Treatment of trichloroethene and hexavalent chromium by granular iron in the presence of dissolved CaCO$_3$

Sung-Wook Jeen [*], YanQi Yang [1], Lai Gui [2], Robert W. Gillham

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

ABSTRACT

Column experiments and numerical simulations were conducted to evaluate the effects of Cr(VI) and dissolved CaCO$_3$ on the iron reactivity towards trichloroethene (TCE) and Cr(VI) reduction. Column experiments included measurements of iron corrosion potential and characterization of surface film composition using Raman spectroscopy. Three columns received different combinations of TCE (5 mg L^{-1}), Cr(VI) (10 mg L^{-1}) and dissolved CaCO$_3$ (300 mg L^{-1}), after short periods of conditioning with Millipore water followed by 10 mg L^{-1} TCE in Millipore water, for a total of 8 months. The results showed that co-existence with TCE did not affect Cr(VI) reduction kinetics, however, the presence of Cr(VI) reduced TCE degradation rates significantly. The formation of Fe(III)/Cr(III) products caused progressive passivation of the iron and was consistent with the increase in corrosion potential. The presence of dissolved CaCO$_3$ resulted in a stable corrosion potential and faster degradation rates of TCE and Cr(VI). Over time, however, the accumulation of secondary carbonate minerals on the iron surface decreased the iron reactivity. Numerical simulation using a reactive transport model reproduced the observations from the column experiments reasonably well. The simulation can be valuable in the design of PRBs or in the development of effective maintenance procedures for PRBs treating groundwater co-contaminated with Cr(VI) and TCE in the presence of dissolved CaCO$_3$.

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1. Introduction

Granular iron permeable reactive barriers (PRBs) have emerged as an accepted groundwater cleanup technology (Blowes et al., 2000; Jeen et al., 2011; Phillips et al., 2010; Warner et al., 2005). Compared to the traditional "pump-and-treat" technology, the installation cost of an iron PRB is somewhat higher, while the operation and maintenance costs are very low. Therefore, the major advantage of this technology depends on its longevity. The longevity of a PRB is mainly controlled by two factors: the reactivity of the granular iron and the effective permeability. Losses of reactivity and permeability have been associated with the groundwater geochemical conditions; thus, it is important to understand how reactivity and permeability change with evolving geochemistry within a PRB.

One of the geochemical conditions affecting the performance of iron PRBs is the presence of co-existing oxidants. Previous studies have indicated that trichloroethene (TCE) dechlorination by granular iron is significantly slowed by the presence of co-existing oxidants, such as hexavalent chromium (Cr(VI)) or nitrate (Lu et al., 2005; Ritter et al., 2003; Schlicker et al., 2000). Ritter et al. (2002) found that the pre-existing passive layer of γ-Fe$_2$O$_3$ (maghemite) and α-FeOOH (goethite) on commercial-grade iron particles was removed by auto-reduction processes, resulting in the formation of magnetite, a semi-conducting oxide that maintained the iron reactivity towards TCE reduction. However, the presence of nitrate

prevented the auto-reduction processes and the passive oxides remained on the granular iron surfaces. As a consequence, the reduction of TCE was largely inhibited (Ritter et al., 2003). Further study by Lu et al. (2005) on TCE degradation in the presence of nitrate indicated that higher nitrate concentration led to a more positive shift in the corrosion potential and an increased amount of the high valency iron oxides and slowed degradation rates of both TCE and nitrate. It was concluded that the oxidizing effect of nitrate controlled the corrosion potential in a range of thermodynamic conditions which was favorable for the formation and stability of higher valency iron oxides (Fe_2O_3, $Fe(OH)_3$ and α-FeOOH) at the iron surface. These passivating oxides acted as a physical barrier and greatly interfered with charge transfer processes, and thus both TCE and nitrate degradation rates declined. Compared to nitrate, research on Cr(VI) has been largely limited to the treatment of Cr(VI) itself, with relatively little attention to the effects of Cr(VI) as a co-existing oxidant on TCE reduction by granular iron, though there are exceptions (e.g., Dries et al., 2005; Lo et al., 2005). As a co-existing contaminant, a difference between the effects of Cr(VI) and nitrate should be expected. In the case of Cr(VI), precipitates of trivalent chromium (Cr(III)) will form in addition to iron corrosion products.

Other geochemical conditions affecting the performance of granular iron PRBs include common groundwater constituents, such as bicarbonate/carbonate. Bicarbonate commonly occurs at concentrations ranging from 5 to 600 mg/L (Freeze and Cherry, 1979). When the groundwater encounters a PRB, an increase in pH resulting from iron corrosion causes a shift in the carbonate-bicarbonate equilibrium, resulting in precipitation of solid phases such as calcium and iron carbonate minerals. The accumulation of precipitates can block access of contaminants to the iron surface and decrease porosity and hydraulic conductivity, which in turn restricts groundwater flow. Numerous studies have shown that the accumulation of carbonate precipitates can cause a decline in both the reactivity and permeability of PRBs (e.g., Jeen et al., 2006; Mackenzie et al., 1999; Phillips et al., 2010; Zhang and Gillham, 2005).

TCE and Cr(VI) are sometimes present as co-contaminants in contaminated sites, such as the Haardkrom site, Kolding, Denmark (Kjeldsen and Fuglsang, 2000) and the Elizabeth site, NC, US (Mayer et al., 2001). Calcium carbonate, on the other hand, is one of the most common constituents of groundwater. Thus, the combined geochemical effects of these co-constituents on the performance of iron PRBs, with regard to both reactivity and permeability, should be evaluated when iron PRBs are considered as a remedial option in this geochemical condition. Though there have been many studies on the treatment of TCE or Cr(VI) as a single contaminant and on the effects of Cr(VI) or carbonate as independent factors on the performance of granular iron, there have been few studies of TCE, Cr(VI), and carbonate as co-constituents of the influent water. Therefore, the first objective of this study was to determine the effects of Cr(VI) and carbonate, as co-constituents, on the reactivity of iron towards TCE and Cr(VI) reduction. The second objective was to provide mechanistic explanations for the observed effects by examining TCE and Cr(VI) degradation kinetics through column experiments, together with corrosion potential measurements and Raman spectroscopic analysis. The third objective was to evaluate the applicability of the reactive transport model of Jeen et al. (2007a) for simulating the long-term performance of iron PRBs in environments where chlorinated solvents co-exist with other oxidants in the presence of a high concentration of dissolved calcium carbonate. The ability of the model to predict long-term performance under this complex set of conditions was of particular interest.

2. Methods

2.1. Column experiments

Three Plexiglas columns were assembled to simulate groundwater flow through iron PRBs and were operated for 8 months. Each column (3.8-cm I.D., 20-cm long) had 5 sampling ports located at 2.5, 5, 10, 15 and 17.5 cm from the influent end, and was packed with commercial-grade granular iron obtained from Connelly-GPM, Inc. (Chicago, IL). The surface area of the iron, determined by the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938), was 1.23 m^2 g^{-1}. Prior to contact with solution, nitrogen gas was passed through each column to remove oxygen from the pore space. Column saturation was achieved by pumping deoxygenated Millipore water through the columns using an Ismatec multi-channel peristaltic pump (Model 78001–12). Pore volumes (PVs), defined as the total volume of voids in a particular column, was determined for each column by measuring the column weights before and after saturation and were calculated to be 136.0, 129.5, and 138.7 cm^3 for C1, C2, and C3, respectively.

The column experiments were divided into three phases (Table 1). After approximately 60 PVs of Millipore water had passed through each column (Phase I), the corrosion potential had reached a quasi-steady state of approximately −540 mV, indicating complete removal of the pre-existing passive films on the iron surfaces by auto-reduction processes (Lu et al., 2005; Ritter et al., 2002). The influent was then switched to a 10 mg L^{-1} TCE solution (Phase II), for approximately 50 PVs, to determine the initial iron reactivity. The flow rate in Phases I and II through the three columns was maintained at 0.10– 0.12 mL min^{-1}. In Phase III, different combinations of TCE, Cr(VI) and dissolved $CaCO_3$ (Table 1) were pumped to the respective columns. The flow rate through the columns was maintained at 0.32–0.38 mL min^{-1}. The primary reason for increasing flow rate for Phase III was to facilitate accumulation of secondary minerals and to reduce the operational time for the experiment, while still maintaining a flow rate within a small range that can represent field conditions. Further details

Table 1
Column operation history.

Column	C1	C2	C3
Phase I	Input~60 PVs Millipore water to auto-reduce pre-existing passivating film on iron surface Flow rate: 0.10–0.12 mL min^{-1}		
Phase II	Input~50 PVs TCE (10 mg L^{-1}) to measure initial reactivity Flow rate: 0.10–0.12 mL min^{-1}		
Phase III	5 mg L^{-1} TCE + 300 mg L^{-1} $CaCO_3$	5 mg L^{-1} TCE + 10 mg L^{-1} Cr	5 mg L^{-1} TCE + 10 mg L^{-1} Cr + 300 mg L^{-1} $CaCO_3$
	Flow rate: 0.32–0.38 mL min^{-1}		