# Effects of ferrous ions on the reductive dechlorination of trichloroethylene by zero-valent iron

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## Abstract

The surface characteristics of zero-valent iron (ZVI) and the efficiency of reductive dechlorination of trichloroethylene (TCE) in the presence of ferrous ions were studied. The experimental results indicated that the acid-washing of a metallic iron sample enhanced the efficiency of TCE degradation by ZVI. This occurred because acid-washing changed the conformation of oxides on the surface of iron from maghemite ($\gamma$-$Fe_2O_3$) to the more hydrated goethite ($\alpha$-FeOOH), as was confirmed by XPS analysis. However, when ferrous ions were simultaneous with TCE in water, the TCE degradation rate decreased as the concentration of ferrous ion increased. This was due to the formation of passive precipitates of ferrous hydroxide, including maghemite and magnetite ($Fe_3O_4$), that coated on the surface of acid-washed ZVI, which as a result inhibited the electron transfer and catalytic hydrogenation mechanisms. On the other hand, in an $Fe^0$-TCE system without the acid-washing pretreatment of ZVI, ferrous ions were adsorbed into the maghemite lattice which was then converted to semiconductive magnetite. Thus, the electrons were transferred from the iron surface and passed through the precipitates, allowing for the reductive dechlorination of TCE.
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## 1. Introduction

During the past decade, permeable reactive barriers (PRBs) have received a great deal of attention as an innovative, cost-effective technology for the in situ remediation of groundwater contaminated with chlorinated solvents [1–3]. Although a variety of materials have been proposed for use in PRBs, zero-valent iron (ZVI) has shown the greatest promise, especially for the reduction of many common environmental contaminants [4,5]. However, due to the thermodynamic instability of ZVI in the presence of the water, changes in environmental conditions encourage the development of a surface layer of corrosion.

It follows that understanding the behavior of such a layer upon contact with the solution to which it is exposed is important, because of chemical deposit that occurs due to iron corrosion can inhibit electron transfer and catalytic hydrogenation between any contaminants and the iron. Several studies have shown that passive films, formed by mineral precipitation on an iron sur-face, can cause a rapid decrease of degradation of chlorinated hydrocarbons, by inhibiting access to the reactive iron surface [6,7]. In addition, one can expect porosity loss and reduced flow in the bulk iron material, meaning that the longevity of favorable barrier hydraulics and reactivity must be compensated for [8,9].

Numerous investigations have demonstrated that various kinds of passive films can be coated on iron. Each has a different structure and composition, which depends upon their formation mechanism [10]. In the case of a fresh cathodically cleaned Fe surface, a quasi-bulk $Fe(OH)_2$/$Fe_3O_4$ film should be expected. An $Fe^{3+}$ film should form on a pre-oxidized Fe surface, which will then be reduced to form a $Fe_3O_4$/$Fe(OH)_2$·$2FeOOH$ film [11]. In both cases, the main surface product of the aged film is magnetite ($Fe_3O_4$). Magnetite, being a denser species, should occupy the inner layer of the film. Magnetite can also be electrically conductive, which allows a charge to be transferred through the interphase, which in turn induces reductive dechlorination. However, the degradation is slower, since the charge transfer rate through an oxide is slower than on a bare metal surface [12]. Bonin et al. [13] identified magnetite, hydrated magnetite [$Fe(OH)_2$·$2FeOOH$] and green rust complexes as being the final

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products of surface redox reactions that occurred in a borate buffer solution after iron was exposed to the contaminant. Aging the film converted the hydrated magnetite to magnetite. Magnetite and green rust are not protective, so that charge transfer and reductive dechlorination continued.

In addition, in natural subsurface environments, high concentrations of dissolved $Fe^{2+}$, related to the reductive dissolution of ferric oxides and oxyhydroxides, are primarily generated by chemical, physical or biological processes. Moreover, in PRB systems, dissolved $Fe^{2+}$ can also be generated and released into the subsurface environment due to the oxidation of metallic iron. Johnson et al. [14] showed that dehalogenation by surface-bond $Fe^{2+}$ appears to happen faster when there is an oxide film on ZVI. $Fe^{2+}$ reacts with the oxide surface, and electrons are transfer between the adsorbed $Fe^{2+}$ and the underlying $Fe^{3+}$ oxide. This electron transfer induces the growth of an $Fe^{3+}$ layer on the oxide surface that is similar to the bulk oxide [15]. The resulting oxide is capable of reducing chlorinated aliphatics, nitrate, nitroaromatics and uranium [16–20]. The degradation rate and efficiency is dependent on the environmental conditions, such as the pH value, concentration of $Fe^{2+}$, the morphologies of the minerals, and the presence of transitional metal ions.

However, the results from the literatures cited above reveal that little attention has thus far been paid to the production and role of $Fe^{2+}$, and, in particular, its interaction with the corrosion products. Consequently, the objective of this study is to understand how ferrous ions may affect the reductive dechlorination of trichloroethylene (TCE) by ZVI and to clarify the relationship between the ZVI and the passive precipitates of iron (hydro) oxides that coat the iron surface, in the presence of ferrous ions.

## 2. Experimental

### 2.1. Chemicals and materials

The laboratory grade iron, purchased from the Riedel-deHaën Company, had the following characteristics: (1) a particle size of between 0.045 and 0.125 mm; (2) a specific surface area of $0.287 \, m^2/g$ (as determined by ASAP 2010 micrometrics using nitrogen BET analysis); (3) a purity >99%, with other trace metals. The TCE (99.5+%, GR grade) was obtained from the Merck Company. Pentane (99.5+%, GR grade), also purchased from Riedel-deHaën, was used as the extractant. Sulfuric acid (97%), purchased from the Osaka Co. (Japan), was used to pretreat the iron. A standard chloride ion solution, obtained from Merck, was used to identify the qualities and quantities of chloride ion, as measured by an ion chromatograph (IC). The ammonium acetate ($C_2H_7NO_2$, Riedel-deHaën), acetic acid ($C_2H_6O_2$, Merck), 1,10-phenanthroline (Riedel-deHaën), ferrous chloride tetrahydrate ($FeCl_2 \cdot 6H_2O$, Fluke) and ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, Ferak) were all GR grade. The DI water had a resistivity of $18.0 \, M\Omega$. The water was obtained from a Millipore-Q system. The Millipore-Q water was sparged with nitrogen gas for half an hour to ensure that the DO concentration remained below 0.5 mg/l, and thus emulated the low oxygen levels that are typical of actual groundwater.

### 2.2. Acid pretreatment of the iron

Acid-washed iron was used in some of the experiments. A 2.0 l beaker containing a known mass of powdered iron (that was measured prior to pretreatment) in 1.5 l of 1N sulfuric acid solution was agitated at 300 rpm for 0.5 h, then rinsed five times in 1.5 l deionized water to prevent any $H_2SO_4$ from remaining on the iron surface. Following the rinsing, the iron was dried for 2 days in a freeze-drying system (Labconco Co.) and then sieved using a 120 mesh screen (opening size of 0.125 mm). To inhibit oxidation, the iron powder was stored in nitrogen-sparged glass jars prior to use.

### 2.3. Dechlorination experiments

Each batch of experiments was conducted using 7.5 g of iron powder in 30 ml serum bottles that were filled with the deoxygenated solution. These deoxygenated solutions were prepared by purging, with $N_2$ (99.995%) at a flow rate of 5 l/min, to remove any trace amounts of oxygen left in the solution [20]. A 90 mg/l of TCE solutions were prepared by injecting appropriate quantities of pure TCE reagent into deoxygenated solutions, which were in the 1 l serum bottles without any headspace. The solutions were then immediately sealed and stirred to dissolve the TCE thoroughly. The ferrous ion solutions were prepared by dissolving $FeCl_2 \cdot 6H_2O$ as the ferrous source. Solutions containing both $Fe^{2+}$ and TCE were prepared, by adding a known mass of $FeCl_2 \cdot 6H_2O$ powder into deoxygenated solutions, after which TCE was injected and then proceeded the same as for the preparation of the TCE solutions. The ferrous iron concentrations in this study were 50, 100, and 300 mg/l.

To begin each batch of experiments, solutions were transferred into serum bottles containing acid-washed or unwashed iron, depending on the experimental requirements, and sealed immediately with Teflon-lined rubber septa. All the bottles were shaken in an orbital shaker at 30 rpm and room temperature (25–30 °C). In addition, control batches, without the addition of iron or ferrous ions, were also conducted. The experimental process lasted for 72 h. The TCE concentrations in the test bottles were measured at intervals time. Fifty microliters aliquots of solution were withdrawn using a 250 µl gastight syringe.

After withdrawing from the solutions, the bottle caps were removed and the pH and redox potential (SUNTEX, SP-701) of the solutions in the bottles immediately were measured. The solutions were then filtered through a membrane filter with a pore diameter of 0.45 µm (ADRANTEC MFS, Inc.). The filtered solutions were collected and the total dissolved iron, ferrous and chloride ion concentrations were determined. Residual particles on the membrane were freeze-dried and prepared for SEM-EDS and XPS observation.

### 2.4. Analytical methods

#### 2.4.1. TCE concentration

TCE was extracted via a liquid–liquid extraction process using pentane. The aqueous samples were then transferred into 1.8 ml vials containing 1.0 ml of pentane. The extraction vials