PROMOTER EFFECT OF ALUMINUM OXIDE ON ENHANCED HYDRODECHLORINATION OF CARBON TETRACHLORIDE WITH ZERO-VALENT ALUMINUM

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ABSTRACT

The transformation of carbon tetrachloride by zero-valent aluminum (Al^0) under various pH conditions has been examined in the presence and absence of Al_2O_3. In the absence of Al_2O_3, carbon tetrachloride was primarily transferred to chloroform (68%) and dichloromethane (16%) at pH 3.0 while little of hydrodechlorination intermediates (7%) was found at pH 10. This indicates that carbon tetrachloride undergoes hydrodechlorination at low pH but not at high pH. The low production of hydrochlorination products could be attributed to the base-catalyzed hydrolysis of carbon tetrachloride resulting in the formation of carbon monoxide at high pH. It can not be detected by the provided analytic methods. In the presence of Al_2O_3, reaction rates increased as increasing the Al_2O_3 loading. Under alkaline conditions, the increase of selectivity towards the hydrodechlorination products was observed as the loading of Al_2O_3 increased. Reactions shifting from the possible base-catalyzed hydrolysis to hydrodechlorination suggested that Al_2O_3 serves as a proton donor in the degradation of carbon tetrachloride. Al_2O_3 is the key component of aluminosilicate, which is a composition of aquifer materials that have been found to increase the effectiveness of zero-valent iron. The present results provide a better understanding of the role of aluminosilicate minerals.
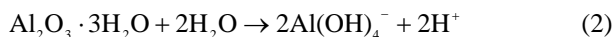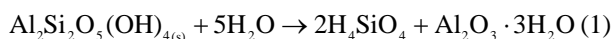
INTRODUCTION

Permeable reactive barrier (PRB) technology represents a promising environmental remedial technology for the remediation of groundwater contamination [1-2]. PRB technology involves the placement or formation of a reactive treatment zone in the path of a contaminant plume in which groundwater passively moves while contaminants precipitate, adsorb or degrade. This technology is attractive relative to other remediation technologies such as pump and treat because PRB treatment occurs in situ. Substantial research efforts have been initiated over the past few years to identify reactive materials/reagents that can be used in PRBs to treat the many contaminants found in groundwater. The reactive media most successfully deployed to date has been zero-valent metals (ZVM) [3-10]. The successful application of ZVM, particularly zero-valent iron (ZVI), in permeable reactive barriers to reductively remediate many contaminants including halogenated organics,

Cr(VI), and nitroaromatics has been widely reported in the literature [1].

Because PRB is an in situ treatment technology, issues such as geochemistry, flow direction, velocity, and contaminant distribution must be thoroughly addressed in order to construct a successful PRB system. Therefore, extensive studies have been conducted to focus on understanding the geochemical effect of aquifer materials that may be potentially beneficial or detrimental to contaminant treatment. For example, aquifer materials have been shown to influence reaction rates in the reduction of Cr(VI) by ZVI in a PRB system [11]. It has been demonstrated that the Cr (VI) reduction rates increase when certain aquifer materials are present in the ZVI system [11]. The increase in reaction rate has been attributed to the presence of aluminosilicate minerals ($Al_2Si_2O_5(OH)_4$) in aquifer materials. Powell and Puls suggested that the proton, which could serve as an electron acceptor, was generated by dissolution of aluminosilicate minerals resulting in the enhancement of Cr(VI)

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reduction by ZVI [11]:

$$Al_2Si_2O_5(OH)_{4(s)} + 5H_2O \rightarrow 2H_4SiO_4 + Al_2O_3 \cdot 3H_2O \quad (1)$$

$$Al_2O_3 \cdot 3H_2O + 2H_2O \rightarrow 2Al(OH)_4^- + 2H^+ \quad (2)$$

However, direct evidence to indicate the role of aluminosilicates as proton donors is still limited.

The difficulty in investigating the role of aquifer materials as the proton donor is related to the pH-dependence of iron corrosion process. Reductive degradation by ZVM involves metal corrosion. ZVM (e.g., iron, zinc, and aluminum) serves as electron donors that release electrons through metal corrosion while contaminants such as carbon tetrachloride undergoes reduction gaining electrons to form less-chlorinated intermediates such as chloroform in the presence of protons:

$$M^0 \rightarrow M^{n+} + ne^- \quad (M = Fe^0, Zn^0, Al^0\ldots) \quad (3)$$

$$CCl_4 + 2e^- + H^+ \rightarrow CHCl_3 + Cl^- \quad (4)$$
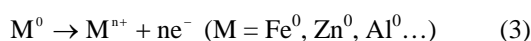
The hydrodechlorination rate could be enhanced by increasing either the proton concentration or the electron activity. Studies have shown that the rate of carbon tetrachloride reduction by iron metal is a function of pH where decreasing pH increases the reduction rate [6]. On the other hand, the electron activity could be increased by increasing the corrosion rate, which is also pH-dependent. The dependence of both metal corrosion rate and carbon tetrachloride degradation rate on pH complicates the interpretation of intrinsic effect of pH on the metal-mediated dechlorination because:

(i) At low pH, the increased degradation rate may not be directly attributed to the decrease in pH. As indicated in Fig. 1a, the corrosion rate of iron increases while pH decreases [12]. Proton- and electron-rich environments are established at low pH. The enhancement of corrosion rate facilitating the release of electrons may also be involved in the increase of the carbon tetrachloride degradation rate.

(ii) The expected decrease of the degradation rate under alkaline conditions did not result from the lack of protons (Fig. 1a). In contrast, at high pH, the formation of iron oxide precipitates on the iron surface develops an electron-deficient condition. Electron transfer by iron dissolution is inhibited by the inert oxide layer [6].

$$Fe^0 + 2H_2O \rightarrow Fe(OH)_2 + H_2 \quad (5)$$
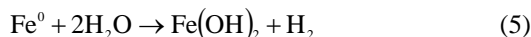
Clearly, neither low nor high pH would be suitable for investigating the role of aquifer materials as the proton donor in zero-valent iron system. At low pH, acidic water itself (H^+) is a strong proton donor that dominates the protonation process. On the other hand, the reduction system fails at high pH because of poor reductive capacity of iron.

Zero-valent aluminum (Al^0), however, provides

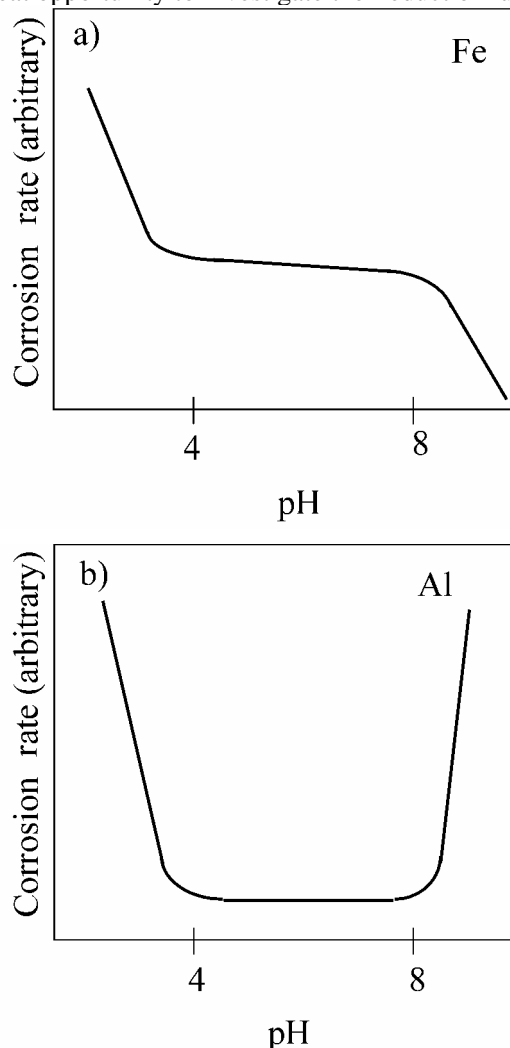a great opportunity to investigate the reduction under

Fig. 1. Dependence of corrosion rates (electron-donating ability) of (a) iron and (b) aluminum on pH. General type of diagrams adapted from Chawla and Gupta [12].

alkaline conditions. As illustrated in Fig. 1b [12], aluminum corrosion proceeds under both acidic and alkaline conditions that lead to yield Al^{3+} ions (which is corresponding to eq 3) and AlO_2^- (aluminate), respectively. At high pH, an electron-rich but proton-deficient environment was created because the presence of OH^- removes the aluminum oxide layer [13]:

$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2O \quad (6)$$
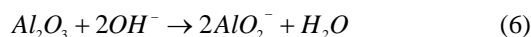
The role of aquifer materials can therefore be investigated by using zero-valent aluminum to create an electron-rich but proton-deficient environment. While the compositions of aquifer materials have been studied by Powell and Puls, a simplified system was carried out by using Al_2O_3, as a substitute in this study. Aluminum oxide was chosen because it is the key component of aluminosilicate indicated in eq 2.

Carbon tetrachloride (CT), a priority pollutant classified by USEPA, was selected as a model compound. CT undergoes a hydrodechlorination under acidic conditions (proton-rich conditions) and a hydrolysis under alkaline conditions [14-15]. Major products from CT hydrodechlorination are less-chlorinated intermediates (e.g., chloroform, eq 4) or methane [16] while carbon monoxide and dissolved organic acids such as formic acid are the dominant products from the CT hydrolysis (eq 7).

$$CCl_4 + 2e^- + 2OH^- \rightarrow CO + H_2O + 4Cl^- \qquad (7)$$

As a result, under the proton-deficient conditions (high pH), the presence of a proton donor could promote eq 4 to compete with eq 7 and therefore increase the product selectivity toward less-chlorinated intermediates. By comparing the product distributions with increasing amounts of Al_2O_3 under alkaline conditions, an expected increase of hydrodechlorination products would provide insight into the function of aluminum oxide.

EXPERIMENTAL METHODS

Treatment of Aluminum. The aluminum metal was treated by sodium hydroxide for the study under alkaline conditions and hydrochloric acid for the study under acidic conditions, respectively. Typically, 20 mL of 0.75 M NaOH aqueous solution was used to clean the surface of aluminum particles at ambient temperature. After vigorous stirring for 3 minutes, the solution was filtered and washed by a large amount of distilled water. Experiments were conducted by base-washed aluminum without further controlling pH. The solution pH was measured before and after reactions.

For the experiment at acidic pH, the aluminum metal was rinsed by 10 mL of concentrated HCl at ambient temperature. As soon as a dynamic reaction was immediately observed, quickly added 40 mL distilled water to cool off the reaction and kept stirring for three minutes. The pH of the solution containing acid-washed aluminum was adjusted with 1N HCl and was measured before and after the experiment.

Batch Experiments. Batch experiments carried out in 150 mL glass vials containing aluminum and/or aluminum oxide at both low and high pH was used to determine reaction rates and product distributions from the CT reduction. For a typical experiment, constant aluminum loading (2 g) was placed while varying the loading of aluminum oxide from 0 to 10 g in the vials containing approximately 30 mg/L of CT in 100 mL distilled water. The vials were sealed with aluminum crimp caps. The vials were mixed with a rotary shaker at room temperature (23 ± 1.5 °C). For each experiment, duplicates were performed to check the reproducibility of the batch results. In addition,

batch bottles containing CT in the absence of aluminum or aluminum oxide were used as controls.

Kinetics Analysis. The rate of transformation for carbon tetrachloride in a batch system is described as a pseudo-first order reaction:

$$\frac{dC}{dt} = -k_{obs}C \qquad (8)$$

Where C is the concentration of carbon tetrachloride (mg/L); k_{obs} is the measured rate constant (hr^{-1}) and t is time (hr).

Methods of Analyses. Concentrations of chlorinated methanes were measured by a HP4890 GC equipped with a DB-624 capillary column (30 m×0.32 mm) and an electron capture detector (ECD). Headspace gas aliquots (5 µL) were withdrawn for the analysis of chlorinated methanes at selected time intervals. Calibration curves for each compound were made initially and the variability was checked daily before analysis (< 15%). Temperature conditions were programmed as follows: oven temperature at 50 °C; injection port temperature at 200 °C; and detector temperature at 300 °C. Carrier gas for GC was ultra-pure nitrogen at a flow rate of 4.86 mL/min.

Hydrocarbon products (e.g., methane) in the headspace were quantified with GC analysis by comparing retention times and peak areas with standard gas samples. The GC was equipped with a flame ionization detector (FID) and an AT-Q column (Alltech, 30 m × 0.32 mm). Oven temperature was set at 30 °C, injection port temperature at 250 °C, and detector temperature at 300 °C.

Chemicals. Carbon tetrachloride (99.5%) was purchased from SHOWA. Chloroform (99%), and dichloromethane (99.9%) were obtained from J. T. Baker. The standard gas mixture for GC analysis was acquired from Supelco, which included 1% of ethane, ethylene, acetylene, and methane. Sodium hydroxide (NaOH, A.C.S. reagent 97+%), aluminum (Al, ~20 micron, 99+%) and aluminum oxide (Al_2O_3, activated, acidic, Brockmann I, ~150 mesh, 58 Å, surface area 155 m^2/g, standard grade) were from Aldrich.

RESULTS AND DISCUSSION

1. Effect of pH on the Effectiveness of Zero-valent Aluminum

The effect of pH on the effectiveness of zero-valent aluminum in the degradation of carbon tetrachloride is shown in Fig. 2. Four sets of different pH conditions were conducted. Carbon tetrachloride was rapidly degraded under both acidic and alkaline conditions. The observed rate constant of carbon tetrachloride degradation was about 0.26 and 0.065 hr^-

[1] at pH 3.0 and 10.0, respectively. However, little reaction was observed at near neutral pH where reaction rate de-
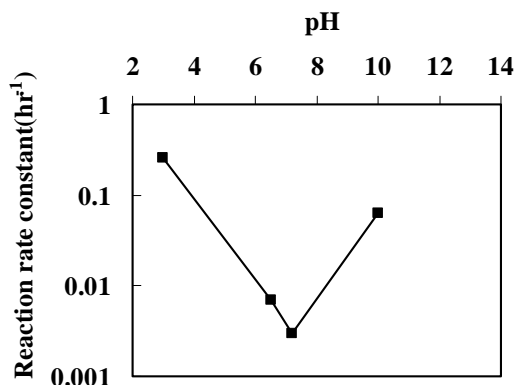

Fig. 2. Effect of pH on the effectiveness of zero-valent aluminum in the degradation of carbon tetrachloride.

creased by a factor of approximately 10-80. It is apparent that Al^0 with a high reductive potential (-1.67 V) could serve as a good electron donor. However, the protective oxide layer readily formed on the surface inhibits the reductive capacity of Al^0 when it reacts with water at near neutral pH. Aluminum corrosion is subject to a very low rate at near neutral pH and its rate becomes increasingly rapid as pH decreases below 4.0 or increases above 8.0 (Fig. 1b). Consequently, the reduction of carbon tetrachloride proceeding under both acidic and alkaline conditions is corresponding to aluminum corrosion. Little degradation of carbon tetrachloride was determined at pH 7.5, which could be contributed to the poor reducibility of Al^0.

2. Transformation of Carbon Tetrachloride by Zero-valent Aluminum

The transformation of carbon tetrachloride by Al^0 was conducted under various pH conditions from approximately 3.0 to 10.0. The results for the degradation of carbon tetrachloride under acidic conditions (pH 3.0) are shown in Fig. 3(a). Carbon tetrachloride was primarily dechlorinated to chloroform and subsequently to dichloromethane. Chloroform was the major byproduct, which accounted for about 68% of the carbon tetrachloride lost. The yield of dichloromethane was about 15.5%. Methane was detected in a minor amount (<1%). The carbon mass balance at the end of the experiment was about 90% (including 6.6% of remaining carbon tetrachloride). This indicates that the hydrodechlorination is the primary reaction in the transformation of carbon tetrachloride by Al^0 at acidic pH.

The results for the degradation of carbon tetrachloride under alkaline conditions (pH 10.0) are

given in Fig. 3(b). Although the same reaction products as described above were found here, the product distribution was quite different. Chloroform, dichloromethane and methane were all detected in minor amounts (< 5%). The carbon mass balance, which is a sum of the
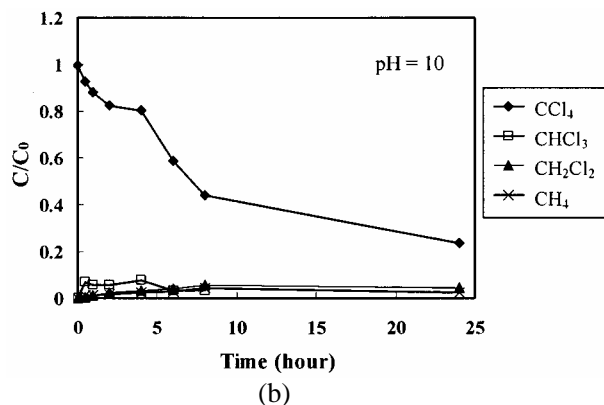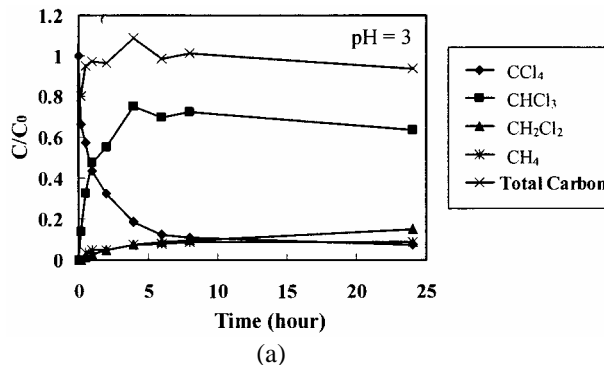

(a)

(b)

Fig. 3. The transformation of carbon tetrachloride by zero-valent aluminum at (a) pH 3.0 and (b) pH 10.0.

lesser-chlorinated intermediates and methane, at the end of the experiment was less than 10%. More than 90% deficit in the carbon mass balance, however, indicates that the hydrodechlorination is no longer the major reaction at high pH.

The low production of hydrodechlorination products also has been observed in the photoreduction of carbon tetrachloride in which it could undergo base-catalyzed hydrolysis to carbon monoxide at high pH [14]. It can not be detected by the provided analytic methods. As a result, the low production of lesser-chlorinated intermediates might suggest that the base-catalyzed hydrolysis dominates at high pH in the degradation of carbon tetrachloride by Al^0.

3. Effect of Aluminum Oxide on the Reaction rate of Dechlorination

No significant impact on reaction rates for the hydrodechlorination of carbon tetrachloride by zero-valent aluminum either in the presence or absence of aluminum oxide under acidic conditions. Nevertheless,

under alkaline conditions (pH 10.0), reaction rates increased as the Al_2O_3 loading increased (Fig. 4). This result suggested that aluminum oxide serves as a proton donor that promotes the degradation of carbon te-trachloride under proton-deficit but not proton-rich conditions.
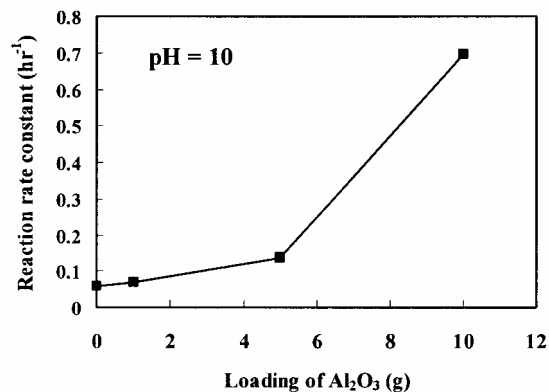

Fig. 4. Effect of aluminum oxide on the degradation rate of carbon tetrachloride with zero-valent aluminum at pH 10.0.
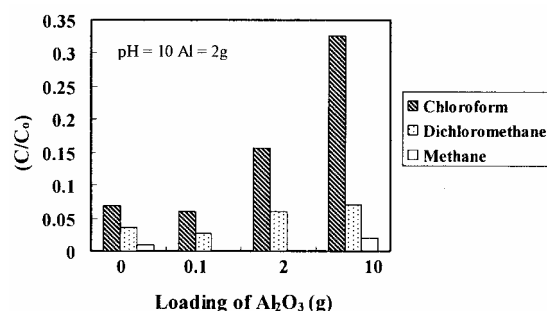

Fig. 5. Effect of aluminum oxide on the product selectivity of hydrodechlorination of carbon tetrachloride under alkaline conditions.

4. Effect of Aluminum Oxide on the Product Selectivity under Alkaline Conditions

Under alkaline conditions, the effect of aluminum oxide on the product selectivity of carbon tetrachloride degradation with zero-valent aluminum is shown in Fig. 5. The increase of selectivity towards the hydrodechlorination products was observed as the loading of aluminum oxide increased. The total measured carbon mass of hydrodechlorination products accounted for about 42% of carbon tetrachloride lost when 10 g of aluminum oxide was added. In comparison, less than 10% of carbon tetrachloride lost was recovered in the form of hydrodechlorination products when the batch system was in the presence of only 0.1 g of aluminum oxide. Reactions shifting noticeably from the possible base-catalyzed hydrolysis to hydrodechlorination suggests that the aluminum oxide may serve as the proton donor that promotes the carbon tetrachloride reduction

toward the hydrodechlorination in the alkaline aqueous solution.

CONCLUSIONS

Aluminum oxide is the key component of aluminosilicate, the compositions of aquifer materials that have been found to increase the effectiveness of zero-valent iron. Although it has been suspected that aluminosilicate serves as a proton donor, direct evidence is limited. By taking advantage of aluminum corrosion behavior, we designed a simple but sound strategy to investigate the role of aluminum oxide in the reduction of carbon tetrachloride with zero-valent aluminum. Zero-valent aluminum is capable of creating electron-rich but proton-deficit conditions at high pH. Carbon tetrachloride undergoes either hydrodechlorination at low pH or base-catalyzed hydrolysis at high pH. Under alkaline conditions, the increase of aluminum oxide loading resulted in the increase of degradation rate of carbon tetrachloride. Further, the increase of aluminum oxide loading led to the increase of selectivity of hydrodechlorination products. This suggested that aluminum oxide serves as a proton donor that promotes hydrodechlorination to compete with base-catalyzed hydrolysis.

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pH   3.0   68%   16%   pH   10
                7%   pH
pH

aluminosilicate