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DECHLORINATION OF CARBON TETRACHLORIDE BY IRON METAL:
 THE ROLE OF COMPETING CORROSION REACTIONS

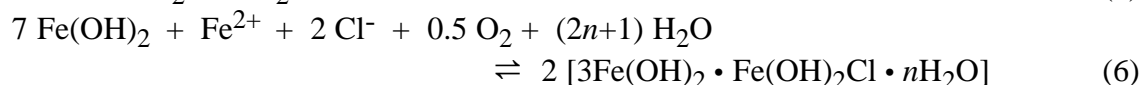
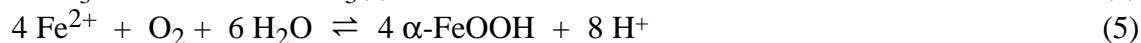
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In waters contaminated with chlorinated solvents, three oxidants are available to drive corrosion of metals: water, dissolved oxygen, and the chlorinated contaminant. The corrosion reaction involving water (eq 1) is slow but presumably ubiquitous, whereas corrosion of Fe⁰ by reaction with dissolved oxygen (eq 2) is very rapid as long as O₂ is available. The presence of chlorinated solvents in an Fe⁰-H₂O system provides another possible reaction (eq 3) that can contribute to the overall corrosion rate. In general, the net rate of corrosion will be rapid at clean Fe⁰ surfaces as long as a strong oxidant such as O₂ or CCl₄ is available.



As corrosion proceeds, however, reaction products will precipitate that are likely to cause passivation of the metal. Of the many solid phases that may form under environmental conditions, three are representative: siderite, goethite, and green rust. Siderite will be favored in carbonate-rich waters (eq 4), and goethite is expected where excess oxidant is available to further react with Fe²⁺ giving Fe³⁺ (eq 5). Green rust 1 (GR1) is a layered oxide containing Fe²⁺, Fe³⁺, and Cl⁻ that commonly forms in corroding metal systems [1] (eq 6), and has recently been discussed in a geochemical context [2].



The preceding discussion reveals several important areas of uncertainty regarding the processes that occur during in situ treatment of halocarbon-contaminated groundwater. Equations 1-3 represent three potentially competing corrosion reactions among which dechlorination is only one. A goal of this study is to assess the relative significance of solvent dechlorination among these three possibilities. Equations 4-6 represent precipitation reactions that will occur under different geochemical conditions, but all three may occur at any particular field site. A second goal of this study is to determine how the accumulation of these precipitates is determined by the chemical gradients created by subsurface barriers of Fe⁰, and how these precipitation zones effect the degradation of chlorinated solvents. Two

column studies have been performed using a configuration that was designed to model a cross section of an in situ permeable iron barrier by including up-gradient, iron-bearing, and down-gradient zones (Fig. 1). The first column received varying amounts of chlorinated solvents in air saturated deionized water for 10 months and provided our first look at the spatial and temporal dependence of chemical processes under these conditions [3]. The second column was designed similarly, but has received only deoxygenated water and CCl_4 to date.

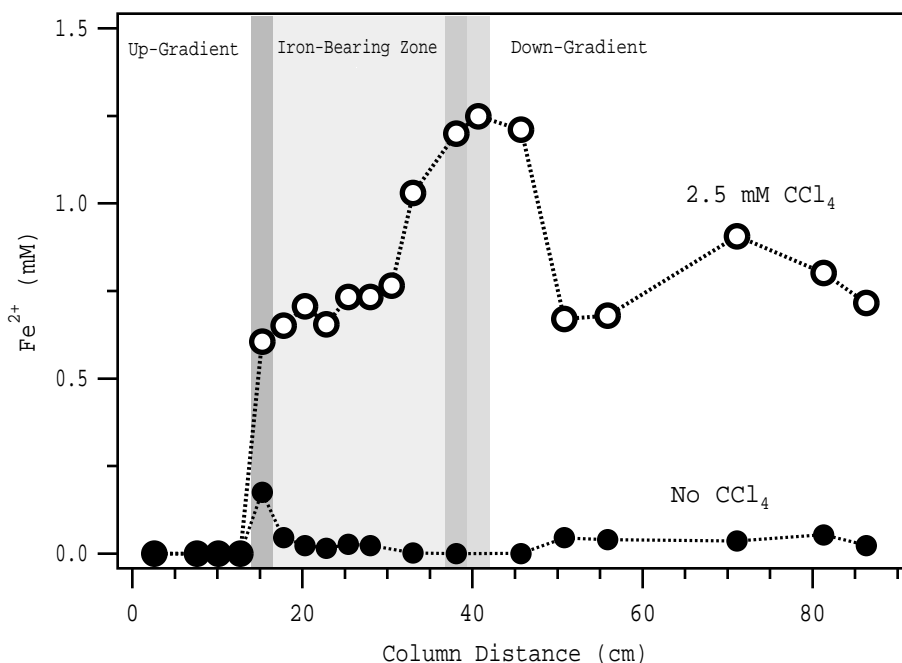


Figure 1. Concentration of iron in pore water sampled along Column I with and without CCl_4 in the influent. Darkly-shaded zones represent regions of visible precipitation. $[\text{O}_2]_0 \approx 0.3 \text{ mM}$, $\text{Fe}^0 = 185 \text{ m}^2/\text{L}$, $v = 30 \text{ cm/day}$.

The unique design of these columns allowed the rates and products of CCl_4 degradation, as well as changes in column chemistry resulting from corrosion and precipitation, to be determined as a function of time and location along the column length. Before CCl_4 was introduced in Column I, very little iron dissolution was observed except at the up-gradient interface of the iron-bearing zone, where dissolved O_2 was consumed by reaction 2 (Fig. 1). When CCl_4 was added, a marked increase in iron dissolution was observed, which we attribute to corrosion by dechlorination of CCl_4 (eq 3). The difference between the two profiles in Fig. 1 indicates that oxidative dissolution of iron is primarily due to reaction with CCl_4 (at 2.5 mM) and not O_2 or H_2O . This interpretation is further supported by the correlation between the concentration of dissolved iron and CCl_4 across the length of the iron-bearing zone (Fig 2). Linear regression on these data gives a fitted slope that is somewhat less than unity, which we attribute to the obvious precipitation of iron in the column. If precipitation in the column were not significant, the slope of Fig. 2 should be greater than one due to additional Fe^0 dissolution by further dechlorination of the CCl_4 reduction products. Analogous correlations can be derived from Column I data by comparing the steady-state concentration of Fe^{2+} at different input concentrations of CCl_4 . The data (not shown) suggest an intercept that is not significantly different from zero, as it should in the absence of any significant corrosion reactions other than eq 3.

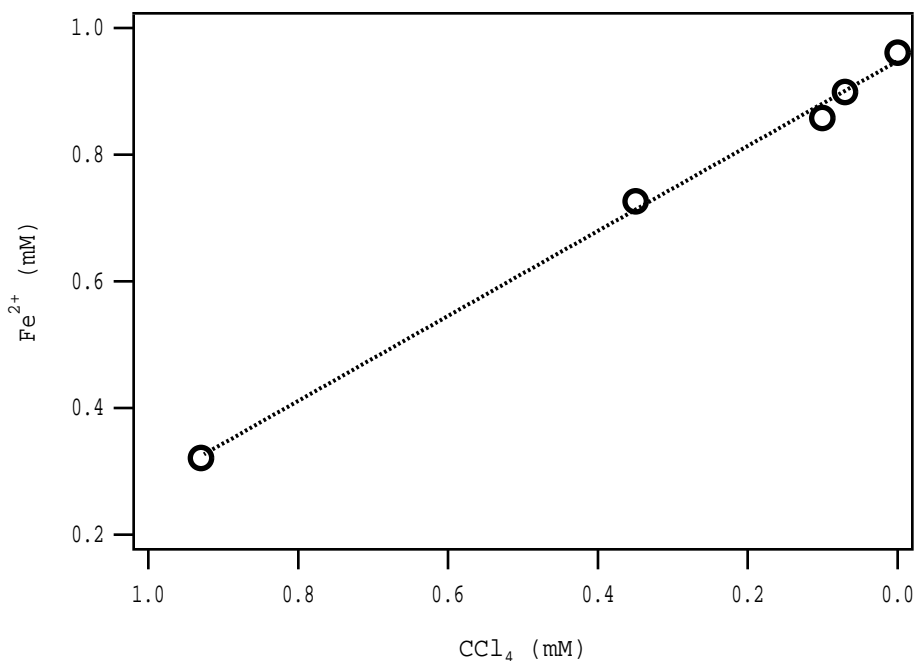


Figure 2. Concentration of Fe^{2+} found in solution at sampling ports throughout the iron-bearing zone of Column II, showing the dependence of iron corrosion on CCl_4 concentration. $[\text{O}_2]_0 < 2 \times 10^{-4}$ mM, $\text{Fe}^0 = 40$ m²/L, $v = 30$ cm/day. The regression line is $[\text{Fe}^{2+}] = (0.95 \pm 0.01) - (0.67 \pm 0.02)[\text{CCl}_4]$.

Of the three corrosion reactions considered above (eqs 1-3), only reduction of H_2O yields H_2 (eq 1). It has been pointed out previously that H_2 and Fe^{2+} are products of corrosion that—in addition to the Fe^0 metal—could serve as direct reductants of chlorinated solvents [4]. However, the conclusion that eq 3 is the dominant reaction in our columns leaves little room for intermediacy of H_2 in the dechlorination process. The additional possibility that Fe^{2+} plays a role in dechlorinating solvents will depend on its reactivity as an adsorbed species or as “structural iron” in the various precipitates that may form (e.g. GR1, eq 6). Either of these reductants could produce dechlorination in the zone of precipitation just down-gradient from the iron-bearing region of our columns. We have preliminary data (not shown) to indicate this process does occur, but also that it contributes little to the net loss of CCl_4 relative to dechlorination that takes place within the iron-bearing zone.

References:

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