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Design Considerations for Groundwater Remediation using Reduced Metals

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Abstract−Use of reduced metals has attracted much attention since it possesses a great potential for eliminating reducible contaminants in groundwater such as heavy metals and chlorinated compounds. However, products of metal-mediated reactions for many chlorinated hydrocarbons have not clearly been identified. In addition, consumption of the metals, generation and release of metal ions, formation of insoluble metal oxides and hydroxides on the clean metal surface, and rise of pH inevitably accompany the reactions. Due to these properties of metal-mediated reactions, the reaction rate could decrease as the reaction proceeds, and effluent quality could decay. It was shown in this study using chlorine mass balance and GC analysis that chloroform is formed from carbon tetrachloride by reduced iron. It is also well-known that nitrate is reduced mostly to ammonia by metals, which indicates that the metal process is inappropriate for denitrification of nitrate-contaminated aquifers. These results indicate that groundwater remediation using metal process requires careful consideration for the safety of reaction products. It was also shown that mixing rate strongly affects reaction rate since metal-mediated reaction occurs on the surface of metals. In addition, reaction rate was decreased due to metal hydroxide deposition on the surface of metal granules that was seen by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Generation of iron ions (consumption of reduced iron) released from reduction of zero-valent iron was also shown by using an ion chromatograph (IC). In this study, some methods were suggested to solve the above-mentioned problems. Acid washing appeared effective for removing corrosion products on the surface of metal granules, by which a reduction rate could be maintained high for an extended time of reaction. Use of iron sulfide decreased an extent of pH rise during metal-mediated reaction; thereby precipitation of insoluble metal (hydr)oxides is expectedly decreased. It was also shown that inexpensive iron scrap instead of fine metal powders can be used for metal processes.

Key words: Metal-mediated Process, Iron Scrap, Metal Loss, Precipitation, pH Rise, Iron Sulfide

INTRODUCTION

Worldwide efforts for developing and cleaning up groundwater are being made to meet water shortage problems. Among technologies for groundwater remediation, conventional pump-and-treat methods [Mackay and Cherry, 1989; NAS, 1994] including pyrolysis [Chang et al., 1986; Hua and Hoffman, 1996], photolysis [Haarstrick et al., 1996], oxidations using ozone [Kong et al., 2003] and plasma [Mok et al., 2003], and biological treatment [Dolan and McCarty, 1995; Fox et al., 1990] are being used or studied. These methods, however, bear technological difficulties such as high energy cost, incomplete transformation of contaminants, narrow substrate ranges, and inconsistent reaction rates caused by variations of reaction conditions such as dissolved oxygen concentration, concentrations of minerals, pH, temperature, and conductivity of groundwater.

Since 1990 when Gillham and his collegues fortuitously found that zero-valent iron eliminated trichloroethylene, use of reduced metals has attracted much attention and is now recognized as a competent alternative for remediation of groundwater that is contaminated with reducible substances including chlorinated hydrocarbons [Gillham and O'Hannesin, 1994; Liu et al., 1995; Agrawal and Tratnyek, 1996]. In addition to chlorinated hydrocarbons, zero-valent metals are known to reduce nitrate [Siantar et al., 1996; Kielemoes et al., 2000; Shrimali and Singh, 2001], nitro aromatics [Agrawal and Tratnyek, 1996], hexavalent chromium [Powell et al., 1995; Blowes et al., 1997, 2000], uranium [Gu et al., 1998], and others. In particular, a permeable reactive barrier (PRB) containing granular iron is believed to be an in situ technology for remediation of contaminated groundwater [Wilson, 1995; Weber, 1996; MSE, 1995; US EPA, 1997, 1998] because it is technologically simple, economically-feasible, generating non- or less-toxic products, applicable to a broad range of substrates, and less vulnerable to environmental conditions.

Metal processes, however, impose fundamental and technical obstacles that should be addressed for successful implementation. For example, generation of metal ions, rise of pH, formation and precipitation of metal hydroxides and oxides, concomitant decrease of reaction rates, high market prices of metal granules are representative difficulties inherent in metal-mediated processes. Furthermore, formation of scales originating from inorganic materials in groundwater can cause problems in terms of hydrology and reaction chemistry in PRB applications. For a long-term operation of a PRB, decreased reaction rates, shortened residence time in the barrier, and decreased conductivity have been reported [Benner et al., 1999; Gu et al., 1999; Blowes et al., 2000], which were probably due to decrease of reactive sites on the metallic surface, channeling of the packed bed, and decrease of ionic species in aqueous media, respectively. These problems are rooted in the reaction chemistry of metals (formation of metal ions and consumption of hydrogen ions).

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In addition, no carbon balances between reactants and products have ever been successfully done for many chlorinated hydrocarbons, which indicates that reduction pathways of metal-mediated reactions are not fully understood yet. Therefore, it is not clear if reaction products are environmentally safe. Reaction rates were also not consistent between technical reports because specific surface areas of metals and mixing conditions (mass transfer rate) were different from each other. For engineers who design a PRB containing metals, this fundamental vagueness imposes difficulties in determining an amount of metals and a thickness of the PRB.

In this study, the above-mentioned engineering and fundamental problems are briefly reviewed and discussed with experimental results. In addition, some methods through which metal processes can gain more application credibility arere proposed as well.

MATERIALS AND METHODS

1. Materials

Distilled deionized water (Milli-Q Plus UV, Millipore, USA) was used throughout the experiments conducted in this study. Carbon tetrachloride (CT, 99.5%, Showa, Japan), perchloroethylene (PCE, 98.0%, Showa), and sodium nitrate (99.0%, Showa) were used as received. 100 mM stock solutions of CT and PCE were prepared in 2.9 mL of methanol in 2.9 mL glass vials with PTFE/silicone septa-lined screw-caps. Experimental solutions of CT and PCE in N_2-sparged water were prepared by diluting the CT or PCE stock solutions. When stored at 4 °C in the dark, CT and PCE solutions were stable for at least 14 days. The metallic iron and zinc were 100-mesh cast iron filling from Fisher (USA) and 100-mesh from Junsei (Japan), respectively. These metallic granules were pretreated prior to use by washing in N_2-sparged 3% (v/v) hydrochloric acid for an hour, then rinsed thoroughly with N_2-sparged deionized water until recovery of pH, and dried at room temperature under a N_2 atmosphere in a glove box. Iron scrap (Fig. 1) used in this study refers to thin (about 0.1-0.2 mm thick) spiral pieces of iron produced as a by-product from cutting process of steel plate. The size (width and length) of iron scrap varied with iron-processing procedure, and 2 mm wide scrap was used in this study. Silica sand (70-mesh) and iron sulfide (170-mesh) were purchased from the Aldrich and Duksan Chemical (Korea), respectively.

Fig. 1. Iron scrap used in this study. This material was obtained from a metal-processing facility and acid washed before use to remove cutting oil on the surface.

2. Batch Studies

Dechlorination of CT and PCE by iron granules in a batch mode was carried out in a 26.6 mL clear borosilicate crimp-top serum vial with the Teflon-lined rubber septum. Vials were filled with 10 mL of deoxygenated water and 1 g of acid-treated iron. Aqueous solutions of CT and PCE were prepared by adding the stock solutions into the vials by using gas-tight syringes. Solutions were agitated by rotating vials in the longitudinal axis on a rotator at varied rpm's at room temperature (28±2 °C). Actual aqueous concentrations of CT and PCE were calculated by applying Henry's law constants [Mackay and Shiu, 1997].

Denitrification of nitrate by granules of iron and zinc or iron scrap in the batch mode was carried out in a 250 mL Erlenmyer flask. Flasks were filled with 150 mL of a nitrate solution and 1, 5, or 10 g of acid-treated metals and were shaken in a shaking incubator at 150 rpm and 30 °C. Periodically, 1 mL of aqueous solution was taken by using a 1 mL pipette into a 2 mL vial for nitrate analysis.

3. Continuous Studies

Continuous reactions of CT and PCE were carried out in glass columns (inner diameter 4 cm×20 cm long) with Teflon Mininert valves on every 4 cm. To prevent physical adsorption of CT and PCE, Viton and Teflon tubings were used. Columns were filled with silica sand, iron or zinc powder, and iron sulfide, if necessary. The porosity of the sand-packed bed was determined to be 0.4 with a liquid volume of 0.3 L.

Water containing CT or PCE was held in a 1.5 L collapsible Teflon bag (Alltech, USA) to minimize losses due to adsorption and volatilization into the head-space as the solution was consumed. The solution was pumped from the collapsible bag to the column at flow rates of 0.35-0.75 mL/min with a peristaltic pump (SMP-3, EYELA, Japan) so that mean residence time of the solution in the column was 6.7-14.3 hrs. Columns were packed with silica sand only (control), 5 wt% 100-mesh iron granules and remaining sand, or 5% of 100-mesh iron powder, 2.5% of 100-mesh iron sulfide powder and 92.5% of sand according to the experimental design. For organic analyses, aliquots were taken from the ports of the column and the influent and effluent lines by using a 2.0 mL gas-tight glass syringe. Prior to sampling, 0.25 mL was withdrawn to remove stagnant water around the port. The syringe was rinsed three times with methanol followed by three rinses with deionized water for every use. 1.5 mL aliquots were transferred to a 2.0 mL vial with screw cap and Teflon-lined septum. Vials were then placed on an orbital shaker for 15 min to allow partitioning of organics between the aqueous and gas phases, and gas phase was analyzed with a gas chromatograph (GC).

For treating nitrate with zinc granules, sand (680 g) and zinc (120 g) were mixed thoroughly and then packed in a rectangular reactor (6×16×7 m) with an open top. Flow rate of nitrate solution was set at 2 mL/min, and the effluent was analyzed periodically with an ion chromatograph (IC). To wash zinc in the reactor, hydrochloric acid (2.5%) or sulfuric acid (1%) solution was filled in the reactor for 1-1.5 hrs, and then eluted the reactor with N_2-sparged deionized Milli-Q water until pH reached a neutral range.

4. Analyses

Particle surfaces and corrosion products of Fe^0 were identified by SEM (scanning electron microscope) and EDX (energy dispersive X-ray analyzer) analyses (Stereouscam 440, Leica, Germany). All samples were placed on aluminum stubs and sputtered with gold to prevent electrical charging during SEM analyses. The images were recorded with 10,000-15,000×magnification. Surface area of metals was measured with a BET analyzer (NOVA 1200, Quantachrome, USA).

To identify gaseous products such as chloroform (CF), methylene chloride (MC) and trichloroethylene (TCE) over the course of reactions, gas chromatographic analyses were carried out. 50 μL of gas taken from the reaction headspace by using a gas-tight syringe were injected into a GC (GC-14B, Shimadzu, Japan) with an AT-502.2 capillary column (30 m×0.25 mm×1.40 μm film thickness, Alltech, USA) and an ECD (electron capture detector). N_2 at 100 kPa was used as a carrier gas. Temperatures for the column, the injector, and the detector were 60 °C, 220 °C, and 250 °C, respectively. GC-Mass analyses were done on a Hewlett-Packard 5793 MSD coupled to a Hewlett-Packard 6890 gas chromatograph with an HP-5MS capillary column (30 m×0.25 mm×0.25 μm film thickness). The column temperature was maintained at 40 °C for 2 min then programmed to 260 °C at 10 °C/min and held isothermal for 20 min. Helium was used as a carrier gas at a flow rate of 1 mL/min.

Chloride (Cl^-) and nitrate (NO_3^-) ions were determined by an ion chromatograph (Waters 432, Waters, USA). This IC was equipped with a conductivity detector and an Anion HR column (Waters IC-pak, 4.6×75 mm). Solutions of 1.6 mM sodium hydrocarbonate and 1.4 mM disodium carbonate were used to elute the column at a flow rate of 1 mL/min. The instrument detection limit was as low as 0.1 mg/L. Ferric (Fe^{3+}) and ferrous (Fe^{2+}) ion analyses were performed on the IC with a Waters M486 UV-Vis detector (540 nm) and a Waters Spherisorb column (Waters S10 SCX 4.6×150 mm). 100 mM tartrate buffer prepared from tartaric acid and lithium hydroxide (pH 3.1-3.5) was used to elute the column at a flow rate of 1 mL/min. PCAS (post column addition system) reagent containing 1 mM bathopheuanthroline-disulfonic acid in 0.2 M ascorbic acid (0.3 mL/min) was mixed with ions directly after they were eluted from the column.

RESULTS AND DISCUSSION

1. Chlorine Balances of Dechlorination Reactions

As similar to previous reports [Metheson and Tratnyek, 1994; Hung and Hoffmann, 1998], CF (35-40% of the initial CT on the molar basis) was formed from CT dechlorination by the granular iron. MC was also detected in the reaction mixture but was trace. This result was similar to Metheson and Tratnyek's [1994] in that 3 hrs of reaction generated a negligible amount of MC. No methane or any other noticeable products except CF and MC were seen from the GC-mass analyses. Since this dechlorination reaction could not be balanced with respect to carbon, a chlorine mass balance was established as Su and Puls [1999] did. Transformation of CT to CF yields a free chloride ion in the aqueous medium, and the other three chlorines remain on a CF molecule. As shown in Fig. 2, all of the chlorines on CT were conserved as atomic chlorines on CF and aqueous chloride ions. Therefore, it seemed that transformation of CT to CF was carried out through hydrogenolysis, but further dechlorination of CF to MC in a large quantity unlikely occurred as experimental results supported.

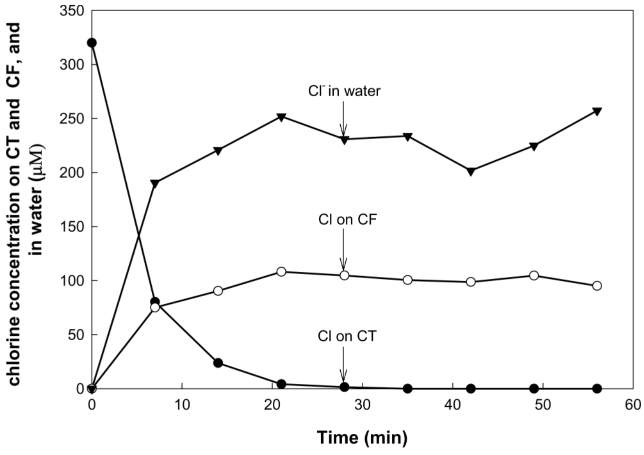
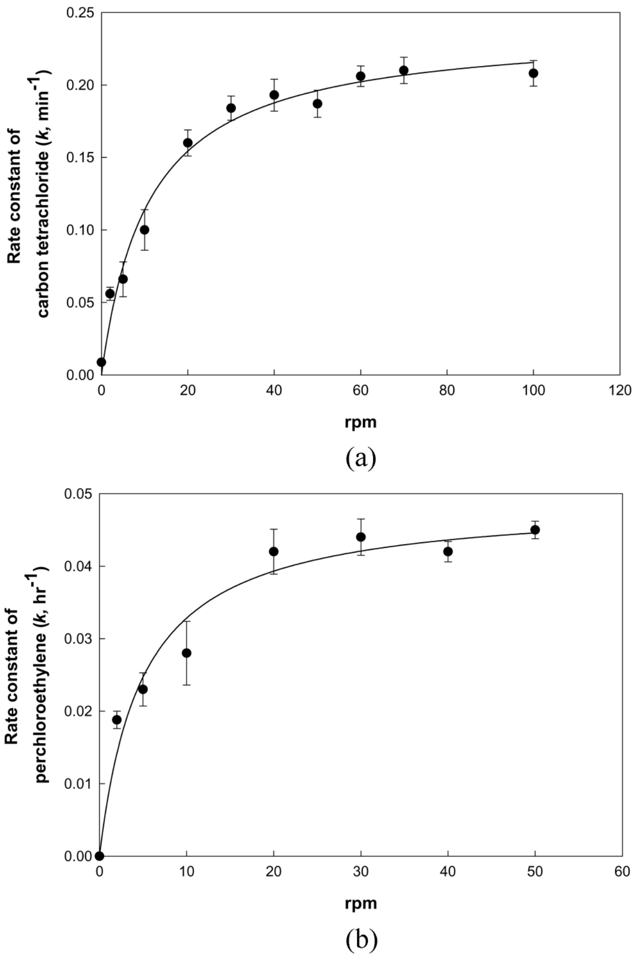


Fig. 2. Generation of chloride ions from the reduction of carbon tetrachloride (CT) to chloroform (CF) by iron granules. Chlorine concentrations on CT and CF were calculated by multiplying number of chlorines on each molecule and concentrations of CT and CF.

In case of PCE, TCE and DCE were not formed. These results indicated that dechlorination of PCE by iron followed the *β*-reductive elimination pathway in which two electrons simultaneously transferred to PCE to remove two chlorines at once. But this hypothesis was not sufficient to explain why ethylene or any other probable hydrocarbons were not detected as a major reaction product. According to Glod et al. [1997], chlorinated ethylenes including PCE and TCE undergo different dechlorination pathways that are partly determined by reaction pH's. Nonetheless, chlorine a mass balance was successfully established for PCE as well (data not shown). Therefore, a successful chlorine balance for metal-mediated reduction of chlorinated contaminants can indirectly indicate that reaction products are not hazardous as much as substrates since halogens usually confer the toxicity of the organic molecules.

2. Mixing Effect on Dechlorination Rates

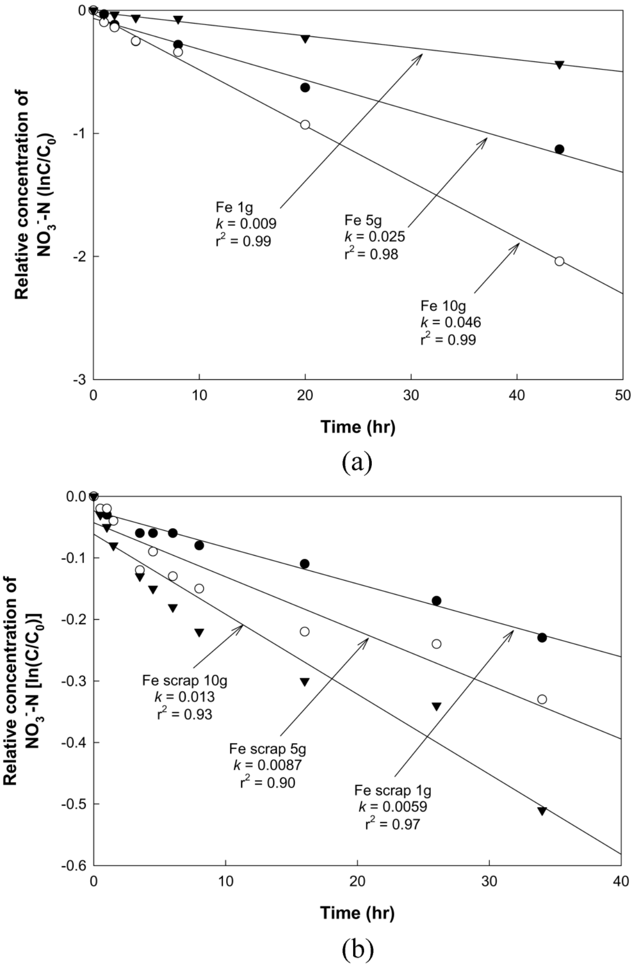
Among three reaction mechanisms previously proposed [Matheson and Tratnyek, 1994] through which dechlorination of chlorinated compounds by iron occurs, electrochemical reactions between substrates and iron on the metallic surface are known to be most important [Matheson and Tratnyek, 1994]. This heterogeneous surface reaction undergoes several steps of physicochemical processes: (i) mass transport of substrate to the metallic surface from the bulk liquid, (ii) adsorption of substrate to the surface, (iii) chemical reactions on the surface, (iv) desorption of reaction products from the surface, and (v) mass transport of the products to the bulk liquid from the surface [Scherer et al., 1998; Fogler, 1992]. In these events, a net velocity of dechlorination reaction will be limited by the mass transport rate of a substrate from the bulk liquid or the chemical reaction rate on the surface. In order to obtain a base reaction rate on the surface, therefore, the mass transfer rate needs to be increased until the reaction rate constant reaches a maximum. In this study, agitation speed of batch reaction vials varied, for which a first-order reaction rate constant was obtained. As shown in Fig. 3, no significant increases of rate constants were observed at 30 and 20 rpm's, which were 0.22 min^{-1} and 0.045 hr^{-1} for CT and PCE, respectively.



(a)

(b)

Fig. 3. Effects of agitation speeds on dechlorination rates of carbon tetrachloride (a) and perchloroethylene (b) by iron granules. Error bars indicate standard deviations of first-order rate constants for 50, 80, and 100 μM of substrates.



(a)

(b)

Fig. 4. Reduction of nitrate by iron granules (a) and iron scrap (b). Denitrification rate constants increased as amounts of metals increased.

These results are essentially the same as Choe et al. [2000] in that rate constants of denitrification rates by nanoscale iron powder remain constant at strongly-agitated conditions.

In a PRB operation for an *in situ* groundwater remediation, mixing as in batch vial reactions is impossible, and, instead, continuous flow of groundwater through the PRB bed provides contacts between substrates and packed metallic materials. Therefore, reaction rates obtained in laboratory batch experiments are not directly applicable for designing PRB (e.g., for determining amounts of metal and a thickness of PRB bed). Instead, the reaction rate in the field scale PRB is thought to be significantly lower than a maximum reaction rate obtained as above.

3. Effects of Metallic Materials on Reaction Rates

One of most important design factors of PRB is the reaction rate constant. As noted above, mass transfer affects reaction rates, but surface area per unit mass of metal also absolutely determines the reaction rate. Gillham and O'Hannesin [1995] reported that dechlorination rate of CT by iron scrap was 5-15 times as slow as iron granule. Choe et al. [2000] also showed that nanoscale iron powder yielded a faster denitrification rate. As a matter of fact, however, surface area does not induce a change in the net specific reaction rate (mol/time·surface area) per se, since mass transfer rate of substrates and surface chemical reaction rates are independent of surface area. But a reaction rate per unit mass of metal is obviously dependent on the surface area. Since fine metallic powders worsen economic feasibility of a metal process, careful consideration should be given in choosing metallic materials. For example, reduction of nitrate was successfully accomplished by iron granules but also by iron scraps (Fig. 4). Although use of iron scrap resulted in slower rate constants than iron granules for the same amount of iron by mass (0.013 hr^{-1} vs. 0.046 hr^{-1} for 10 g of iron), it seems that iron scrap is usable for PRB applications since inexpensive materials will be useful for designing a field-scale PRB.

4. Consumption of Metals and Precipitation

Since the reduced metal is an electron donor for the reduction of oxidized substrates, metal consumption is inevitable as indicated in the reactions (1) to (3). In many research papers on metal reactions, however, this problem has not been seriously discussed. This is partly because halogenated compounds that are usually contaminated at ppb levels in groundwater have been major concerns for the use of metal.

$$Fe^0+CCl_4+H^+\rightarrow Fe^{2+}+CHCl_3+Cl^- \quad (1)$$

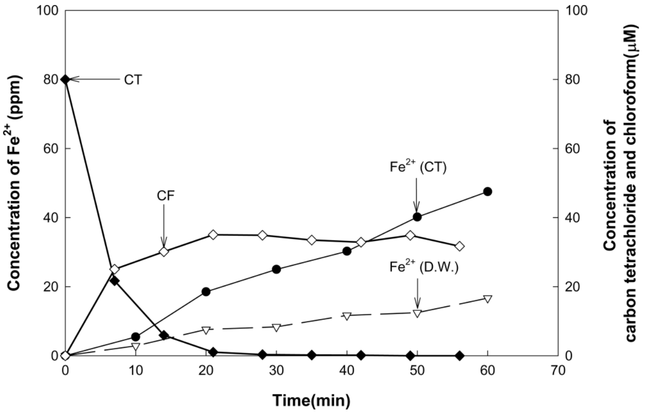


Fig. 5. Generation of ferrous ions from carbon tetrachloride reduction by iron granules. Iron in the distilled water without carbon tetrachloride also produced ferrous ions. Ferric ions were not detected.

$$4Fe^0+C_2Cl_4+4H^+ \rightarrow 4Fe^{2+}+C_2H_4+4Cl^- \tag{2}$$

$$4Fe^0+NO_3^-+6H_2O \rightarrow 4Fe^{2+}+NH_3+9OH^- \tag{3}$$

However, metal is obviously consumed as reaction proceeds. As shown in Fig. 5, ferrous ions were produced in the course of CT reduction by the zero-valent iron. For CT at the initial concentration of 80 μM, 18.5 ppm of ferrous ions were produced in 20 min. In addition, the rate of ferrous ion generation was positively dependent on CT concentrations (for 300 μM of CT, ferrous ion production at 20 min was 38.4 ppm), which also represented first-order behavior with respect to the substrate concentration. According to a field test report for an iron-filled PRB [Puls et al., 1999], ferrous ion concentration and pH of groundwater increased, whereas conductivity of metal decreased. In reality, furthermore, more iron would be required for a field PRB because significant amount of iron is thought to be inactivated due to gradual deposition of insoluble materials on the iron granules.

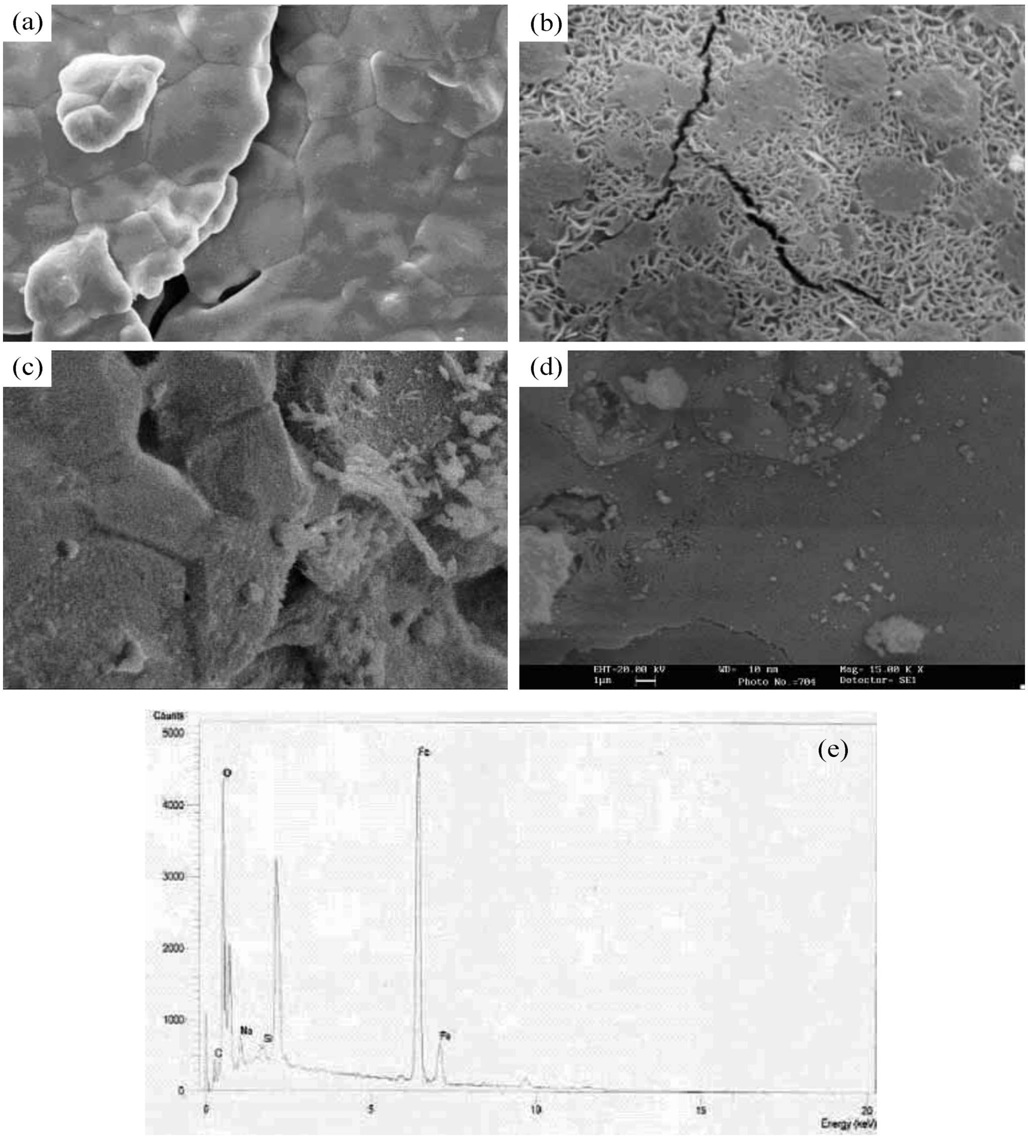


Fig. 6. SEM micrographs for fresh iron without acid treatment (a), acid-treated iron granule (b), iron granule used for CT reduction for 24 hrs in a batch vial (c), iron granule used for CT reduction for 20 days in a continuous column (d), and EDX diagram for 24-hr used iron granules (e).

Decrease of mass of metal in a PRB could be overcome simply by packing a large amount of metal that is more than enough for a long-term operation. But metal consumption causes other problems that could be more problematic. For instance, metal ions generated form precipitated layers of metal hydroxides or metal oxides on the reactive metal surface, which would result in decreased reaction rates. Insolubilization of metal ions is even accelerated at alkaline pHs that are accompanied by the consumption of hydrogen ions or generation of hydroxide ions as seen in the reactions (1) through (3). Changes of metal surfaces due to precipitations of insoluble metal species are shown in Fig. 6. As reaction proceeded, surface morphology changed in that smooth surface became coarse and crevices were filled [(Fig. 6(a), (c), and (d)]. After 24 hours of dechlorination reaction of CT [Fig. 6(c)], the iron surface looked similar in some extent to the original iron surface, but it looked very different for 20 day reacted iron [Fig. 6(d)]. Since iron and oxygen were found on the surface by the EDX analyses [Fig. 6(e)], precipitated materials were likely to be iron hydroxides or iron oxides as predicted. Gotpagar et al. [1999] also reported that surface morphology of metal was changed as the reactions were carried out.

Acid washing of unused metal slightly increased specific surface area of 100-mesh iron granules from 0.19 m^2/g to 0.21-0.22 m^2/g according to BET analyses [Fig. 6(b)]. Precipitation on the used metal could be removed by acid washing as well. As shown in Fig. 7, nitrate removal efficiency sharply decreased as reaction time increased due to precipitation of non-reactive metal species. After acid washing of the column, the rate of nitrate reduction recovered and was maintained for several days. But repeated acid washing was required periodically. Although acid washing can clean the metallic surface, metal loss will be larger and large quantities of metal ions in the effluent into the environments may evoke secondary contamination.

Since deionized water containing only chlorinated compounds or nitrate was used in this study, a limited number of precipitated species was formed. But there are extremely diverse ionic materials in natural groundwater so that many different precipitates can be formed due to high pH and abundant metal ions, for which metallic carbonate, calcium carbonate, magnesium hydroxide, and calcium hydroxide are examples [US EPA, 1997; 1998; Vogan et al., 1999; Puls et al., 1999a, b]. These precipitates can lower the reaction rates and hinder hydraulic flow of groundwater toward the PRB. For field scale operations, installation of a limestone bed upstream of the PRB [Palmer, 1996] can be considered for removing magnesium and calcium ions in groundwater before these precipitable ions reach the reactive zone.

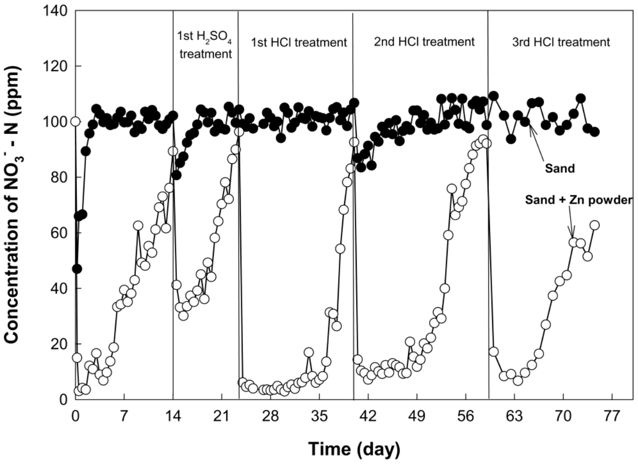


Fig. 7. A long-term operation of a zinc column for continuous denitrification. Acid washing using sulfuric acid was less effective than hydrochloric acid. Without acid washing, denitrification activity of zinc decayed rapidly after a several days of operation.

5. Increase of pH

Iron spontaneously ionized as in the reactions (4) and (5) even in the absence of reducible substrates except water. As zero-valent iron is oxidized, hydroxyl ions are produced (or hydrogen ions are consumed), thereby pH increases.

$$Fe^0+2H_2O \rightarrow Fe^{2+}+2OH^-+H_2 \qquad \text{(anaerobic)} \tag{4}$$

$$Fe^0+H_2O+0.5O_2 \rightarrow Fe^{2+}+2OH^- \qquad \text{(aerobic)} \tag{5}$$

In dechlorination of CT and PCE and reduction of nitrate by metals, pH increased up to 8.5-10 depending on reaction conditions. As mentioned earlier, the formation of metal precipitates is accelerated at alkaline conditions; hence high pH exerts adverse effects on the long-term operation of metal processes. In short, dechlorination rate increased as pH decreased [Deng et al., 1999; Gu et al., 1999; Hung and Hoffman, 1998; Chen et al., 2001]. Since pH control is practically difficult for an in situ PRB, incorporation of pyrite or iron sulfide in the PRB with metals could be a way to alleviate pH increase as presented in reactions (6) and (7).

$$FeS_2\ \text{(pyrite)}+3.5O_2+H_2O \rightarrow Fe^{2+}+2SO_4^{2-}+2H^+ \tag{6}$$

$$FeS+1.5O_2+H_2O \rightarrow Fe^{2+}+SO_4^{2-}+2H^+ \tag{7}$$

Although dissolved oxygen concentration of groundwater is usually low, continuous flow of fresh groundwater into the PRB is expected to sustain pH-lowering activity of pyrite and iron sulfide. In the laboratory, 1 g of iron sulfide in 100 mL of distilled water increased hydrogen ion concentration from pH 6.2 to pH 4 in 3 min. It has been reported that 2 wt% pyrite in a batch reactor maintained pH 6.4-6.7 for 456 hrs of reaction, whereas pH of an iron reaction without pyrite increased to pH 9 [Burris et al., 1995]. In addition to pH control activity, ferrous ions generated from dissolution of pyrite and iron sulfide were thought to enhance the reaction rate by reducing substrates at the expense of oxidation of Fe^{2+} to Fe^{3+} [Butler and Hayes, 1998]. In long-term continuous experiments, iron sulfide-containing column showed lower effluent pH and higher CT conversion (Fig. 8). As shown in Fig. 8, reaction rate was sharply decreased in a day for iron without iron sulfide so that CT concentration gradually increased, and CF concentration decreased as dechlorination rate of CT slowed down. Hydrogen ion concentration remained above pH 10.5 after a day of reaction. On the other hand, iron sulfide-containing column maintained a high dechlorination rate up to 4 days, and slope of CT increase was lower than that of iron only. Accordingly, CF concentration maintained higher and pH was lower. These better performances of the iron sulfide-containing column were thought to be due to a lower pH. In the field, low pH will help in preventing formation of insoluble precipitates.

CONCLUSION

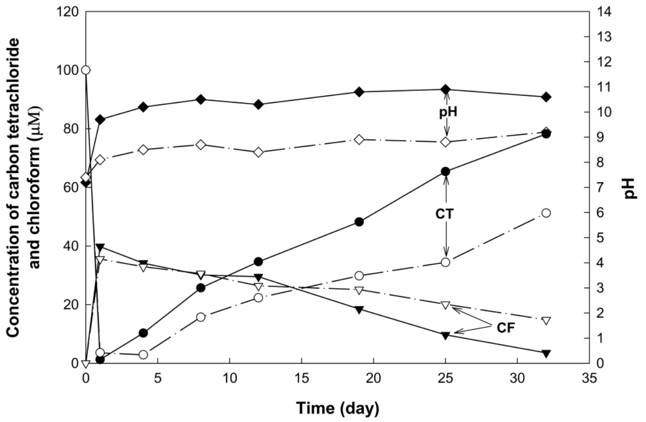


Fig. 8. Effect of iron sulfide on CT reduction, CF formation and pH in a long-term dechlorination of CT by iron granules. Iron sulfide-containing column showed faster dechlorination and a lower pH. Open and filled symbols represent experiments with and without iron sulfide, respectively.

Although metal processes have great potential for remediation of groundwater, it is necessary for successful field applications to overcome intrinsic obstacles posed by reaction chemistry. Consumption of metal, concomitant generation of metal ions, formation of metal precipitates on the metallic surface, and rise of pH are examples of the problems. These problems are interconnected with each other and eventually reduce the reaction rates, possibly cause a secondary pollution (release of metal ion-containing alkaline effluents), and worsen economic feasibilities (repeated supply of fresh metals). As shown in this study, use of inexpensive materials like iron scrap, periodic acid washing of used metals, and co-use of iron sulfide with metals can improve the metal process in terms of field applications. For groundwater, in particular, ionic and nonionic substances probably evoke other problems like formation of scales that lower the reaction rate and block the hydraulic flow. Much effort is necessary to solve these problems for successful applications of metal-mediated processes.

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