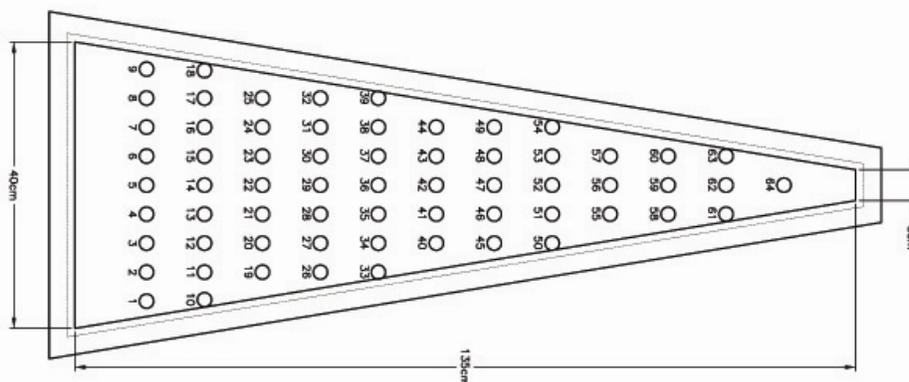

Fig. 1. Sampling locations for each of the five levels in the flow cell

The porous media samples from the columns and flow cell were analyzed for iron using an inductively coupled plasma mass spectrometer (ICP-MS) after treatment with HCl (5 M) for two weeks to dissolve the iron. All reported

Fe^0 concentrations are in % w/w and were corrected for native iron oxide content of the porous media.

3. Results and Discussion

The short-column experiments with H-200 iron in Accusand yielded unfavorable results. The polymer solutions were unable to carry the iron particles homogeneously through the 20-cm columns. Right after entering the column, the H-200 particles settled to the bottom. This iron type could not be transported uniformly because of the relatively large size of the particles (43 ± 5 μm). Because the iron was displaced non-uniformly in the columns for both polymers at the highest concentration, H-200 was removed from consideration. The 20-cm-column experiments with the S-3700 iron did not show the density effects observed for the H-200 iron. In all experiments, the iron particles appeared to move through the column uniformly.

The iron concentrations for the S-3700 treatments in 12/20 Accusand were always higher in the first section and the concentrations generally increase with an increase in injected pore volumes. The highest concentrations were obtained for cases receiving the largest number of pore volumes of treatment. The 0.02 cm/s flow rate produced generally higher amended iron concentrations in the second section than the 0.01 and 0.05 cm/s applications. The slowest flow rate applications show large differences between the first and second section. The highest flow rate resulted in smaller concentrations in both compartments compared to the 0.02 cm/s. The results show no obvious differences between the polymer types, although the highest polymer concentration applications appear to deposit more iron. Based on these results using Accusand, it was decided to conduct the 20-cm column experiments with Ringold sediment without considering the 3 pore volume, the 0.01 cm/s and 0.05 cm/s applications. The results of these small-column experiments show that the 30 pore volume injection resulted in larger amended iron concentrations. No clear differences between the two polymers were observed although the highest polymer concentrations yielded larger iron concentrations in the second compartment. Based on these results, it was decided to use the application with a velocity of 0.02 cm/s and duration of 30 pore volumes for both polymers at the highest concentration in the 1-m-long columns.

The results of the four 1-m-long column studies are shown in Fig. 2. The results show a larger decline in iron concentrations for the AMPS applications, relative to the SP treatment, for both the 12/20 and the Ringold sediment. The iron concentrations for the Ringold material settled at a value slightly above 0.6% (w/w). The results of the 1-m-long column application show that the SP polymer suspensions provided better results than the AMPS applications. The combined results of the short and long column experiments indicated that the 30-pore volume application at a 0.02 cm/s flow rate with the 0.02% SP polymer would provide the best chance of a successful application in the intermediate-scale wedge-shaped flow cell.
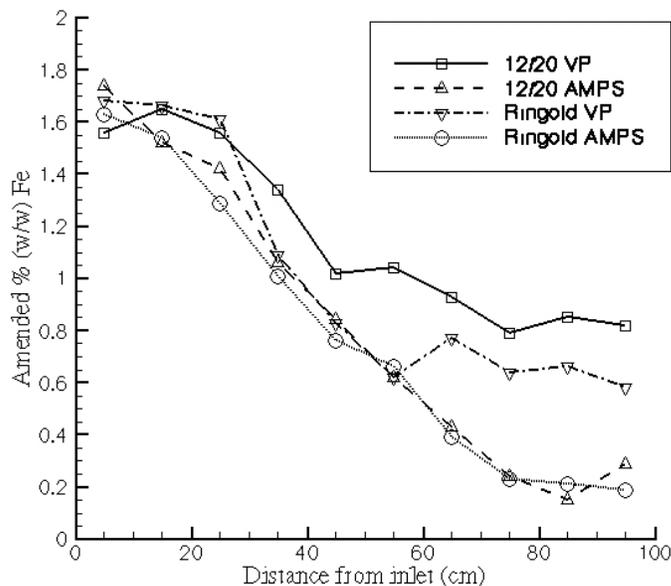
Fig. 2. Amended % (w/w) Fe^0 as function of distance from inlet for SP and AMPS treatments using 12/20 Accusand and Ringold sediment after 30 pore volumes.

The flow rate for the flow cell experiments was assumed to apply to the outflow end of the flow cell. The injection rate for Experiment 1, with a 200 cm^2 zone of highly permeable Ringold, was 240 mL/min. In Experiment 2, with a 400 cm^2 zone of high-permeability Ringold, the injection rate was 480 mL/min. The duration of Experiment 1, with an estimated pore volume of 5.8 L, was 12 hours. Experiment 2, with a pore volume of 7.7 L, lasted 8 hours. The injection rates were ramped up linearly to the intended rate over 15 minutes to avoid excessive initial pressures in the system. Fluid pressure measurements near the injection location show that in Experiment 1 the pressure slowly increased to ~20 KPa (~3 psi) and in Experiment 2 to ~25 KPa (~3.5 psi) above background pressure. These elevated pressures appear to be related to the increased viscosity of the polymer solutions. No obvious negative effects of reduced saturated hydraulic conductivity were observed in either experiment.

Iron distributions as a function of distance from the inlet are shown in Fig. 3 for Experiment 1 and Fig. 4 for Experiment 2. Both plots show that the differences in iron content for the various Ringold levels (Level 2, 3, and 4) are minor, indicating that the iron has been transported relatively uniformly as a function of elevation. Another observation is that only small amounts of iron have moved into the lower permeability zones (Level 1 and 2). Although the iron concentrations generally decrease as a function of distance from the injection location, the iron concentrations at the downstream half of the flow cell seem to level out at concentrations of about 0.6% in both experiments.
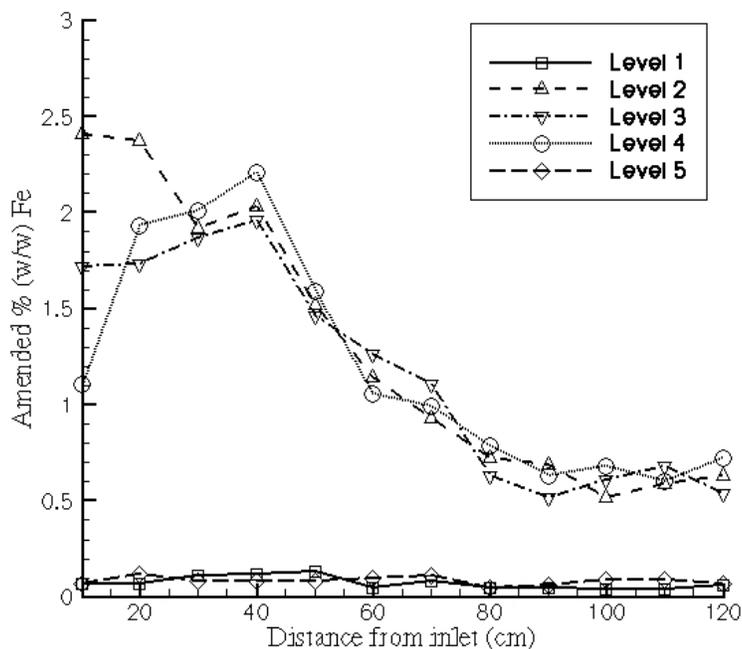
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Fig. 3. Amended % (w/w) Fe^0 at all five levels as a function of distance from injection location (Experiment 1)
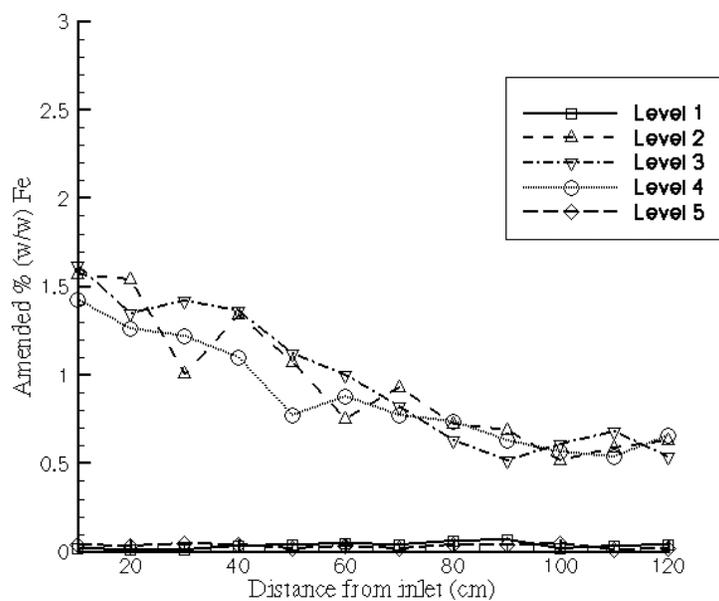

Fig. 4. Amended % (w/w) Fe^0 at all five levels as a function of distance from injection location (Experiment 2)

Based on amended concentrations of 0.6% w/w zero-valent iron, barrier longevity calculations can be performed, similar to Szecsody et al. (2005). The longevity of a zone containing Fe^0 iron can be determined from the ratio of the

iron in the sediments to the electron acceptors in the aquifer. The identified electron acceptors are dissolved oxygen (8 mg/L), nitrate (60 mg/L) and chromate (2 mg/L). Assuming a representative dry bulk density of 2300 kg/m^3, a porosity of 0.14 (Szecsody et al. 2005), and 3 moles of electrons per mole of iron, 0.6% Fe^0, with a molecular weight of 55.85 g/mol can donate (0.006 × 2300 × 3/55.85) × 1000 = 740 mol e$^-$/m^3 of porous medium. Assuming that oxygen (molecular weight: 32 g/mol) accepts 4 mol e$^-$/mol, nitrate (molecular weight: 62 g/mol) 2 mol e$^-$/mol, and chromate (molecular weight 117 g/mol) 3 mol e-/mol, a unit volume of porous medium with a saturated porosity of 0.14 is able to accept (8 × 4/32 + 60 × 2/62 + 2 × 3/117) × 140/1000 = 0.28 mol e$^-$. The ratio of 740/0.28 indicates that 2640 pore volumes of ground water have to flow through a treated zone before breakthrough is observed. The longevity of a zero-valent iron barrier with length *p* m (*p*/0.305 ft) and groundwater velocity of *k* m/day (*k*/0.305 ft/day) is (2640 × *p*)/(365.25 × *k*) years. For instance, a 1 m Fe^0 amended zone with an average concentration of 0.6% w/w iron subject to a pore water velocity of 1 m/day will have longevity of 7.2 years.

4. Summary and Conclusions

At the Hanford Site, a field-scale ISRM barrier was installed to prevent chromate from reaching the Columbia River. However, chromium has been detected in several wells, indicating premature loss of reductive capacity in the aquifer. One possible cause for premature chromate breakthrough is associated with the presence of high-permeability zones in the aquifer. One way enhancement of the current barrier reductive capacity can be achieved is by the addition of micron-scale zero-valent iron. The potential emplacement of zero-valent iron into high-permeability Ringold Unit E gravels using shear-thinning fluids containing polymers was investigated in three-dimensional wedge-shaped aquifer models. The primary reason for using polymers was to create a suspension that is both viscous enough to keep the Fe^0 in solution for extended time periods, improving colloid movement into the porous media, while not causing a detrimental decrease in hydraulic conductivity.

The flow cell experiments indicate that iron concentration enhancements of at least 0.6% (w/w) could be obtained using moderate flow rates and injection of 30 pore volumes. Calculations show that the longevity of a 0.6% amended zero-valent iron zone will provide 2640 pore volumes of treatment before breakthrough is observed, assuming groundwater flowing through the treatment zone contains 8 mg/L oxygen, 60 mg/L nitrate, and 2 mg/L chromate, and assuming a complete reduction of these redox-reactive species. To provide an example of comparable scale to that which would be required at the 100-D Area ISRM barrier site, a 10-m-long amended zone with an average concentration of 0.6 w/w % zero-valent iron subject to a typical groundwater velocity of 0.3 m/day would have an estimated longevity of 240 years. The 0.6% amended Fe^0 concentration would provide approximately 20 times the average reductive capacity that is provided by the dithionite-reduced Fe(II) in the ISRM barrier.

5. Acknowledgements

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