

Destruction of TCE Using Oxidative and Reductive Pathways as Potential In-Situ Treatments for the Contaminated Paducah Groundwater

Prepared by
Kentucky Research Consortium for Energy and Environment
233 Mining and Minerals Building
University of Kentucky, Lexington, KY 40506-0107

Prepared for
United States Department of Energy Portsmouth/Paducah Project Office
Acknowledgment: This material is based upon work supported by the Department of Energy under
Award Number DE-FG05-03OR23032.



January 2007

**Destruction of TCE Using Oxidative and Reductive Pathways as
Potential In-Situ Treatments for the Contaminated Paducah
Groundwater**

By

PI: Dibakar Bhattacharyya
University Alumni Professor
Email: db@engr.uky.edu
Phone: 859-257-2794

Post Doc: D. Meyer

Ph.D. Students: S. Lewis, Y. Li, J. Xu, Y. Tee

Undergraduate: Andrew Lynch

Dept. of Chemical & Materials Engineering
University of Kentucky

January 2007

Nanoparticle-Based Dechlorination. When considering reductive technologies for ground water remediation, it is important to understand the underlying principles that govern the kinetics of zero-valent metal dechlorination. Studies involving the use of nanoscale metals (characteristic length < 100 nm) for chloro-organic degradation have increased reaction rates by 1-2 orders of magnitude with minimal intermediate formation. Typically, these metals are synthesized using modifications of the aqueous phase reduction of metal ions using sodium borohydride presented by Glavee and coworkers. The use of a bimetallic system (Fe + Pd or Ni, etc.) increases the reactivity of the particle surface by incorporating a second metal that can typically act as hydrogenation promoter. The presence of the hydrogenation catalyst is believed to alter the mechanism for dechlorination, promoting a faster dechlorination reaction. Given iron is the active reactant, it is reasonable to assume that the quantity and quality of exposed Fe surface area will impact the rate of dechlorination. This is because the first step of the dechlorination mechanism involves the generation of hydrogen and electrons through the corrosion reaction involving water and Fe. To verify this, the rate of hydrogen generation has been monitored through headspace analysis for Fe/Ni nanoparticle systems operating under anaerobic conditions. Changes in this rate resulting from pH effects have been studied during the dechlorination of TCE to determine how hydrogen production impacts the dechlorination rates. The influence of the bimetallic ratio on dechlorination rates was also studied.

For experiments involving no TCE, the initial hydrogen generated by the anaerobic iron oxidation increased linearly with time within the first two hours for four of the bimetallic systems (20 wt%, 25 wt%, 50 wt%, and 75 wt% nickel), with the 20 wt% and 25 wt% Ni nanoparticles being two of the highest hydrogen generating systems (Figure 1). Lower hydrogen generation with increase in nickel content can be explained by the enriched nickel concentration at the edge of the particles that act as a protective layer to minimize the oxidation of iron. It is interesting to observe that in Figure 1 the total hydrogen generation for Ni = 20 wt%, 25 wt%, and 50 wt% falls on a relatively linear trend line ($r^2 = 0.905$) when normalized by the iron mass and the obtained iron-normalized hydrogen generation rate, k_{H_2} , based on the regression line is $63.20 \mu\text{mol H}_2/\text{g Fe hr}$. This shows that the bimetallic system with up to 50 wt% nickel content still provide satisfactory iron surface concentration for producing the necessary hydrogen for reaction under anaerobic condition. In contrast, the 75 wt% Ni nanoparticles has had significantly lower iron-normalized H_2 generation ($k_{H_2} = 6.70 \mu\text{mol H}_2/\text{g Fe hr}$). Analysis of the hydrogen generated by the 20 wt% Ni nanoparticles and nanoiron under TCE-free anaerobic conditions at different solution pH (5.0, 6.5, and 8.0) shows that the total H_2 generation for the buffered solution is not a strong function of the solution pH over the range tested. Similar trends will be expected with Fe + Pd. As expected, the iron corrosion rate increases in the presence of a catalytic metal such as Ni or Pd based on the galvanic cell hypothesis, where iron is the sacrificial metal protecting the nickel.

For the studies involving TCE degradation, complete conversion of TCE to ethane was achieved in under 2 hrs with minimal accumulation of toxic intermediates. Table 1 shows that a strong correlation exists between the surface area-normalized TCE reaction

rate (k_{SA} , L/m² hr) and hydrogen generation ($k_{H_2}^*$, $\mu\text{mol H}_2/\text{m}^2 \text{ hr}$) for the Ni/Fe nanoparticles with different nickel content. Reported literature results of k_{SA} and $k_{H_2}^*$ for iron, nanoiron and Ni/Fe systems are also listed in Table 1 and show the influence of synthesis techniques and particle purity on particle reactivity. However, the presence of nickel as a catalyzing agent is clearly demonstrated by the observed results between the acid-treated nanoiron and 50 wt% Ni nanoparticles. Both of these nanoparticles obtained similar $k_{H_2}^*$ values, but the bimetallic Ni/Fe system demonstrated a dechlorination rate an order of magnitude higher than the nanoiron. Figure 2 shows that both of the surface area-normalized degradation and hydrogen generation rates goes through a maximum. Based on this observation, derivation of a functional reaction rate constant that incorporates relevant parameters such as the hydrogen generation rate and bimetallic composition is a better representation for bimetallic systems.

Researchers working with bimetallic nanoparticle systems have recently began questioning the relevance of a simple surface-area-normalized rate constant for describing such systems. The present work has provided a more-meaningful way to predict nanoparticle performance during dechlorination by incorporating the particle reactivity into the rate constant as a function of hydrogen production and consumption. This is an important contribution to the study of dechlorination kinetics because the modified rate constant can be used to better model and predict nanoparticle performance during injection for contaminated-plume detoxification. In addition, the influence of pH has been shown to be negligible for anaerobic conditions, like what would be expected *in-situ*.

Oxidative-Based Dechlorination. The other pathway being considered for potential remediation of chloro-organics is their oxidative destruction through the use of hydroxyl radicals (OH•). The most common oxidative destruction technique used is the Fenton reaction, which produces hydroxyl radicals and destroys TCE.

To address the potential for two-phase (DNAPL) systems, experiments involving the standard Fenton reaction have been performed *in vitro* using distilled water containing a concentration of TCE well above its saturation limit. Specified amounts of Fe²⁺ and H₂O₂ are added to obtain complete destruction of TCE in reaction times ranging from 5-20 hours, depending on the quantities of reactants used. Based on the results of these tests, the minimum ratio required to remove all TCE present is between 1:1:1 and 1:1:2 (TCE:Fe²⁺:H₂O₂). For the case of the modified Fenton reaction, a suitable chelate (citrate or gluconic acid) has been added to prevent the loss of Fe through precipitation of Fe(OH)₃. The chelate also allows the reaction to take place at near neutral pH and controls H₂O₂ consumption by binding to Fe²⁺. Results involving the modified Fenton reaction kinetics with citrate as the chelate show that increasing the chelate:Fe²⁺ molar ratio reduces the amount of H₂O₂ used to degrade 1 mol TCE. Because the presence of other impurities in the water at the test site can reduce the efficiency of the Fenton reaction by consuming hydroxyl radicals before they can be used to oxidize TCE, tests have been conducted using non-contaminated water from the Paducah site containing alkalinity and hardness and spiked with TCE. Comparison of results for this matrix with the control matrix (deionized, ultrafiltered water) indicate that impurities present in the

Paducah water have no significant effect on the performance of the modified Fenton system for TCE dechlorination. For groundwater remediation applications kinetic model for the dechlorination reaction (to form chloride) is important. For the modified Fenton reaction we have established the model using the simultaneous numeric solution of nonlinear equations for equilibrium reactions involving chelation and the ordinary differential equations for the free radical reactions. This kinetic model also provides fundamental information to demonstrate an increase in the superoxide radical $[O_2^{\bullet-}]$ as the pH is increased. This leads to the possibility for $O_2^{\bullet-}$ to act as a reactive reductant.

Conclusions:

- For bimetallic nanoparticle reactions with chloro-organics, increasing the surface loading of the 2nd metal will eventually result in a decline in the hydrogen generation rate because of the lack of available exposed Fe surface area for corrosion. The influence of pH on hydrogen generation is insignificant over a broad range (5-8), indicating the ability of bimetallic nanoparticles to dechlorinate over this range.
- Dechlorination rates involving bimetallic systems are more accurately represented as a strong function of the rate of Fe corrosion with water because the generated hydrogen interacts with the 2nd dopant metal (Pd, Ni, etc.) to form highly active H where it undergoes reaction with chloro-organics. This is a significant finding that will allow for more accurate modeling of ground water remediation involving bimetallic systems.
- The use of the modified Fenton reaction system for the in-situ destruction of TCE at Paducah should not be influenced by impurities in the water based on the results for reactions carried out in this matrix.
- A model has been developed to describe modified Fenton reaction kinetics and the build-up of the superoxide radical at elevated pH. This radical is a potential reductant that is capable of degrading more challenging compounds such as carbon tetrachloride. Application of this model to in-situ applications will be used to predict necessary dosing for groundwater treatment.

Table 1. Surface area-normalized reaction rate and hydrogen generation rate constant for Fe and Ni/Fe nanoparticles

Iron – based nanoparticles	Surface area-normalized hydrogen generation rate ^{**} k_{H_2} ($\mu\text{mol H}_2/\text{m}^2 \text{ hr}$)	Surface area-normalized TCE degradation rate k_{SA} ($\text{L}/\text{m}^2 \text{ hr}$)
Acid-washed Fe from Fisher ¹	0.01	0.03×10^{-2}
Fe/B nanoparticles ²	0.85	1.40×10^{-2}
Fe nanoparticles ³	1.03	0.05×10^{-2}
Acid-treated Fe nanoparticles	1.78	0.72×10^{-2}
Ni/Fe nanoparticles ⁴ (Ni = 25 wt%)	0.20	9.80×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 20 wt%)	2.23	3.50×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 25 wt%)	2.57	5.75×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 50 wt%)	1.90	2.35×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 75 wt%)	0.25	1.25×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 80 wt%)	0.04	0.09×10^{-2}

^{**} initial H_2 generation rates were determined from measurements obtained up to 120 minutes where linear increase with time was observed. Initial pH = 6.5

¹ k_{SA} from Su et al. *Environ. Sci. Technol.* 1999, 33, 163.

² k_{SA} and k_{H_2} from Liu et al. *Environ. Sci. Technol.* 2005, 39, 1338.

³ k_{SA} from Tee et al. *Ind. Eng. Chem. Res.* 2005, 44, 7062.

⁴ k_{SA} and k_{H_2} from Schrick et al. *Chem. Mater.* 2002, 14, 5140.

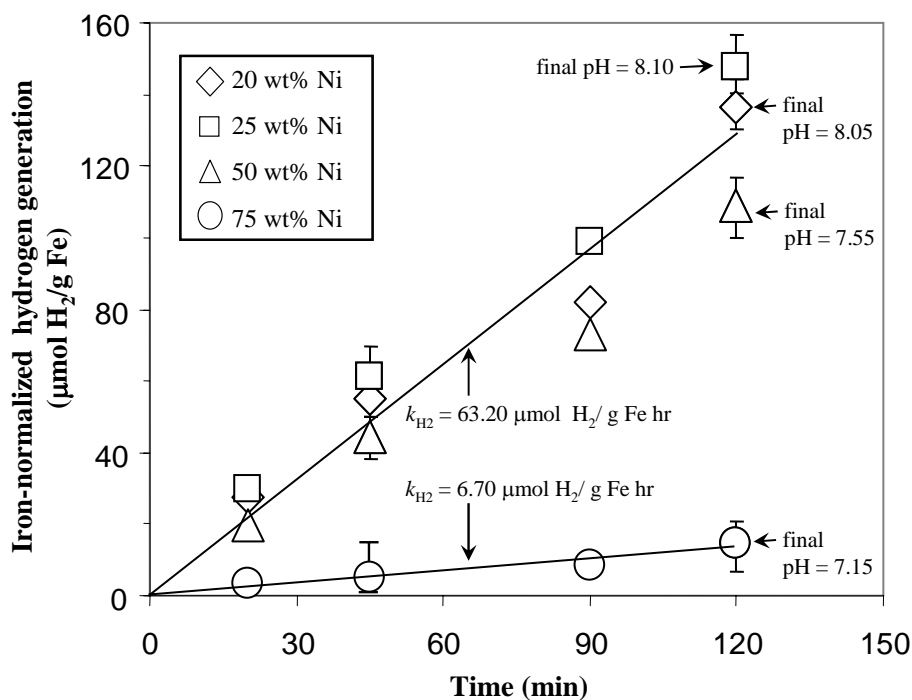


Figure 1. Total hydrogen generation normalized with iron for different bimetallic Ni/Fe nanoparticles versus time under anaerobic aqueous solution. Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.

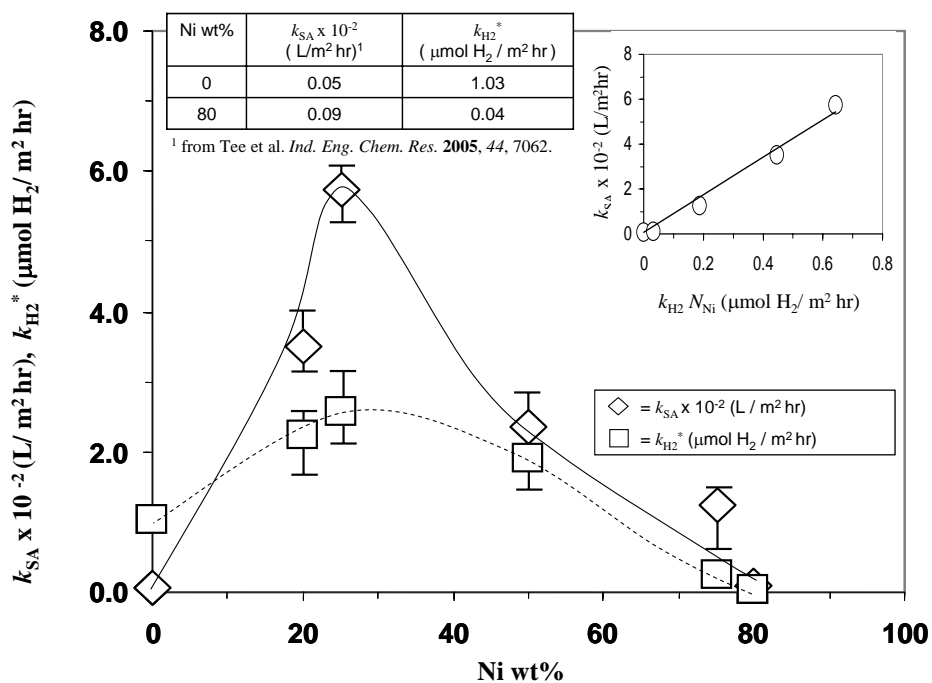


Figure 2. Profile of surface area-normalized TCE reaction rate and hydrogen generation rate with respect to Ni wt% of the Ni/Fe nanoparticles. Insert is the linear correlation between k_{SA} and $(k_{H_2} N_{Ni})$.