Performance evaluation of granular iron for removing hexavalent chromium under different geochemical conditions

Sung-Wook Jeen, David W. Blowes *, Robert W. Gillham

Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Abstract

Long-term column experiments were conducted under different geochemical conditions to estimate the longevity of Fe^0 permeable reactive barriers (PRBs) treating hexavalent chromium (Cr(VI)). Secondary carbonate minerals were precipitated, and their effects on the performance, such as differences in the mechanism for Cr removal and the changes in system hydraulics, were assessed. Sequestration of Cr(VI) occurred primarily by precipitation of Fe(III)–Cr(III) (oxy)hydroxides. Trace amounts of Cr were observed in iron hydroxy carbonate presumably due to substitution of Cr^{3+} for Fe^{3+}. The formation of Fe(III)–Cr(III) (oxy)hydroxide greatly decreased the reactivity of the Fe^0 and thus resulted in migration of the Cr removal front. Carbonate minerals did not appear to contribute to further passivation with regard to reactivity toward Cr removal; rather, the column receiving high contents of dissolved calcium carbonate showed slightly enhanced Cr removal by means of a higher corrosion rate of Fe^0 and because of sequestration by an iron hydroxy carbonate. Precipitation of carbonates, however, governed other geochemical parameters. The porosity and hydraulic conductivity in the column receiving high contents of dissolved calcium carbonate did not indicate a great loss in system permeability because the accumulation of carbonates declined as the Fe^0 was passivated over time. However, the accumulated carbonates and associated Fe(III)–Cr(III) (oxy)hydroxide could cause problems because the presence of these solids resulted in a decline in flow rate after about 1400 pore volumes of operation.
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1. Introduction

Permeable reactive barriers (PRBs) composed of granular iron can be an effective option for remediation of groundwater contaminated by electroactive chemicals. The use of granular iron for treatment of inorganic contaminants (e.g., Cr, Cu, Hg, Mo, Tc, and U) by reductive precipitation has been investigated at the laboratory scale, and field-scale PRBs have been used for the treatment of As, Cd, Cr, Cu, Hg, Mn, Mo, Se, Tc, U, V, and Zn (Cantrell et al., 1995; Blowes et al., 2000; Morrison et al., 2002). Among four types of iron-bearing solids (i.e., iron filings, iron chips, pyrite, and siderite), Blowes and Ptacek (1992) found fine-grained iron filings to be the most effective in treating hexavalent chromium, Cr(VI). In addition, the rate of Cr(VI) reduction by granular iron and removal through precipitation were observed to be sufficiently rapid for use in groundwater remediation (Blowes and Ptacek, 1992; Blowes et al., 1997). The removal mechanism for Cr(VI) by Fe^0 is through the oxidation of Fe^0 to Fe(II) and Fe(III), coupled with the reduction of Cr(VI) to Cr(III), and the subsequent precipitation of a sparingly soluble solid (Pratt et al., 1997;

* Corresponding author. Tel.: +1 519 888 4878; fax: +1 519 746 3882.
  E-mail address: blowes@sciborg.uwaterloo.ca (D.W. Blowes).

Blowes et al., 2000). Under moderate pH conditions (between pH 5 and 11), removal of Cr(III) can occur through the precipitation of Cr(OH)$_3$ or mixed Fe(III)–Cr(III) hydroxide (Eary and Rai, 1988), or through the precipitation of mixed Fe(III)–Cr(III) (oxy)hydroxide (Schwertmann et al., 1989).

Field evidence has demonstrated that PRBs of granular iron can be effective for Cr removal over extended periods of time (Blowes et al., 1999; Wilkin et al., 2003, 2005); however, uncertainties remain concerning effectiveness under various hydrogeochemical conditions, and the length of time that a barrier will maintain its effectiveness. The longevity of Fe^0 PRBs may be limited by the declining reactivity of Fe^0 due to the precipitation of secondary minerals, whose presence leads to a decrease in reaction rate. Decreases in porosity and hydraulic conductivity may also limit the longevity through changes in system hydraulics.

Chromate reduction contributes to passivation of the Fe^0 surface because of the build-up of an electrically insulating surface film of Fe (oxy)hydroxide (Blowes et al., 1997; Pratt et al., 1997; Schlicker et al., 2000; Melitas et al., 2001). Thus, the estimated longevity of Fe^0 PRBs is commonly based on the passivation rate of Fe^0 and the time of Cr breakthrough under specific experimental conditions. For example, under the particular conditions of a set of column tests, Bennett et al. (1997) estimated that a 60 cm-thick barrier would have a useful lifetime of about 20 years. Also, Schlicker et al. (2000) proposed a general formula for chromate breakthrough time on the basis of the migration rate and concentration of Cr. However, effects of other secondary minerals, such as carbonates, on Cr removal have not been evaluated in detail. Although the presence of carbonate minerals is frequently reported in granular iron PRBs (McMahon et al., 1999; Vogan et al., 1999; Phillips et al., 2000, 2003), few previous studies provided detailed descriptions of the geochemical and permeability changes in granular iron used for the treatment of hexavalent chromium in the presence of dissolved calcium carbonate. Calcium and bicarbonate are among the most common groundwater constituents, and thus their effects on PRB performance are important for the application of the granular iron PRB technology.

The objective of this study was to evaluate the long-term performance of granular iron under different geochemical conditions, for the purpose of estimating the longevity of Fe^0 PRBs that treat Cr(VI). The effects of secondary carbonate minerals on the performance of Fe^0 were of particular interest. Column experiments were conducted over a period of 2 years, and differences in the mechanism of Cr removal and the changes in reactivity and permeability were assessed.

2. Materials and methods

2.1. Column experiments

Two Plexiglas™ columns, 2.54 cm in internal diameter and 50 cm in length, were packed with as-received granular iron obtained from Connelly-GPM, Inc. (Chicago, IL). The grain size was 14–80 mesh (0.17–1.41 mm), and the specific surface area, measured by the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938), was 2.52 ± 0.25 m^2 g^{-1}. The average particle density, calculated from bulk density and porosity, was 7.60 g cm^{-3}. The initial porosity was 0.55 for both columns. Each column had a total of 11 sampling ports located at 2.5 cm intervals up to 10 cm from the influent end and located at 5 cm intervals thereafter along the column. To serve as ports for sampling the solids for mineralogical examination, stainless steel plugs having an outer diameter of 1.27 cm were threaded into the wall of each column at locations between the solution sampling ports and on the opposite side of the column.

Column I received 10 mg L^{-1} Cr(VI) in de-ionized water, and column II received 10 mg L^{-1} Cr(VI) in a calcium carbonate solution of 500 mg L^{-1} alkalinity as CaCO$_3$. The feed solution for column I was deoxygenated by purging with oxygen-free N$_2$ gas for about 2 h. For the preparation of the feed solution for column II, a pre-calculated amount of analytical grade CaCO$_3$(s) was added to a 22 L glass carboy containing 18 L of de-ionized water. The solution was then purged with CO$_2$ gas to dissolve the CaCO$_3$, followed by oxygen-free N$_2$ gas to adjust the pH to 6.4 ± 0.2. Finally, a concentrated stock solution of K$_2$Cr$_2$O$_7$ was spiked to both feed solutions. Stainless steel tubing was used for delivering the solutions to the columns, except for short lengths of Ismatec 2-stop Viton® tubing (Cole–Parmer) that passed through the pump. A Mylar™ balloon filled with oxygen-free N$_2$ gas was connected to the feed bottle to avoid oxygen contamination. The feed solution was pumped at a flow rate of 0.4 mL min^{-1} using an Ismatec multi-channel peristaltic pump (Model 78001-12). This gave a velocity within the columns of approximately 2.3 m d^{-1}.

Hydraulic conductivity across the column was calculated from the Darcy equation using the hydraulic head gradient and solution flux. The hydraulic head difference across each column was measured from manometers installed near the inlet and outlet of each column. The gases evolved from the effluent were trapped using a sealed glass tube before the gases entered the waste bottle. The volume difference in the sealed glass tube over a given time interval was then used to calculate the rate of gas production. Samples were collected for analyses of Cr and