

## Development of Activity Enhanced Zero Valent Metals for Permeable Reactive Barrier

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(Manuscript received 13 December , 2002 ; Accepted 14 February, 2003)

The dechlorination of chlorinated methanes by iron powder and palladium coated iron (Pd/Fe) was studied in batch experiments. Iron powder dechlorinated carbon tetrachloride (CT) with a half-life of 4 days. Three chloromethane was found as major product and less chlorinated daughters. Mass balance found was to be about 93-99%. Pd/Fe showed very enhanced reactivity for CT in comparing with plain iron. The major dechlorination products of CT were also less chlorinated methanes with Pd/Fe. Pd/Fe also degrade the produced less chlorinated compounds. Sequential reactions were occurred on Pd/Fe. As the Pd/Fe content increased, the reaction rate was increased linearly.

Key words: Zero-Valent Metals, Reduction, Dechlorination, Carbon tetrachloride, Palladium

### 1. Introduction

Zero valent metals (ZVMs) have been known to reductively dechlorinate chlorinated organic pollutants. Many laboratory and field scale demonstrations of contaminated groundwater remediation showed that ZVMs could be an alternative reductants for chlorinated organic solvents such as tetrachloroethene (PCE), trichloroethene (TCE), and carbon tetrachloride (CT)<sup>1-6</sup>. Currently ZVMs are using as media for permeable reactive barrier (PRB). Common intermediates are less chlorinated compounds and a thicker wall is required for complete dechlorination of these degradation intermediates in remediation using the a PRB<sup>7</sup>. Reactivity enhanced ZVMs are required for fast and complete dechlorination reactions and a compact design of PRB. The preparation of bimetals is one of the most promising technology to enhance the reactivity of zero valent metals (ZVMs). Usually bimetals consists of more than 99% of a primary metal as electron source and

less than 1% of a secondary metal for surface coating. Iron<sup>1,4</sup>) and zinc<sup>8-9</sup>) were common primary metals while palladium<sup>1,4,8-9</sup>), and nickel<sup>9-10</sup>) have been tested as secondary metals. Tested bimetals enhanced the dechlorination reactivities for a variety of chlorinated compounds such as PCE, TCE, and polychlorinated biphenyls (PCBs). In spite of the enhanced reactivity, the lack of understanding of the reaction mechanism and effects of environmental factors has been the reason for the delayed the practical application.

Palladium is a well known hydrogenation and reduction catalyst<sup>11-12</sup>). Palladium deposited alumina or activated carbon has been studied as a dehalogenation catalyst for treating halogenated contaminants<sup>13-14</sup>). Hydrogen was the most common electron donors with the catalyst.

Identification of the intermediate was important in understanding dechlorination mechanism. However, no chlorinated intermediates were observed in previous results in which bimetals were used<sup>1,9</sup>). Pd/alumina catalyst also found no chlorinated intermediate<sup>1,14</sup>).

The objective of this work was to study the degradation of chlorinated methanes by Fe and Pd/Fe. The experiments provided kinetic data for CT and daughter compound distribution. Rate information was also obtained with dif-

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ferent dose of iron. Based on the observed results, effectiveness of palladium was discussed.

## 2. Experimental Methods

### 2.1 Materials

CT (99.9+%, Aldrich), methanol (99.8%, HPLC grade, EM), toluene (99.9%, gas distilled, EM), palladium chloride (5% by weight solution in 10% HCl, Aldrich), hydrochloric acid (Aldrich), pentane (99.9%, HPLC grade, EM), and iron powder (electrolytic, -100 mesh, Fisher Scientific) were used without further purification. The iron surface area measured by BET were  $0.098 \pm 0.003 \text{ m}^2 \text{ g}^{-1}$ .

### 2.2 Preparation of Pd/Fe

Pd/Fe was prepared by spontaneous adsorption of Pd on the Fe surface. Pd stock solution (5% Pd in 10% HCl solution) were diluted in 250 ml flasks with water and mixed with acid washed iron powder. Then the flasks were placed on an orbital environmental shaker at 215 rpm for 30 minutes. The prepared Pd/Fe was rinsed with deoxygenated water and acetone, sequentially. The rinsed Pd/Fe was dried in air and stored in an amber vial. A batch of 0.051% Pd coated Pd/Fe was used in this study.

### 2.3 Reactor system

The prepared Pd/Fe was weighed and added to EPA 20 mL VOA amber vials (23.4 mL observed). The vials were placed in an anaerobic bag for 3 hours to remove oxygen from the vials and metal surfaces. The vials were filled with deionized and deoxygenated water allowing minimal headspace ( $< 0.5 \text{ mL}$ ) and reactions were initiated by injecting an aliquot of target compounds in methanol with a microsyringe. The vials were sealed with open top caps and lead foil lined PTFE/Silicone septa and placed on an orbital shaker at 200 rpm and room temperature ( $23 \text{ }^\circ\text{C}$ ). Triplicate samples and controls were analyzed at each sampling time.

### 2.4 Analysis

All chlorinated methanes were determined by pentane extraction and GC analysis. An aqueous sample (1.5 mL) was transferred into 4-mL

vials containing 1.5 mL of pentane and toluene ( $10\text{-}40 \text{ mg l}^{-1}$ ) dissolved as an internal standard. The extraction vials were placed on an orbital shaker at 215 rpm for 30 minutes. The compounds were identified and quantified with a HP-5890 GC with an ECD and a FID ( $30 \text{ m} \times 0.25 \text{ mm}$ ,  $1.8 \text{ }\mu\text{m}$  film thickness, J & W Scientific). The oven temperature was 8.0 minutes at  $80 \text{ }^\circ\text{C}$ ,  $20 \text{ }^\circ\text{C min}^{-1}$  to  $160 \text{ }^\circ\text{C}$ , and 2.0 minutes at  $160 \text{ }^\circ\text{C}$ . The injector and the detector temperatures were  $230 \text{ }^\circ\text{C}$  and  $300 \text{ }^\circ\text{C}$  respectively. The peaks were identified by comparison with the retention times of known standards and mass spectra analysis.

## 3. Results and Discussion

CT was dechlorinated with iron powder and the result was summarized in Fig. 1. CT was gradually disappeared and trichloromethane and dichloromethane was found as daughter products. Trichloromethane was the major product and dichloromethane followed. Trace amount of monochloromethane was detected but not quantified. The produced daughters were accumulated indicating further reaction rate was small or no additional reaction occurred. The mass balance, sum of CT, trichloromethane, and dichloromethane, was about 96-103% over the experimental period. The high mass balance indicate dechlorination was the major reaction and no significant volatile loss occurred. The degradation followed a pseudo first order reaction

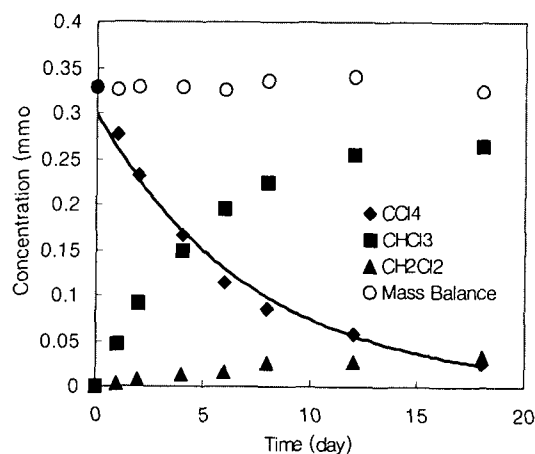


Fig. 1. Reductive dechlorination of carbon tetrachloride using zero valent iron powder.

kinetics. Previous studies also showed pseudo first order reaction to the metal surfaces<sup>1-5</sup>.

It is hard to directly compare the first order rate constants ( $k_{obs}$ ) from different studies with different ZVMs because the reaction rate usually depends on several parameters such as the metal surface area per volume of solution. Kinetic rate constants normalized by surface area per unit volume of aqueous solution ( $k_{SA}$ ) have been suggested as unifying values for a specific metal<sup>1)</sup> in ZVM studies. In this study, the primary metals (Fe) had same specific surface areas before coating and were coated with similar low mass fractions of Pd. Therefore, for purposes of comparison, authors assumed the change in specific surface area due to coating by the secondary metal is negligible and normalized  $k_{obs}$  values by the primary metal surface area. The  $k_{obs}$  and  $k_{SA}$  values obtained are in Table 1.

Table 1. Dechlorination reaction kinetic constants for chlorinated methanes using zero valent metals

Compounds	Metals	Kinetic constants ( $d^{-1}$ )	Surface area normalized kinetic constants ( $L/m^2 hr$ )	$R^2$
Carbon tetrachloride	Fe	0.139	0.681	0.99
Trichloromethane	Fe	0.023	0.112	0.96
Dichloromethane	Fe	0.006	0.029	0.92
Carbon tetrachloride	Pd/Fe	6.14	30.086	0.98

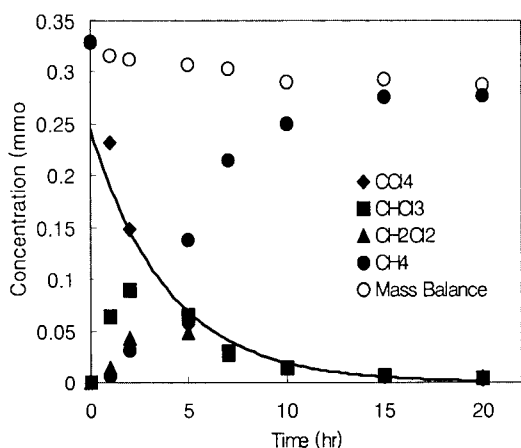


Fig. 2. Reductive dechlorination of carbon tetrachloride using zero valent iron powder.

Pd/Fe was tested for CT to compare with Fe (Fig. 2). Pd/Fe showed the faster degradation rate. Note the experimental term is in hours while the reaction term was days with Fe. The surface area normalized kinetic constants showed 1-2 order higher values in comparing with that of Fe (Table 1). Palladium worked as catalyst for dechlorination of CT. It is reported that palladium coated iron showed very enhanced reactivity for TCE and PCE in previous studies. The exponential fit shown in Fig. 1 indicates that the reaction by Pd/Fe also followed pseudo first order kinetics. Trichloromethane, dichloromethane, and methane were found and quantified as product. The less chlorinated daughters were produced and disappeared indicating the less chlorinated daughter react with Pd/Fe. Finally, no chlorinated and non-toxic compound, methane was detected and it is accumulated. The mass balance was about 91-100% over the experiments indicating no significant loss.

Trichloromethane and dichloromethane was degraded by Fe in the same condition used for CT (Fig. 3). The degradation rates were very lower than that of CT indicating longer term is required to complete dechlorination. The kinetic constants were compared in Table 1. Dichloromethane has about one order lower degradation rate in comparing with CT. This trend is similar with the result for dechlorination of chlorophenols<sup>12)</sup>. Less chlorinated phenol had lower degradation rate while PCP had fastest reaction rate. In general, it is difficult to

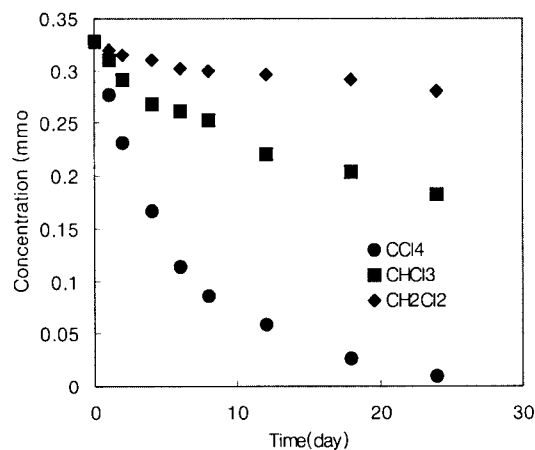


Fig. 3. Reductive dechlorination of chlorinated methanes using zero valent iron powder.

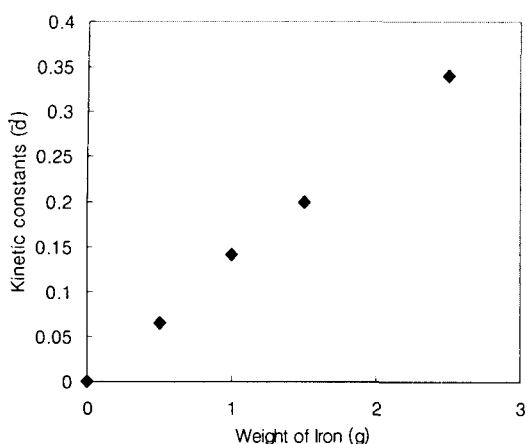
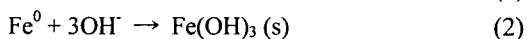
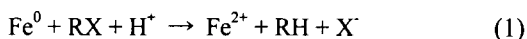


Fig. 4. The effect of metal dose for degradation of carbon tetrachloride using zero valent iron.

remove chlorine from lower chlorinated carbon in the stepwise dechlorination. In design of PRB, the slow degradation of less chlorination daughter compound could be the limiting factor.

In Fig. 4, the kinetic constants in varying metal dose is linearly increased. A few previous result also showed similar results<sup>12)</sup>. The solution pH was monitored during the experiments. The pH of Pd/Fe containing vials ranged between 5.3-7.1 without any pH buffer. However, the pH of the Fe containing solution increased to near 10 in this study (data not shown). The lower pH is preferred for dechlorination reactions and because the overall hydrodechlorination reaction consumes protons and high pH make inactive coating on the metal surface as shown below.



A high pH accelerates metal hydroxide precipitation and lead to problems such as the clogging of flow reactors.

#### 4. Conclusions

CT and its less chlorinated methane was successfully tested with Fe and Pd/Fe. Fe dechlorinated CT and produced less chlorinated daughter compounds. Fe which is the most commonly used ZVM for PRB has lower reactivity for less chlorinated daughter. However,

Pd/Fe showed very enhanced reactivity for CT and stepwise dechlorination occurred indicating small amount of palladium worked as catalyst and increased orders of reaction rate. This results implicate that Pd/Fe could be an excellent PRB media.

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