

사)한국지하수토양환경학회  
춘계학술대회 2001. 4.13-14  
한양 대학교 신소재공학과

## Degradation of Chlorinated Organic Compounds by Zero Valent Metals and an Electron carrier

YoungHun Kim

*Department of Environmental Engineering, Kyungpook National University, Taegu, Korea,  
(E-mail: kimyounghoonsi@hotmail.com)*

### Abstract

The degradation of tetrachloroethene (PCE) and trichloroethene (TCE) by vitamin B<sub>12</sub>, an electron mediator was examined when zero valent metals (ZVMs) were used as bulk electron donors. Dechlorination of PCE and TCE by iron and zinc in the presence of vitamin B<sub>12</sub> showed that the zinc and vitamin B<sub>12</sub> combination greatly enhances the reaction rates for both PCE and TCE, but iron and vitamin B<sub>12</sub> result in an increase in reactivity only for PCE degradation, not for TCE degradation in comparing with metals only. This result indicates vitamin B<sub>12</sub>(I) is active towards both PCE and TCE degradation while vitamin B<sub>12</sub>(II) is active only towards PCE. Calculated activation energies for the dechlorination of PCE in the presence of Vitamin B<sub>12</sub> showed that vitamin B<sub>12</sub> lowered the activation energy about 40-60 kJ/mol for the both metals.

**Key words:** reductive dechlorination, degradation, zero valent metals, iron, zinc, vitamin B<sub>12</sub>, electron carrier

### 1. Introduction

The use of zero valent metals (ZVMs) such as iron and zinc is a new technology for remediation of groundwater contaminated with chlorinated organics. The oxidation of some ZVMs is a thermodynamically favorable reaction under environmental conditions, and ZVMs can reduce chlorinated compounds detoxifying the compounds in most cases. Matheson and Tratnyek proposed three reaction pathways for the dechlorination of chlorinated compounds by iron. The first was direct electron transfer on the metal surface and the second and third were reduction by Fe<sup>2+</sup> and H<sub>2</sub> produced in an aqueous system. If the major pathway is direct electron transfer, target contaminants must contact the metal surface regardless of the electron transfer ways (e.g. innersphere or outersphere) and the activation energy for the electron transfer must be overcome. Weber indirectly demonstrated that the first pathway (direct electron transfer by the metal surface) is probably the major mechanism for reduction by zero valent iron and that the reduction can be mediated by electron carriers. This study was conducted to evaluate the extent to which vitamin B<sub>12</sub> could be reduced by ZVMs and to assess the

catalytic role of vitamin B<sub>12</sub> for PCE and TCE dechlorination when ZVMs were used as bulk electron donors.

## 2. Materials and Methods

The kinetic studies were conducted using 20 mL (23.4 mL measured) EPA sampling vials as the reactors. The vials containing metals were placed in an anaerobic chamber for 5 hours to remove oxygen adsorbed on the vial glass surface and metal. The reaction vials were filled with 23.4 mL of vitamin B<sub>12</sub> aqueous solution, which was purged in the anaerobic chamber. The reaction was initiated by injecting an aliquot of stock solutions with a gas-tight microsyringe. Immediately after the injection, the vials were capped with lead foil and Teflon lined septa. The prepared vials were placed on an end-over-end tumbler that rotated at 25 rpm at room temperature (23°C). Triplicate samples were taken from the table and analyzed at each time point.

## 3. Analytical methods

All samples were extracted by liquid-liquid extraction using pentane. From each vial, about 1.5 mL of sample was transferred using a gas-tight syringe to a 4 mL analysis vial containing 1.5 mL of pentane. Toluene was added as an internal standard before the sample addition. The exact volume of the sample and solvent were corrected by gravimetric measurements. The analysis vials were capped with Teflon lined septa and shaken for 30 minutes on a shaker table at 220 rpm. The solvent layer was transferred to a GC auto-sampler vial for analysis. Standard curves were prepared for PCE, TCE, and each daughter compound using 6 different concentrations and linear relations over the relevant concentration range was shown. An HP G1800A GCD (mass selective detector) equipped with a DB-VRX (60m x 0.25mm I.D., J&W) column was used. The oven temperature program was 8 minutes at 80°C, ramped of 20 °C/minute to 160°C, and 2 minutes at 160°C. The carrier gas (UHP He) flow rate was 1 mL/minute. The detector mass range was 45-200 m/z and the detector was turned off from 5 to 5.75 minutes for solvent delay. Inlet and detector temperatures were 230 and 300 °C, respectively, and the inlet split ratio was 30:1.

## 4. Results and Discussion

The degradation rate of PCE was increased by the both combination of zinc-vitamin B<sub>12</sub> and iron-vitamin B<sub>12</sub> in comparing with ZVMs only. Zinc-vitamin B<sub>12</sub> showed dramatically increase dechlorination of TCE while zinc only has a very low reactivity. Iron-vitamin B<sub>12</sub> has a same or a little lower reactivity toward TCE dechlorination than iron has indicating that Co(II) is not an active species for TCE dechlorination.

The pseudo first order rate constant,  $k_{obs}$ , can be hypothesized to be the sum of rate constants for reduction by ZVMs only and by vitamin B<sub>12</sub> reduced by ZVMs; i.e.  $k_{ZVM \cdot VB_{12}} = k_{ZVM} + k_{VB_{12}}$ . If no changes in the dehalogenation rate occur due to competition between vitamin B<sub>12</sub> and the chlorinated organics for ZVM surfaces, then  $k_{VB_{12}}$  values can be calculated using this relationship. For PCE degradation, vitamin B<sub>12</sub> increased the reaction rates about 10 times in combination of both metals and for TCE degradation, it increased the rate about 50 times in combination with zinc.

The activated PCE and TCE can receive a second electron from the oxidation of Co(II) to Co(III) or from zinc to complete the hydrodechlorination reactions. If the second electron is transferred from Co(II), the re-reduction of the Co(III) must be so fast that Co(III) was not observed in the spectroscopic study. The electron transfer from bulk electron donor to alkylcobalamin was also proposed by Glod. The first electron source will be the shuttle between Co(II) and Co(III) or from the bulk electron donor. The activated state of PCE will receive additional electrons and protons to complete the reaction.

The reaction rate constants also depended on the concentration of vitamin B<sub>12</sub>. The reaction rate at a fixed zinc dose gives a linear correlation to the concentration of vitamin B<sub>12</sub>. Based on the dependence of the rate on both zinc surface area and vitamin B<sub>12</sub> concentration, the rate of disappearance of TCE could be described by a pseudo first order rate law:

$$\begin{aligned} -d[\text{TCE}]/dt &= k_{obs}[\text{TCE}] \\ &= k[\text{TCE}][\text{surface area of zinc}][\text{vitamin B}_{12}] \end{aligned}$$

This result has important implication in reactor design and applications because reaction rates can be controlled not only by the surface area of the metals added but also by the concentration of electron carriers added.

The activation energy calculated from the Arrhenius equation were of 9.6 kJ/mole for zinc-vitamin B<sub>12</sub> < 70.7 kJ/mole for zinc-only < 153.9 kJ/mole for iron-vitamin B<sub>12</sub> < 191.2 kJ/mole for iron-only. This order is opposite to the reaction rates; zinc-vitamin B<sub>12</sub> showed the highest reaction rate and iron only was slowest. Surface mediated reactions, including PCE and TCE reduction on ZVMs surfaces involve physical and chemical steps of diffusion of the reactants to the surface and chemical reactions on the surface. The overall reaction rates can be controlled by either step. Mass transport-controlled reactions have activation energy of about 10-42 kJ/mole and less. Current study indicate that zinc-vitamin B<sub>12</sub> can be a mass-transport controlled reaction and all three other systems have sufficiently large activation energy to indicate that chemical reaction on the surface, rather than the diffusion to the surface is rate-limiting step.

## 5. References

1. Gillham RW, O'Hannesin SF. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* 32, 958-967, (1994).
2. Arnold WA, Roberts AL. Pathways of chlorinated ethylene and chlorinated acetylene reaction with Zn(0). *Environ. Sci. Technol.* 32, 3017-3025, (1998).
3. Schwarzenbach RP, Stierli R, Lanz K, Zeyer J. Quinone and iron porphyrin mediated reduction of nitroaromatic compounds in homogeneous aqueous solution. *Environ. Sci. Technol.* 24, 1566-1574, (1990).