

## REDUCTIVE DECHLORINATION OF TRICHLOROETHYLENE BY VARIOUS HEMATITE (Fe<sub>2</sub>O<sub>3</sub>)/Fe(II) SYSTEMS

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### Abstract

Experiments were conducted to evaluate the degradation efficiency of TCE in various hematite (Fe<sub>2</sub>O<sub>3</sub>) and Fe(II) systems. Several hematite minerals were prepared and confirmed by using XRD. However, TCE degradation efficiencies varied for various hematite/Fe(II) systems that differed in the method of synthesis and in the specific surface area. The effect of surface area on the degradation efficiency was not clear. However, it appeared that hematite synthesized by calcination showed high TCE degradation efficiency. It was surmised that calcination process seems to remove some impurities which interfere the reaction/sorption of Fe(II) with the reactive site in hematite. A hematite/Fe(II) system was selected and the effect of pH on the TCE degradation kinetics was evaluated. pH was controlled by CaO and KOH, respectively. When pH was controlled by CaO, TCE degradation efficiency increased with the increase of pH. However, when pH was adjusted by KOH an opposite tendency was observed, i.e., increasing reaction rates with the increased pH. CaO appears to play a certain role in forming a reduction system formed by hematite/Fe(II). Hematite/Fe(II) system dechlorinated TCE to yield ethylene as a major product and acetylene as a minor product.

### Introduction

Chlorinated organic compounds are by far the most prevalent contaminants in groundwater and soil. TCE was known as one of priority groundwater pollutants because of its toxicity and recalcitrant. Sites causing groundwater pollution levels to exceed safety standards account for 4.8% of all groundwater monitoring points according to recent survey of the Korean Ministry of Environment.<sup>1</sup> Although the number of contaminated sites is small, it may read serious problems because groundwater pollution could be spread out through aquifers easily.

Many previous studies reported that some Fe(III) oxides such as hematite and goethite showed high reductive dechlorination efficiency for aromatic chlorinated compounds when it reacts with liquid phase Fe(II).<sup>2,3</sup> When liquid phase Fe(II) reacts with Fe(III) oxides, Fe(II)-Fe(III) hydroxides or other Fe(III) oxide minerals were formed after Fe(II) adsorption on Fe(III) surface.<sup>4,5</sup> The mechanism of these reductive dechlorination based on the reaction of Fe(III) oxide with liquid phase Fe(II) were not well defined. Recent researches focused on mineral structure and minerals newly formed on the Fe(III) oxides after reaction with Fe(II).<sup>6-8</sup> Reactive site based on understanding of mineral structure was also reported.<sup>9,10</sup> Each Fe(III) oxides have their own unique structure and particular newly created minerals on the Fe(III) oxide were formed by adsorption and oxidation of Fe(II) injected as a liquid phase. This forming was affected by mineral's own structure. Furthermore, some faces of minerals have been reported as sites favorable to iron adsorption and attachment compared to other faces due to the atomic structure and surface coordination of oxygen of the face. These faces were called reactive sites which were suspected to degrade the contaminants effectively.

As mentioned above, reductive dechlorination efficiency was affected not only by difference of iron oxide species, but also other factors which was caused by difference of faces in the same Fe(III) iron oxide.

In this study, hematite was selected main reactive Fe(III) oxide mineral based on our previous results.<sup>11</sup> Several types of hematite were prepared or purchased. Then mineralogical analysis was performed to characterize each hematite. Then TCE degradation efficiencies of different hematite/Fe(II) were evaluated.

### Materials and Methods

#### 1. Materials

Five kinds of hematite (Fe<sub>2</sub>O<sub>3</sub>) were used. Bayferrox 110M (Bayer), Bayferrox 180M (Bayer), Bayferrox 4110 (Bayer), Kanto hematite (Kanto) were purchased. Synthesized hematite was also used.<sup>12</sup> Each mineral was confirmed by using XRD.

## 2. Experimental procedures

Batch slurry experiments were conducted using clear borosilicate glass vials ( $23.9 \pm 0.1$  mL) with triple seals that were designed to minimize intrusion of oxygen and volatilization losses of TCE and its degradation products. All samples were prepared in duplicate or triplicate and controls contained only deionized water and TCE. The mass ratio of the solid to solution was 0.1. Slurry samples were prepared by filling the vials with appropriate aliquots of the water, Fe(II) stock solutions, base solution, as needed for pH control. CaO and KOH were used to control pH, respectively. Initial concentration of TCE was 0.25 mM. At each sampling event, duplicate or triplicate samples were sacrificed for the analysis of TCE and its degradation products.

CG equipped with flame ionization detector, HP-VOC and GS-Alumina was used to analyze TCE and its degradation products, respectively. XRD and SEM analyses were conducted to characterize the each hematite. BET analysis was conducted to measure the surface area.

## Results and Discussion

### 1. Mineralogical and physical characteristics of various hematite

Our previous study evaluated TCE degradation efficiencies using various Fe(III) oxides such as goethite, hematite, maghemite and magnetite with Fe(II) and revealed that hematite showed highest degradation efficiency. Unexpectedly, some experimental results indicated that purchased and synthesized hematite showed obviously different degradation efficiencies. It means that there are other factors affect to degradation efficiency. Several hematite were purchased or synthesized (Bayferrox 110M, Bayferrox 180M, Bayferrox 4110, kanto hematite, synthesized hematite). XRD analysis was conducted to identify the mineralogical characteristics. SEM analyses were partially conducted to observe shape of hematite and measure predominant particle size. The representative XRD and SEM data (Bayferrox 110M) are shown in Fig. 1. XRD results of all hematite were nearly the same. Furthermore, no obvious differences among hematites were found in SEM analyses. Through these analyses it was confirmed that all minerals were hematite. Other characteristics such as particle size, surface area and synthesis method were investigated prior to degradation kinetic experiments. Main process of synthetic methods divided two ways, calcination and reaction in solution. Bayferrox 110M and 180M were produced by calcination, other hematites were by reaction in solution. Particle size and surface area were shown in table. 1.

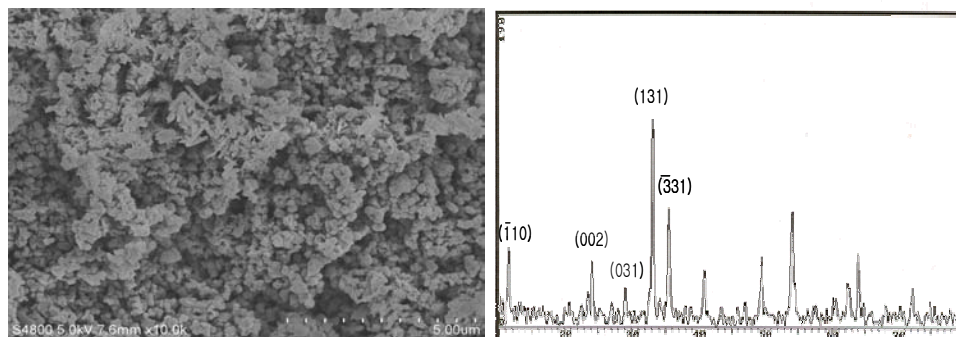


Fig. 1 SEM and XRD analyses of hematite (Bayferrox 110M). SEM and XRD data of other hematites were similar to hematite (Bayferrox 110M).

Table. 1 Particle size, surface area and k value of various hematite

Exp	Type	Predominant particle size ( $\mu\text{m}$ )	BET surface area ( $\text{m}^2/\text{g}$ )	k ( $\text{day}^{-1}$ )	$k_{\text{sur}}^{\text{a}}$ ( $\text{day}^{-1}\text{g}/\text{m}^2$ )
1	Bayferrox 110M hematite	0.09	$13.87 \pm 0.02$	0.511	0.037
2	Bayferrox 180M hematite	0.7	$3.81 \pm 0.01$	0.390	0.1
3	Bayferrox 4110 hematite	0.05	-	0.112	-
4	Kanto hematite	0.15	$8.53 \pm 0.01$	0.004	0.0005
5	Synthesized hematite	0.1	-	0.002	-

<sup>a</sup>Normalized k to surface area

## 2. Degradation experiment using various hematite

Through the previous study, hematite/CaO/Fe(II) system showed highest degradation efficiency. CaO was added in every system commonly to increase the pH and showed increase of efficiency. TCE degradation experiments were conducted using various hematites which were mentioned earlier. The result was shown in Fig. 2 (a) and the prediction with the rate law which was shown by solid lines is generally in good agreement with the observed data. The pseudo-first-order rate constants were obtained by nonlinear regression using the Matlab program (version 7.1, The Mathworks, Inc.). As shown in Fig. 2 (a), initial concentration of TCE (0.25 mM) was completely removed in about 6 days in hematite(Bayferrox 110M)/CaO/Fe(II) system while other hematite systems showed just little reactivities.

Furthermore, result revealed that certain factors can affect to TCE degradation efficiency even in the same experimental condition. Some results (comparison between exp.1 and 2) consistent with that large surface area caused by small particle size affect to increase of the  $k$  value. However, the  $k$  value of exp.1 was higher than that of exp.3 although particle size of exp.1 was about two times bigger than that of exp.3. Although hematite used exp.1, 2, 3 were purchased same company (Bayer), relationship between particle size and degradation efficiency ( $k$  value) showed opposite tendencies. This may be due to differences in the preparation methods for different types of hematite. According to the company (Bayer Korea co.,Ltd) which produced Bayferrox 110M, 180M and 4110 hematite, Bayferrox M series was synthesized using calcination process while Bayferrox 4110 was synthesized by composition in the solution. Based on this result, the hypothesis was established that calcination process seems to remove some impurities which interfere the reaction with Fe(II) on the reactive site in hematite. Future study needs additional experiments that evaluate the effect of calcination process.

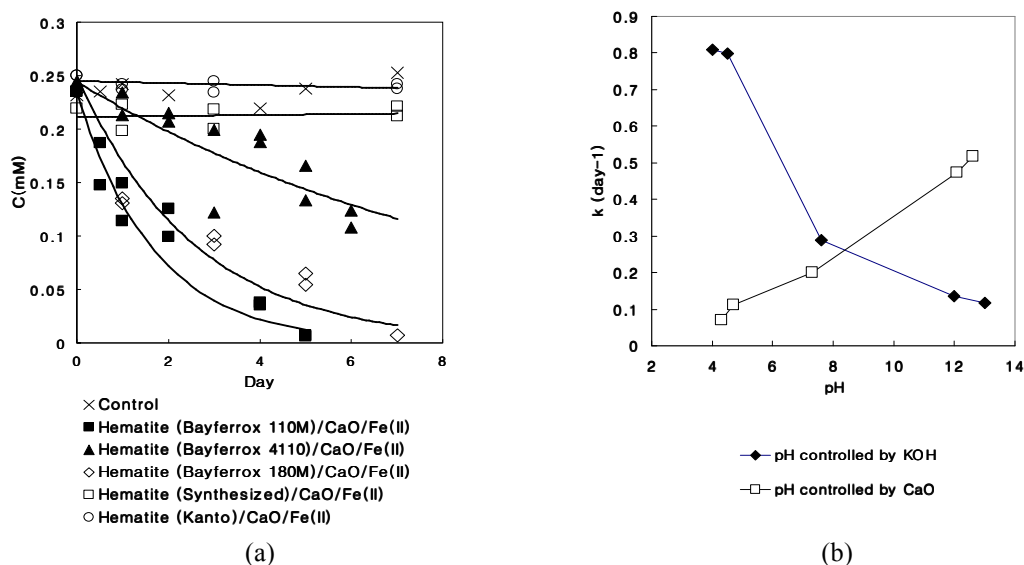


Fig. 2 (a) TCE degradation kinetics in various hematite systems, (b) The pH effect controlled by CaO and KOH, respectively, on pseudo-first-order rate constants of TCE degradation in the hematite/Fe(II) systems

## 3. The effect of pH on TCE degradation

Based on previous study, CaO was added. However, high pH caused by addition of CaO was found. It needed to clear the effect of pH. The experiments were conducted to evaluate the effect of pH for TCE degradation using CaO and KOH as a pH buffer, respectively. Bayferrox 110M Hematite was used. Different amount of CaO and KOH were added to control the pH range from 4 to 12. As shown in the Fig. 2 (b), in the case of CaO, TCE degradation efficiencies were increased with increase of pH that was brought about by increase of CaO dose. The result that degradation efficiency of chlorinated contaminant using Fe(III) oxide was in proportion to pH is similar to result reported by Danielsen and Hayes.<sup>13</sup> It was not clear that TCE degradation was caused by some effect of added CaO or just effect of pH increase. In the case of KOH, systems showed opposite degradation tendency. The TCE degradation efficiency decreased with increase of pH that was caused by increase of KOH dose. These results seem to be affected by the form of pH buffer. CaO was added as a solid

phase while KOH was added as a solution. It was suspected that solid phase CaO has a certain role in TCE degradation.

#### 4. Analysis of degradation products

Degradation products of TCE (DCEs, VC, ethylene, ethane and acetylene) were analyzed to observe that hematite (Bayferrox 110M)/CaO/Fe(II) system could degrade TCE to nonchlorinated products and to get some information about reaction mechanism and degradation pathways. As a result, approximately 91.6% of TCE initially presented was transformed into nonchlorinated products (ethylene, ethane and acetylene) for 6 days (Table. 2), and chlorinated products (1,1-DCE, cis-DCE, trans-DCE and VC) were found below the detection limits.

Reduction of TCE produced ethylene as a major, which accounted for 78.8% of the final products, and ethylene (12.8%) as minor products. Acetylene that was reported to be the major product in the TCE reduction experiments with iron sulfide, green rust, cement/Fe(II), and steel converter slag/Fe(II) system was not detected in hematite (Bayferrox 110M)/CaO/Fe(II) system.<sup>14-17</sup> According to previous studies reported Arnold and Roberts, observation of acetylene and no detection of chlorinated intermediates imply that TCE reductions occurred through reductive  $\beta$ -elimination pathways.<sup>18</sup> Although chlorinated intermediates were not detected in the hematite (Bayferrox 110M)/CaO/Fe(II) system, also acetylene was not detected as a final major degradation products. So it is not clear that this system degrade TCE to nonchlorinated products through reductive  $\beta$ -elimination pathways.

Table. 2 Final products of hematite (Bayferrox 110M)/CaO/Fe(II) system

Exp	Compound	Conc. (mM)	Distribution(%)
-	Ethylene	0.197	78.8
-	Acetylene	0.032	12.8
-	Ethane	ND <sup>a</sup>	-
-	Total carbon	0.229	91.6

<sup>a</sup>Detection limit of ethane was 0.01 mM.

#### References

1. Korean Ministry of Environment, 2005.
2. Williams A.G.B, Scherer M.M. *Environ. Sci. Technol* 2001; 35:3488
3. Jeon B.H, Dempsey B.A, Bursos W.D. *Environ. Sci. Technol* 2003; 37:3309
4. Elsner M, Schwarzenbach R, Haderlein S. *Environ. Sci. Technol* 2004; 38:799
5. Elsner M, Haderlein S, Kellerhals T, Luzi S, Zwank L, Angst W, Schwarzenbach R. *Environ. Sci. Technol* 2004; 38:2058
6. Taylor, H.F.W. *Thomas telford*, Londen, England 1997
7. Wiedler P.G, Hug S.J, Wetche T.P, Hiemstra T. *Geochimica et Cosmochimica Acta*. 1998; 62:3407
8. Williams A.G.B, Scherer M.M. *Environ. Sci. Technol* 2004; 38:4782
9. Chun C.L, Penn R.L, Arnold W.A. *Environ. Sci. Technol* 2006; 40:3299
10. Philip L.C, Scherer M.M. *Environ. Sci. Technol* 2007; 41:471
11. Kim H.S, Lee Y.J, Kim H.Y, Hwang I. *J. KoSSGE* 2007;11:35
12. Cornell R.M, Schwertmann U. *VCH* Weinheim 1996
13. Danielsen K.M, Hayes K.F. *Environ. Sci. Technol* 2004; 38:4745
14. Butler E.C, Hayes K.F. *Environ. Sci. Technol* 1999; 33:2021
15. Lee W, Batchelor B. *Environ. Sci. Technol* 2002; 36:5348
16. Hwang I, Park H.J, Kang W.H, Park J.Y. *J. Hazard. Mater* 2005; B118:103
17. Kang W.H, Hwang I, Park J.Y. *Chemosphere* 2006;62:285
18. Arnold W.A, Roberts A.L. *Environ. Sci. Technol* 2000; 34:1794