Reductive dechlorination of DNAPL mixtures with Fe(II/III)-L and Fe(II)-C: Evaluation using a kinetic model for the competitions

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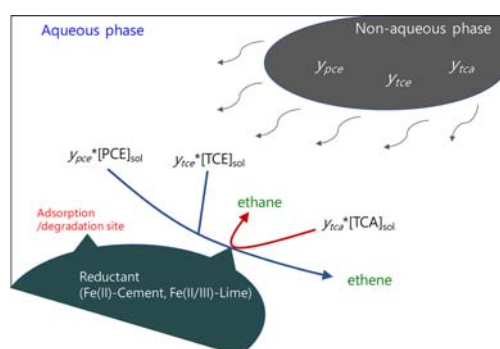[b] Refinery Research Group, BIO R&D Center, CJ CheilJedang, Seoul 100-400, Republic of Korea
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HIGHLIGHTS

- A kinetic model is developed for dechlorination of tertiary DNAPL mixtures.
- Degradation rates are in order 1,1,1-TCA > PCE > TCE.
- The effective solubility determined by DNAPL composition is simulated over time.

GRAPHICAL ABSTRACT

ABSTRACT

A kinetic model for the competitions was applied to understand the reductive dechlorination of tertiary DNAPL mixtures containing PCE, TCE, and 1,1,1-TCA. The model assumed that the mass transfer rates were sufficiently rapid that the target compounds in the solution and the DNAPL mixture were in phase equilibrium. Dechlorination was achieved using either a mixture of Fe(II), Fe(III), and Ca(OH)$_2$ (Fe(II/III)-L) or a mixture of Fe(II) and Portland cement (Fe(II)-C). PCE in the DNAPL mixtures was gradually reduced and it was reduced more rapidly using Fe(II)-C than Fe(II/III)-L. A constant total TCE concentration in the DNAPL mixtures was observed, which implied that the rate of loss of TCE by dechlorination and possibly other processes was equal to the rate of production of TCE by PCE dechlorination. On the other hand, 1,1,1-TCA in the DNAPL mixtures was removed rapidly and its degradation rate by Fe(II/III)-L was faster than by Fe(II)-C. The coefficients in the kinetic model (k_i, K_i) were observed to decrease in the order 1,1,1-TCA > PCE > TCE, for both Fe(II/III)-L and Fe(II)-C. The concentrations of target compounds in solution were the effective solubilities, because of the assumption of phase equilibrium and were calculated with Rault's Law. The concentration changes observed were an increase and then a decrease for PCE, a sharp and then gradual increase for TCE, and a dramatic decrease for 1,1,1-TCA. The fraction of initial and theoretical reductive capacity revealed that Fe(II)-C had ability to degrade target compounds.

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1. Introduction

Remediation of dense nonaqueous phase liquids (DNAPLs) in subsurface is challenging. Depending on the site characteristics and

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DNAPL distribution in subsurface, not only the source zone but also the plume can be needed for remediation (Kaye et al., 2008; Soga et al., 2004; Wilking et al., 2013). Substantial DNAPL source depletion can be achieved either by extraction or degradation (U.S. EPA, 2003). However, lack of depletion for the sorbed mass phase or the entrapped DNAPL lead several obstacles including the uncertainty of the long-term effectiveness (U.S. EPA, 2003). Effects of site characteristics such as ununiform groundwater flow and aquifer heterogeneity on the DNAPL dissolution has been addressed (Powers et al., 1991, 1994; Wilking et al., 2013). Methodology for comparing source and plume remediation is suggested (Falta, 2008), and the contaminant mass discharge from DNAPL source has been adapted to assess remediation performance (Johnston et al., 2014; Zhu and Sun, 2016). A containment of the source zone and/or management of the dissolved plume can achieve the cost-effective risk reduction and regulatory compliance (U.S. EPA, 2003).

Various technologies are available to destroy DNAPL (e.g. perchloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA)) (Arnold and Roberts, 2000; Christ et al., 2005; Crimi and Siegrist, 2005; Matheson and Tratnyek, 1994; Quinn et al., 2005). Reductive dechlorination using various iron-based solids (e.g. zero-valent iron, iron oxides, iron sulfides, and other iron minerals) has been accepted as one of the effective methods for removal by degradation (Erbs et al., 1999; Jeong and Hayes, 2007; Lee and Batchelor, 2002; Pecher et al., 2002; Song and Carraway, 2005). Among reductive dechlorination technologies, reductants produced by the reaction of Fe(II) and cement (Fe-C) have been studied intensively (Do and Batchelor, 2012; Ghorpade et al., 2013; Hwang and Batchelor, 2000, 2001; Hwang et al., 2005; Jung and Batchelor, 2008, 2009; Kim et al., 2008; Ko and Batchelor, 2007).

Hwang and Batchelor (2000) proposed a first-order kinetic model with a partitioning factor to describe the equilibrium among the gas, solid, and aqueous phases in the slurry reactor, and they reported that PCE dechlorination was enhanced by increasing the concentration of Fe(II) in Fe(II)-C. Moreover, three hypotheses were proposed and evaluated for the reaction mechanism: reductive dechlorination by Fe(II) hydroxides, by mixed Fe(II)-Fe(III) (hydr)oxides and by sorbed Fe(II) (Hwang and Batchelor, 2000). In addition, it was found that degradation PCE in soils by Fe(II)-C was effective and did not result in production of chlorinated intermediates. They concluded that kinetics of PCE degradation was controlled by a surface reaction rather than by mass transfer to the reactive surface (Hwang and Batchelor, 2001).

Various chlorinated hydrocarbons besides PCE (e.g. TCE, 1,1-dichloroethylene (1,1-DCE), vinyl chloride (VC), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), 1,1,1-TCA, 1,2-dichloroethane (1,2-DCA), carbon tetrachloride (CT) and chloroform (CF)) were evaluated as targets for Fe(II)-C (Hwang et al., 2005; Jung and Batchelor, 2008, 2009). Hwang et al. (2005) reported that the order of reactivity was TCE > 1,1-DCE > PCE > VC, and they suggested that the effectiveness of adding Fe(III) to Fe(II)-C might depend on the source of the cement and/or the types of chlorinated hydrocarbons. Jung and Batchelor (2009) analyzed the kinetics of the conversion of 1,1,1-TCA to 1,1-dichloroethane (1,1-DCA) and ethane and found that the conversion of 1,1,1-TCA was better described by a parallel reaction mechanism (1,1,1-TCE → 1,1-DCA and 1,1,1-TCA → ethane) than by a consecutive reaction mechanism (1,1,1-TCA → 1,1-DCA → chloroethane (CA) → ethane). Moreover, it was shown that the pseudo-first-order rate constants for reductive dechlorination of seven chlorinated hydrocarbons were correlated with the lowest unoccupied molecular orbital energies (E_{LUMO}) rather than other thermodynamic parameters (i.e. one-electron reduction potential, two-electron reduction potential, and bond dissociation energy) (Jung and Batchelor, 2008).

Despite the complexity of cement constituents and their hydration reactions, identification of the solids responsible for reductive dechlorination in Fe(II)-C were continuously investigated (Ghorpade et al., 2013; Kim et al., 2008; Ko and Batchelor, 2007, 2010). Ko and Batchelor (2007) examined the solids produced from 1) the reaction of Fe(II), Ca(OH)$_2$ and the acid-digested Portland cement solution, 2) the reaction of cement hydration products (aluminate-ferrite-mono (AFm) phases) and Fe(II) or Fe(II) + Fe(III), and 3) the reaction of the synthesized cement extract and Fe(II). They found that Fe was associated with hexagonal particles, which was determined as one of AFm phases, so they suggested that AFm phases were possibly responsible for PCE degradation. Furthermore, they evaluated the effect of using different types of Portland cement and repeatedly observed that Fe was likely associated with hexagonal thin plate particles (Ko and Batchelor, 2010). Additionally, AFm phases, either calcium aluminum hydroxide hydrate or calcium chloroaluminate (Freidel's salt), were produced depending on the type of cement used (Ko and Batchelor, 2010).

On the other hand, Kim et al. (2008) evaluated various potential agents for TCE dechlorination, including four types of iron oxides and three cement hydrates containing Al and SO_4^{2-} (ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; Friedel's salt, $Ca_4Al_2Cl_2(OH)_{12}$; hydrocalumite, $Ca_2Al(OH)_6(OH) \cdot 3H_2O$). They found that mixtures of Fe(II), CaO, and hematite (α-Fe$_2$O$_3$) (i.e. Fe(II)-hematite) showed dechlorination rates, Fe(II) dose dependence, and final products distribution similar to those of Fe(II)-C. SEM analyses suggested a sulfate green rust with a hexagonal plate particle as a reactive reductant in both Fe(II)-hematite and Fe(II)-C and the formation of a sulfate green rust was enhanced by the amendment of CaO. However, other observations indicated that the reactive species might be some other compound. Those observations included the fact that there were fewer of the hexagonal plate particles in Fe(II)-C than in Fe(II)-hematite and that identification of crystalline minerals in Fe(II)-C using X-ray diffraction (XRD) analysis was unclear (Kim et al., 2008).

Recently, the effects of cement types (i.e. ordinary Portland cement (OPC), two types of calcium aluminate cements, and calcium sulfoaluminate cement (CSA)) on TCE dechlorination were evaluated in presence of Fe(II) (Ghorpade et al., 2013). In both OPC and CSA, they observed aluminite-ferrite-tri (AFt) phases with a hexagonal rod-like structure and Fe-ettringite. Fe-ettringite is the compound produced when Al^{3+} is replaced in ettringite by Fe^{3+}. Moreover, the mixtures of OPC and CSA gave enhanced TCE dechlorination and this was explained by theoretical calculations which showed that the form of Fe-ettringite depended on the relatively amounts of iron oxide and sulfate that were available. They speculated that Fe-ettringite associated with Fe(II) could be the active reducing agent in Fe(II)-C.

Reductive dechlorination of PCE, TCE and 1,1,1-TCA as a single-component DNAPL was conducted with various Fe(II)-based reductants (Do and Batchelor, 2012). Representatively, one (Fe(II)-C) was a mixture of solids produced from Fe(II) and Portland cement and another (Fe(II/III)-L) was a mixture of solids produced from Fe(II), Fe(III) and Ca(OH)$_2$. An extraction procedure was applied using two solvents (hexane and methanol) to measure the total concentration of chlorinated hydrocarbon in both the aqueous and non-aqueous phases. Kinetic models were developed to describe the degradation in the presence and absence of the dense non-aqueous phase liquid (DNAPL). It was found that the relative reactivities of Fe(II/III)-L and Fe(II)-C depended on the target compound, with Fe(II/III)-L being more reactive with 1,1,1-TCA DNAPL and Fe(II)-C being more reactive with PCE DNAPL and TCE DNAPL. Moreover, the dosage of Portland cement also affected both the yield of intermediates produced by degradation of PCE DNAPL and the degradation rates of 1,1,1-TCA DNAPL. This indicated that increasing cement doses facilitated both β-elimination and hydrogenolysis pathways (Do and Batchelor, 2012).

The goal of this research is to evaluate the reductive dechlorination of DNAPL mixtures composed of PCE, TCE, and 1,1,1-TCA using Fe(II/III)-L (solids formed from a mixture of Fe(II), Fe(III) and Ca(OH)$_2$) and Fe(II)-C (solids formed from a mixture of Fe(II) and Portland cement). A kinetic model was developed, and model coefficients were determined and interpreted. The results with multi-component DNPALs were compared with the previous results with a single-component DNAPL, if necessary.