

PREPRINT EXTENDED ABSTRACT  
Presented Before the I&EC Special Symposium  
American Chemical Society  
Atlanta, GA            September 17-20, 1995

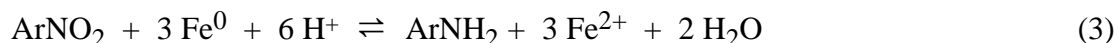
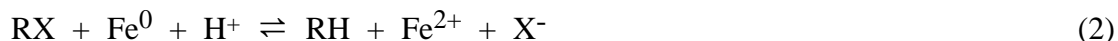
INTERFACIAL PHENOMENA AFFECTING CONTAMINANT REMEDIATION  
WITH ZERO-VALENT IRON METAL

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Over the last several years, a great deal of interest has developed in the groundwater remediation community over the prospects of new treatment strategies based on contaminant degradation by granular iron metal. These developments have created a need for process-level insight into the chemistry of these systems in order to explain, predict, and/or enhance their performance. To this end, we have been investigating various aspects of the reduction of organic substances at the iron-water interface. Recent results have demonstrated the importance of corrosion, precipitation, and mass transport in determining the reactivity of granular iron [1-4]. The purposes of this paper are to discuss the importance of oxygen (or anoxia) in these systems, and to explore the various ways in which all of these processes reflect interfacial phenomena.

In subsurface applications, oxidative dissolution of iron metal occurs when coupled to the reduction of a suitable oxidant. The most generally important oxidant is dissolved oxygen (eq 1), but oxidation by some halocarbons (eq 2) and nitroaromatic compounds (eq 3) can also be very rapid.



All of these reactions favor increased pH, which, in turn, will favor precipitation of iron hydroxides. In addition, further oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  will lead to rapid and extensive precipitation of ferric (oxy)hydroxides. Dissolved  $\text{O}_2$  accounts for most  $\text{Fe}^{2+}$  oxidation under natural conditions, and presumably will be the dominant oxidant where it is in contact with iron-containing reactive barriers.  $\text{RX}$  and  $\text{ArNO}_2$  can also oxidize  $\text{Fe}^{2+}$  and thereby contribute to ferric oxide precipitation, but the possibility of these reactions in  $\text{Fe}^0$ -based remediation systems has only just been recognized, and their importance remains to be determined.

The processes described above occur at, or define, the various interfaces associated with iron-containing reactive barriers. These interfaces range in scale from cm to  $\mu\text{m}$  or less. The large scale interfaces occur between *zones* created by the construction of any in situ permeable barrier; intermediate scale interfaces occur at the boundaries between *grains* (of iron or matrix material) and the surrounding pore water; and small scale interfaces involve thin *films* of precipitate and boundary layers of solution that develop between the metal and the contacting electrolyte. Recognition of this range of scales over which important interfacial processes occur is an

important element in relating results of the various laboratory and field studies currently being reported on reactive barrier remediation systems.

The importance of zone-scale interfaces is illustrated by the results of two column studies. The columns were designed to model a cross section of an in situ permeable iron barrier by including up-gradient, iron-bearing, and down-gradient zones. The first column received various concentrations of  $\text{CCl}_4$  in air-saturated deionized water and developed a dramatic series of precipitation zones that have been described previously [1, 2]. At the up-gradient interface, all dissolved  $\text{O}_2$  was consumed by reaction with  $\text{Fe}^0$  (eq 1) and oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Thus, the region down-gradient from this zone was anoxic. The second column was designed similarly, but the iron-bearing zone was longer and diluted by mixing with sand (Fig. 1). In addition, Ar-sparged deionized water and lower concentrations of  $\text{CCl}_4$  were applied as the influent. A less dramatic, broad black precipitation zone developed gradually over 9 months of operation. Since  $\text{O}_2$  should be absent in Column II, this zone probably reflects the impact of  $\text{CCl}_4$  as an oxidant of  $\text{Fe}^{2+}$ .

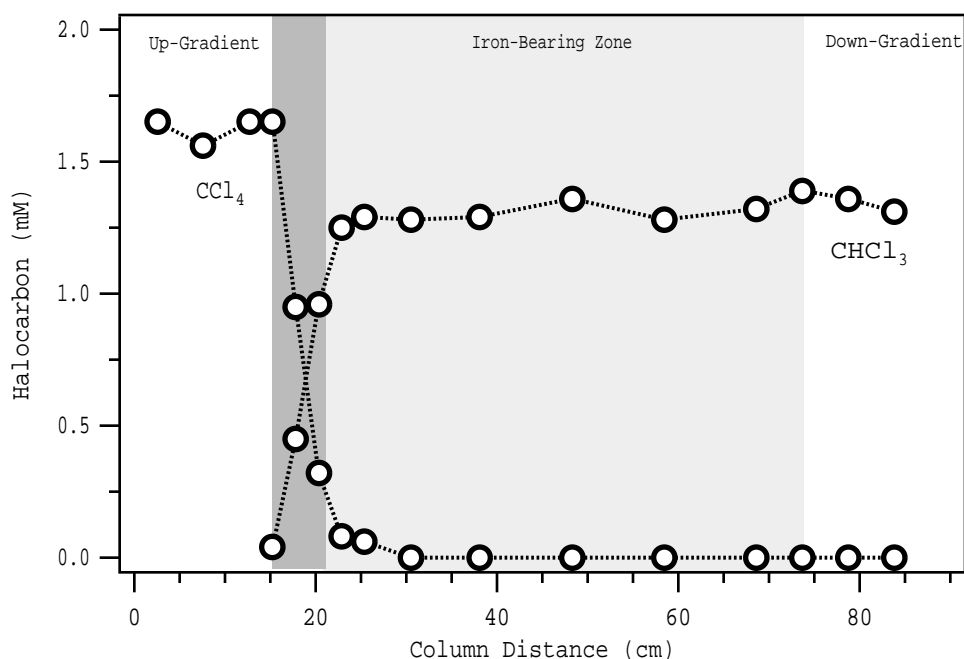


Figure 1. Reduction of  $\text{CCl}_4$  to  $\text{CHCl}_3$  in a column with anoxic influent. The darkly-shaded zone represent a zone black precipitation. Maximum  $[\text{Fe}^{2+}] = 1.4 \text{ mM}$  and  $\text{Cl}^- = 2.1 \text{ mM}$ .

At the grain-scale, interfacial effects can be due to layers and rinds of precipitate, corrosion pits and crevices, etc. These effects have received the greatest attention in studies of  $\text{Fe}^0$ -based remediation systems to date. In particular, many studies that have employed batch model systems have found grain-scale interfacial effects on contaminant reduction rates [3-7]. In general, clean metal surfaces have been found to give faster reduction rates (Fig. 2). This is primarily due to the removal of precipitates that block access to reactive surface sites, although other factors such as increased surface area due to etching of the metal and abrasion may play a role [3, 4].

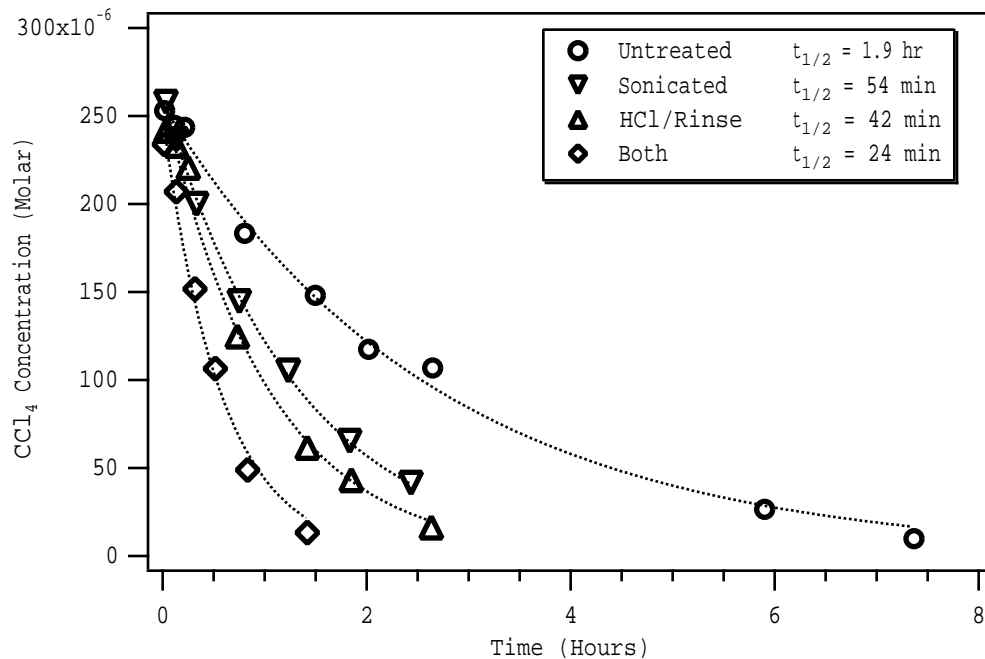


Figure 2. Effect of pretreating iron on rates of  $\text{CCl}_4$  dechlorination by  $\text{Fe}^0$ . Method was based on batch experiments similar to [4, 5]. 16.7 g/L of 325 mesh sieved Fisher electrolytic  $\text{Fe}^0$ , rpm = 36.

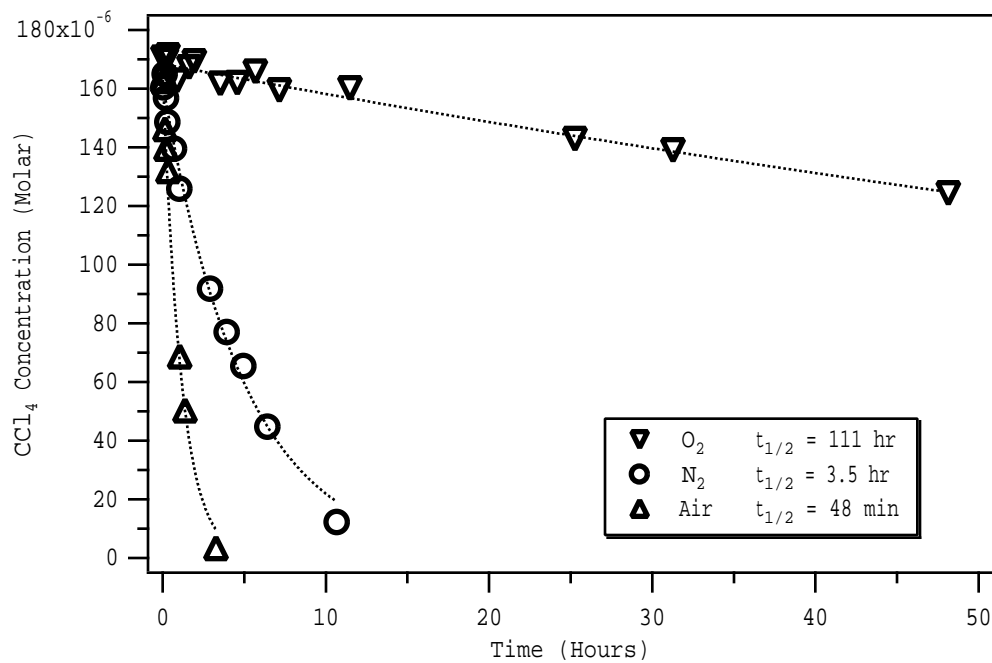


Figure 3. Effect of purge gas on rates of  $\text{CCl}_4$  dechlorination by  $\text{Fe}^0$ . Method was based on batch experiments similar to [4, 5]. 16.7 g/L of 325 mesh sieved Fisher electrolytic  $\text{Fe}^0$ , rpm = 36.

The effect of O<sub>2</sub> on dechlorination rates in batch experiments is illustrated by Fig. 3. Serum bottles were purged with the N<sub>2</sub>, air, or O<sub>2</sub> prior to addition of CCl<sub>4</sub>. The dissolved O<sub>2</sub> reacts rapidly with the iron, and dechlorination occurs more slowly. The strong inhibition of dechlorination in a bottle that had been saturated with O<sub>2</sub> is likely to be due to extensive precipitation of oxides on the Fe<sup>0</sup> grains. In contrast, the smaller amount of O<sub>2</sub> introduced by purging with air appears to have accelerated the rate of CCl<sub>4</sub> dechlorination. This might be an effect of pH due to carbonate introduced with the air, but the addition of carbonate generally results in slower reaction rates [4]. Other possibilities include changes in the dechlorination reaction pathway [8], a catalytic role of small amounts of Fe<sup>2+</sup>, or a mechanism by which aggressive reaction with O<sub>2</sub> creates active corrosion sites that, in turn, facilitate CCl<sub>4</sub> dechlorination. If either of the two effects do occur, they are likely to favor good and sustained remediation performance under microaerophilic groundwater conditions.

#### *References:*

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