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PART III: Remediation

Chapter 7

DECHLORINATION OF PENTACHLOROPHENOL BY ZERO VALENT IRON AND BIMETALS: EFFECT OF SURFACE CHARACTERISTICS AND BIMETAL PREPARATION PROCEDURE

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ABSTRACT

Treatment of Pentachlorophenol (PCP) is challenging due to its hydrophobic nature and the stability of the carbon-chlorine bond, particularly in aromatic molecules. Zero Valent Iron (ZVI) has been used as an effective in situ passive treatment process for PCP contaminated groundwater. However, ZVI applications can experience a decrease in degradation rates over time due to: ZVI surface passivation, the formation of non-conducting iron oxides on the ZVI surface, and the accumulation of less chlorinated intermediates. In this study, ZVI modification by acid washing and formation of bimetallic systems by the incorporation of Nickel (Ni) was explored to overcome these limitations.

PCP degradation was investigated in batch tests using ZVI as received (unwashed or UW) and acid washed (AW) ZVI. Two forms of bimetals were tested - one in which the Ni powder and ZVI (UW or AW) were physically mixed (Ni_S/Fe) and the other in which the Ni was coated onto acid washed ZVI (Ni_C/Fe) by reacting ZVI with $NiSO_4$ solutions. PCP dechlorination was confirmed by gas chromatography quantifying PCP and all intermediates formed. Raman spectroscopy was used to characterise the ZVI surfaces.

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The effectiveness of dechlorination was largely dependent on the composition of the iron oxides on the particle surface. The presence of magnetite was associated with an enhancement in PCP dechlorination while the presence of wustite, maghemite, lepidocrocite or hematite resulted in surface passivation. Complete PCP dechlorination was achieved using the Ni_S/Fe system. After 7 days, Ni_S/Fe with ZVI (AW) completely dechlorinated PCP forming phenol and cyclohexanol (96% and 3% respectively) as the major products. ZVI (UW and AW) and Ni_C/Fe bimetal showed partial PCP degradation with accumulation of less chlorinated phenols. The Ni_S/Fe system offers a simple way of effectively treating PCP without the limitations of other ZVI based procedures currently used.

Keywords: Catalyst, Dechlorination, Iron oxides, Passivation, Pentachlorophenol, Zero Valent Iron

1. INTRODUCTION

Chlorinated phenols (CPs) have been widely used as disinfectants, biocides, wood preservative and pesticides and are byproducts of industrial processing such as the bleaching of pulp using chlorine or chlorine dioxide and during the production of higher chlorinated phenols. CPs have been detected in groundwater, surface water, wastewater, air and soils as a result of improper disposal, leaching from landfills, and incineration of chlorinated wastes (ATSDR 1999). Among all CPs, pentachlorophenol (PCP) has been identified as the most toxic (Tanjore and Viraraghavan 1994) and is considered a possible human carcinogen from exposure via inhalation and dermal contact (USEPA 2010). PCP has a solubility of 14 mg/L in water (Arcand et al., 1995) and tends to bind to organic matter in soil further reducing its water availability and subsequent mobility. It has been identified as a contaminant in New Zealand soils, especially around industries where sawmilling and logging operations were conducted. PCP is listed as a priority pollutant by the United States Environmental Protection Agency (USEPA) and the maximum PCP level in drinking water is defined as 1 ppb (USEPA 2011). PCP is difficult to degrade due to its low water solubility, high degree of chlorination and the chemical stability of chlorinated aromatic compounds.

The use of zero valent iron (ZVI) is a practical effective treatment technology for dechlorination of many organic chlorinated contaminants due to ZVI's relatively high reactivity, inexpensiveness and low environmental impact (Choi et al., 2008). However, only a few studies have focused on PCP degradation by ZVI (Cheng et al., 2010, Kim and Carraway 2000, Marshall et al., 2002, Morales et al., 2002). PCP degradation by ZVI occurs through reductive dechlorination, though

loss of PCP from solution involves a combination of dechlorination and sorption onto ZVI surface (Kim and Carraway 2000). The application of ZVI is limited by several factors (Kim et al., 2007) including (i) decrease in rate of PCP degradation over time due to increase in solution pH and ZVI surface passivation from iron oxide formation on reactive sites and (ii) accumulation of lower chlorinated compounds over time. Furthermore, the rate of dechlorination is highly influenced by ZVI surface characteristics such as morphology, the presence of impurities and oxides, specific surface area and crystallinity (Su and Puls 1999). Low rates of dechlorination by ZVI have also been partly attributed to excessive sorption of the contaminant to nonreactive sites and the impeding of electron transfer by oxide layers (Gotpagar et al., 1999). The reactivity of ZVI surface can be sustained in the presence of oxides such as magnetite (Fe_3O_4) and green rust (Fe [II]/Fe [III] hydroxide), while the presence of goethite (α-FeOOH) and hematite (α-Fe_2O_3) decrease the reactivity (Farrell et al., 2000, Huang et al., 2003, Satapanajaru et al., 2003). Magnetite is a semiconductor with a small band gap of 0.1 eV and has the highest conductivity of all iron oxides (Cornell and Schwertmann 2003). Iron oxides such as hematite, goethite, maghemite and wustite have higher band gaps compared to magnetite (2.2 eV, 2.10 eV, 2.03 eV and 2.3 eV, respectively) and have very low conductivities at room temperature (Cornell and Schwertmann 2003).

The use of modified iron particles is being explored as a means to overcome the above limitations. Acid pretreatment of ZVI has been shown to increase the specific surface area of ZVI (Agrawal and Tratnyek 1996, Lin and Lo 2005) affecting the dechlorination rates. In addition, acid washing of ZVI can remove the oxides present on the surface and also cause the formation of different oxides resulting in a change of surface reactivity and leading to either higher or lower dechlorination rates depending on the conditions (Liu et al., 2006). The introduction of a hydrogenation catalyst such as Nickel (Ni) can enhance the PCP dechlorination efficiency by ZVI. Physically mixing nano-scale Ni and ZVI increased the PCP dechlorination rates (Cheng et al., 2010), whereas some studies have reported that bimetals prepared by coating a catalytic metal on ZVI were poorer at PCP dechlorination than unmodified iron (Kim and Carraway 2000).

In this study, PCP dechlorination was investigated using ZVI with and without its modification as a means to overcome the limitations to using ZVI as a reductant. Unwashed (UW) and acid washed (AW) ZVI were tested under anoxic conditions to study the effect of acid washing and various iron oxides on PCP dechlorination by ZVI. Bimetals of ZVI were tested for enhanced PCP dechlorination with Ni used as the catalyst. Bimetallic systems with either physically mixing Ni and ZVI (Ni_S/Fe) or Ni coated ZVI (Ni_C/Fe) were tested to

investigate their potential for enhanced PCP dechlorination and the effect of bimetal preparation procedures.

2. MATERIALS AND METHODS

2.1 Materials

The zero valent iron (ZVI) used was electrolytic iron powder with particle size 100 mesh and smaller. ZVI powder was sourced from two suppliers: ACROS, Thermo Fisher Scientific (ZVI-T) and North American Höganäs (ZVI-H). Analytical grade solvents (ethyl acetate and acetone), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were obtained from Ajax Finechem. Nickel powder (<150 µm, 99.99%), PCP powder (ACS grade, 98%), standard solutions of PCP, phenol, cyclohexanol and chlorophenol isomers in methanol and $NiSO_4.6H_2O$ (>98%) were purchased from Sigma-Aldrich. Deionised (DI) water (resistivity of 18.20 MΩcm, Millipore-Q system) was used in the experiments. Deoxygenated DI water was prepared by degassing DI water at 80^0C and 100 kPa for 1 hour and then sparging with nitrogen gas for half an hour. A 5000 ppm PCP stock solution was prepared in ethyl acetate.

2.2 ZVI modifications

ZVI particles were acid washed in 1N H_2SO_4 solution using the method described by Liu et al (2006). The Ni coated iron particles (Ni_C/Fe) were prepared using a reductive adsorption process involving acid washed ZVI-T and ZVI-H and a stock solution of 2.4% Ni (as $NiSO_4$) in 10% H_2SO_4. An aqueous solution of $NiSO_4$ (2 mL of Ni stock solution in 200 mL of degassed DI water) was prepared and added to a container with 100 g of acid washed ZVI. The contents were mixed at room temperature for 1 hour at 100 rpm on a rotary shaker. All modified ZVI particles were rinsed with deoxygenated DI water and acetone, dried in air at room temperature and stored in an anaerobic chamber under nitrogen until use. Analysis of solutions (using atomic absorption spectrophotometer, AAS) before and after Ni coating showed 92% and 85% removal of Ni from solutions with acid washed ZVI-T and ZVI-H respectively.

2.3 Iron surface characterization

The surface area of iron, nickel and Ni_C/Fe bimetallic particles was measured using BET N_2 adsorption analysis with the Micromeritic Tristar 3000 surface area analyzer. Specific surface area of ZVI, Ni, and Ni_C/Fe bimetallic particles are presented in Table 1. Environmental Scanning Electron Microscopy (ESEM- FEI

Quanta 200 F) coupled with SiLi (Lithium drifted) Energy Dispersive Spectroscopy (EDS) was used to obtain surface topography, characteristics and elemental information of selected regions of each material's surface. Images were collected using the back-scattered detector at a beam potential of 20 kV.

Table 1. Specific surface area of metal particles

Material	**Specific surface area (m^2/g)**
ZVI-T (UW)	0.2505 ± 0.0037
ZVI-T (AW)	2.3182 ± 0.0122
ZVI-H (UW)	0.2117 ± 0.0018
ZVI-H (AW)	0.9104 ± 0.0033
Nickel powder	0.3854 ± 0.0035
Ni_C/Fe (with acid washed ZVI-T)	4.4668 ± 0.0209
Ni_C/Fe (with acid washed ZVI-H)	2.6957 ± 0.0108

The iron oxides present on ZVI (unwashed and acid washed) and Ni_C/Fe bimetallic particles before and after exposure to PCP solution were identified using Raman spectroscopy (Renishaw Raman system 1000 spectrometer). Nine oxides commonly found on iron surfaces (akaganeite, maghemite, hematite, magnetite, wustite, lepidocrocite, goethite, feroxyhyte and ferrihydrite) were used as the reference iron oxides in Raman analysis (Cornell and Schwertmann 2003). Quantification of iron oxides was performed using Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) within MATLAB (Mathworks®) (Jaumot et al., 2005).

2.4 Experimental procedure

Experiments were carried out in batch reactors using Wheaton amber vials (30 mL). To each reactor 1.00 (±0.01) g of unwashed or acid washed ZVI or 1.00 (±0.01) g of Ni_C/Fe bimetal or 1.00 (±0.01) g of Ni powder was added. For the experiments with Ni_S/Fe bimetal, 1.00 (±0.01) g or 0.10 (±0.01) g of Ni powder was mixed with 1.00 (±0.01) g of unwashed or acid washed ZVI-H. Mixture of 1 g of ZVI and 1 g of Ni is referred to as Ni_S (1.0)/Fe and the mixture of 1 g of ZVI and 0.1 g of Ni is referred to as Ni_S (0.1)/Fe. Then the reactors were filled with 10 mL of deoxygentated DI water and spiked with 10 μL of PCP stock solution (5000 ppm) prepared in ethyl acetate. Immediately after spiking with PCP stock solution, reactors were sealed with aluminum caps and PTFE/silicone septa and agitated on a rotary shaker at 100 rpm at 23 (±1)°C until sampled. Control vials were prepared similarly, except that no solid was added. Four reaction vials and

two controls were sacrificed for analysis at each sampling time. The pH of the reaction solutions was measured in situ in all reactors.

2.5 Analysis

An acid modified liquid-liquid extraction procedure was followed to determine the total (dissolved + sorbed) concentration of PCP and degradation products (Kim and Carraway 2000). For this, 5 mL of ethyl acetate was added to each reactor, which were then placed on a rotary shaker for 30 minutes followed by addition of 1 mL of concentrated HCl and mixing for an additional 10 minutes. The ethyl acetate phase (1.5 mL) was collected using a glass syringe and filtered using 0.2 µm RC (Regenerated Cellulose) membrane filters for analysis. The PCP and degradation products' concentrations were measured with gas chromatography-mass spectrometry analysis (GC/MS-Shimadzu model GCMS-QP2010S) with ZEBRON ZB5-msi capillary column (30 m L x 0.25 mm ID x 0.25 µm thickness) using the Selected Ion Monitoring (SIM) analysis method. Hydrogen gas was analysed using SRI 8610C gas chromatograph with Thermal Conductivity Detector (TCD). A HayeSep Q 80/100 column (Alltech, 6' x 1/8" x 0.085" SS) was used at a temperature of 24 ^{0}C. Nitrogen was used as the carrier gas at a flow rate of 10 mL/min.

3. RESULTS AND DISCUSSION

3.1 Effect of surface characteristics on PCP degradation by ZVI and bimetals

Figure 1 presents the PCP degradation by ZVI-T and ZVI-H (unwashed and acid washed) and Nickel coated iron (Ni_C/Fe) prepared using acid washed ZVI-T and ZVI-H. The two ZVI samples behave surprisingly differently. With no Ni, ZVI-H (UW) showed the highest PCP degradation with 79% PCP degraded after 25 days. In contrast, ZVI-T (UW) showed the least PCP degradation with 34% PCP degraded after 25 days. Acid washing enhanced the PCP degradation by ZVI-T achieving 62% PCP degraded by ZVI-T (AW) after 25 days. Acid washed ZVI-H showed a decrease in the performance with 74% PCP degraded after 25 days (Figure 1). PCP dechlorination was confirmed by quantifying the less chlorinated compounds produced during each treatment using GC/MS analysis and mass balance recoveries were all within 92% to 96% (data not shown). Previous studies showed enhanced trichloroethylene (TCE) dechlorination with acid washed ZVI (Lin and Lo 2005, Liu et al., 2006).

Nickel coated acid washed ZVI-T (Ni_C/Fe (ZVI-T)) showed the highest efficiency among all treatments tested (Figure 1). After 25 days, Ni_C/Fe (ZVI-T) resulted in 97% PCP degradation; phenol was the major degradation product (69% of the end products) while trace amount of tetra-, tri-, di- and mono-CPs were measured (data not shown). Nickel coating on acid washed ZVI-H (Ni_C/Fe (ZVI-H)) did not increase the performance of ZVI-H; in fact, a decrease in PCP degradation (Figure 1) and accumulation of tetra-, tri- and di-CPs were observed. It is interesting to observe that a deposited Ni coating enhanced PCP dechlorination by ZVI-T, but inhibited dechlorination by ZVI-H. Similarly coating ZVI with Pd or Ni has been reported to enhance dechlorination of TCE (Kim 1999), though Kim and Carraway (2000) reported slower PCP degradation rates with Ni/Fe bimetallic particles in comparison to unamended iron.

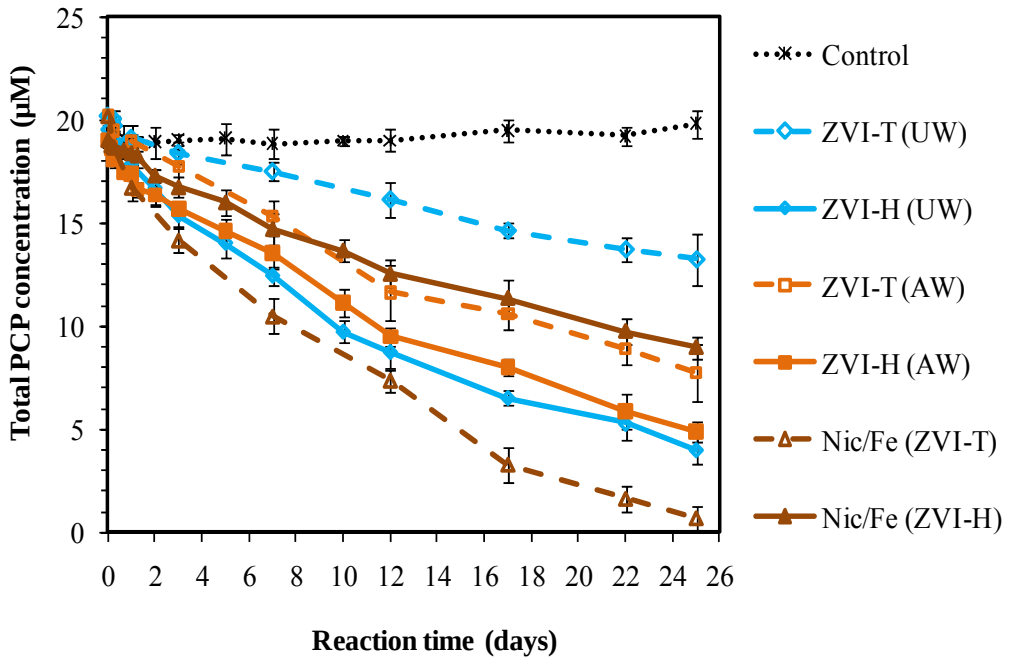

Figure 1. PCP degradation by ZVI and Ni_C/Fe bimetals

Raman spectra were measured to characterize the iron oxides present on the ZVI surfaces for all samples before and after reaction with PCP. For almost all samples, a mixture of iron oxide phases were observed and MCR-ALS was used to determine the sample composition. Figure 2 shows the Raman spectra for the pure oxides and typical sample spectra ranging from before reaction to after 25 days of reaction. A mixture of oxides (wustite, magnetite and ferrihydrite) was observed on unwashed ZVI surfaces. While ZVI-H (UW) was predominantly covered with magnetite, wustite was observed as the major oxide on ZVI-T (UW). Both wustite and magnetite are semiconductors. The magnetite band gap is only

0.1 eV and it is almost metallic with the highest conductivity of all iron oxides. The wustite band gap is 2.3 eV and wustite has a much lower conductivity than magnetite (Cornell and Schwertmann 2003). Hence, the lower reactivity of ZVI-T (UW) was attributed to the presence of wustite on the surface hindering electron transfer process. Acid washing of ZVI-T removed wustite while increasing the amount of magnetite on the surface. Magnetite is electrically conductive and allows electron transfer facilitating the dechlorination reaction (Ritter et al., 2002). Therefore, higher reactivity of ZVI-H (UW) as well as ZVI-T (AW) was attributed mainly to the presence of magnetite. For the ZVI-H PCP degradation was almost unchanged before and after acid washing. This observation is consistent with the Raman spectra showing the ZVI-H having a magnetite oxide layer both before and after acid washing.

A definitive explanation for the different effect of Ni coating on the two ZVI materials is not clear from the work; however, some possibilities are noted. In the present study, AAS analysis of the solutions as well as the ESEM/EDS analysis of Ni_C/Fe particles showed less Ni deposition on ZVI-H (AW) surface compared to ZVI-T (AW) surface (data not shown). Moreover, the specific surface area of Ni_C/Fe (ZVI-H) was smaller than the surface area of Ni_C/Fe (ZVI-T) (Table 1).

Hydrogen gas (H_2 (g)) production was seen in all treatments with the exception of ZVI-T (UW) (data not shown). It was observed that H_2 (g) production in Ni_C/Fe (ZVI-H) system was lower than the H_2 (g) measured in Ni_C/Fe (ZVI-T), indicating lower reactivity or inhibition of hydrogen production due to Ni deposition on reactive sites of ZVI-H (AW). Therefore, the lower PCP degradation by Ni_C/Fe (ZVI-H) could be a result of lower Ni deposition and specific surface area, inhibition of hydrogen production and excessive formation of iron oxides (predominantly magnetite) on the Ni/Fe surface interfering with the Fe^{2+} movement.

3.2 Effect of bimetallic preparation procedure on PCP degradation

Bimetallic systems prepared by physically mixing Ni with ZVI were compared with the Ni coated ZVI described in Section 3.1 to investigate the effect of bimetallic preparation procedure on PCP dechlorination. Physical mixing used Ni powder (Ni_S) with ZVI in either a 1:1 or a 0.1:1 Ni_S/Fe ratio (w/w). Figure 3 presents the PCP degradation by just ZVI and both different bimetallic systems. The Ni particles, when used without ZVI, showed the least PCP degradation (Figure 3). The standard reduction potential of Ni is higher than that of Fe, meaning that Ni is a poorer electron donor for PCP dechlorination, as indicated by the lower PCP degradation.

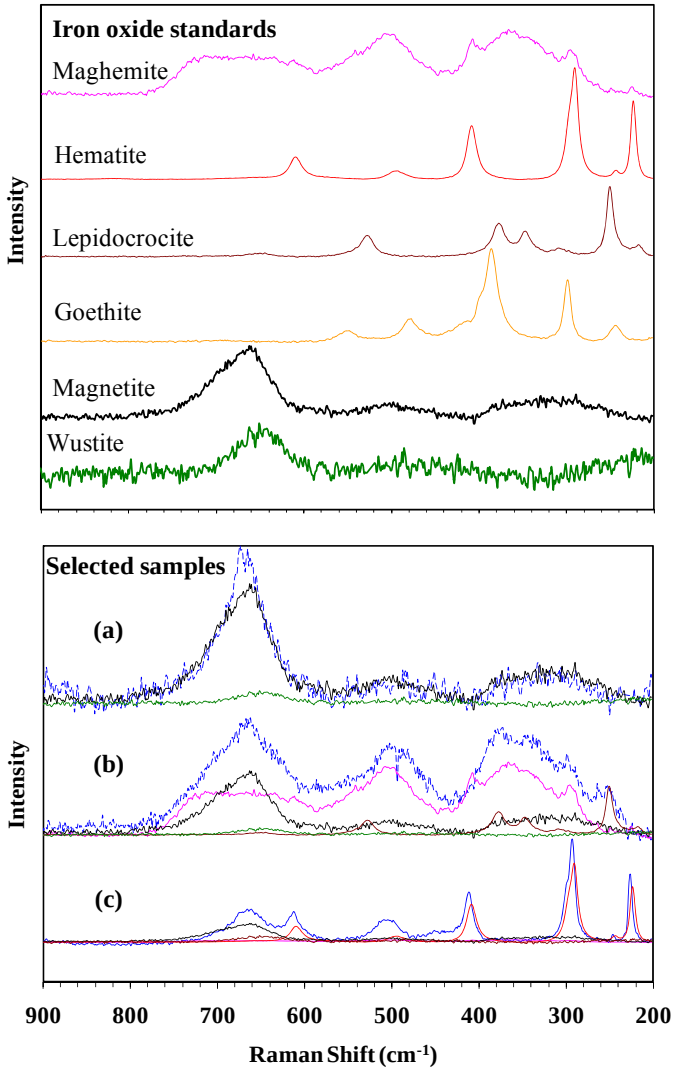

Figure 2. Raman spectra of pure iron oxides and typical sample spectra (ZVI-T AW) that was (a) unreacted (b) after 1 day and (c) after 25 days reaction. Sample Raman spectra are shown in blue with their fitted components in colours as per the oxide standards.

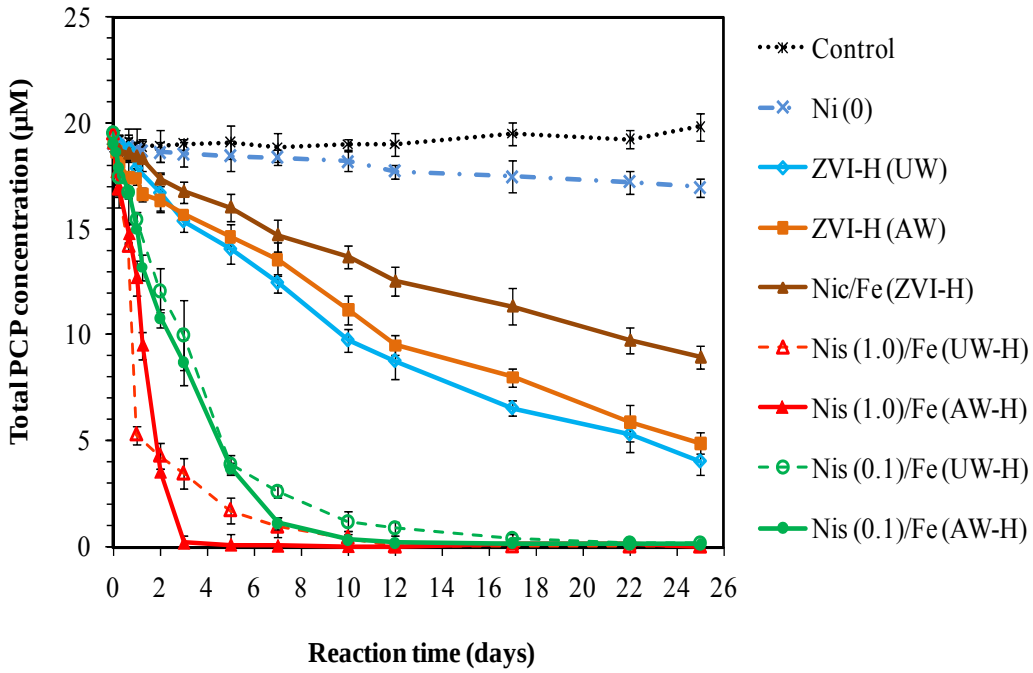

Figure 3. PCP degradation by ZVI and different Ni-ZVI bimetallic systems

Physically mixing Ni and ZVI (Ni_S/Fe) significantly enhanced the PCP dechlorination compared to ZVI (UW and AW) and Ni_C/Fe treatments. For example, with Ni_S/Fe using ZVI-H (AW) and a 1:1 w/w Ni_S/Fe, complete dechlorination of PCP to phenol and cyclohexanol (96% and 3% of the end products, respectively) was observed after 7 days. In comparison, after 7 days, the nickel coated ZVI treatment (Ni_C/Fe) resulted in only 27% PCP degradation while accumulating tetra-, tri- and di-CPs as degradation products in the solution. Similarly, ZVI-H (UW and AW) treatments resulted in partial PCP degradation (Figure 3) and accumulation of tetrachlorophenols in the solution. The Ni_S/Fe system resulted in complete PCP dechlorination and also in complete degradation of intermediate CP's such that after 25 days' reaction in all Ni_S/Fe systems, the final degradation products were either just phenol or were phenol and cyclohexanol. In addition, the rate of dechlorination was substantially faster with the Ni_S/Fe than with the Ni coated ZVI. The amount of Ni added to the system affected the rate of PCP dechlorination and the intermediate byproducts distribution with higher PCP degradation rates being observed by mixing 1 g of Ni compared to 0.1 g of Ni (Figure 3).

Figure 4 presents an example of the PCP degradation products from a Ni_S/Fe treatment. This illustrates the rapid production of phenol through the less chlorinated phenol intermediates. The concentrations of intermediates indicate

their relative rates of production and destruction, and the most prominent intermediates were the CP's with 4 chlorines followed by those with 3 then 2 and lastly 1 chlorine. The mass balance achieved in these Ni_S/Fe systems was consistently ≈ 90 %, which could be due to (1) incomplete recovery of non-chlorinated compounds (that are formed during rapid dechlorination of PCP) during chemical extraction and/or (2) possible loss of the more volatile non-chlorinated compounds during sample handling.

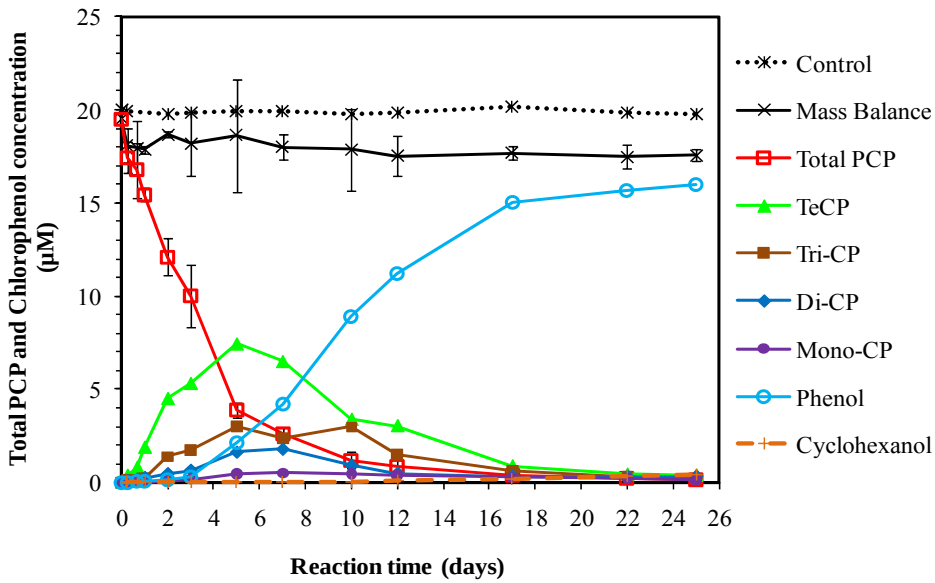

Figure 4. PCP degradation by Ni_S/Fe bimetal (physical mix of 1 g ZVI (UW) + 0.1 g Ni powder) and intermediate products distribution

Hydrogen gas production was seen in treatments with ZVI-H (UW and AW), Ni coated ZVI-H and physical mix of Ni and ZVI-H, but not when Ni powder was used without ZVI (data not shown). The highest H_2 (g) production was observed with the Ni_S/Fe systems and more H_2 (g) was produced with 1 g Ni than with 0.1 g Ni. For example, after 25 days reaction, Ni_S/Fe systems with ZVI-H (AW) produced 201% (i.e. the H_2 partial pressure in the vessel was 2.01 atm) and 106% H_2 (g) with 1 g Ni and 0.1 g Ni, respectively. The lowest H_2 (g) production (45% after 25 days reaction) was seen with the Ni_C/Fe (ZVI-H) treatment.

Another important difference between the Ni_S/Fe samples and Ni_C/Fe samples was the iron oxide phases formed on the surface after reaction with PCP as determined by Raman spectroscopy. Prior to reaction with PCP, a mixture of magnetite and/or wustite was observed on ZVI (UW) while only magnetite was present on the ZVI (AW) and Ni_C/Fe surfaces. After 25 days reaction with PCP several iron oxides, including lepidocrocite, magnetite, hematite, wustite and

ferrihydrite, were found on the Ni_C/Fe bimetallic particles. Oxides such as lepidocrocite, hematite, wustite and ferrihydrite have low conductivity at room temperature (Cornell and Schwertmann 2003). Formation of these oxides can decrease the number of reactive sites on the ZVI surface and electron transfer process hindering PCP dechlorination. However, in the treatments with physically mixing Ni particles and ZVI, only magnetite was present on ZVI (UW) and ZVI (AW) consistent with an increase in PCP dechlorination compared to Ni coated Fe system.

In a ZVI/H_2O system, although ZVI acts as the main reductant, there are also other reducing agents, Fe^{+2} and H_2, which were produced during iron corrosion, and are available for PCP reduction. However, the reaction of Fe^{+2} with the chlorinated compound is known to be a slow process, and H_2, in the absence of a catalyst, is not an effective reductant (Matheson and Tratnyek 1994). When Ni particles are physically mixed with ZVI, Ni acts as an effective catalyst, resulting in higher H_2 (g) production, and potentially increasing the ratio of indirect reduction of PCP by H_2. Feng and Lim (2005) reported enhanced reduction of chlorinated compounds by nano-scale Nickel-iron bimetal as compared to unmodified ZVI, and the effect was attributed to indirect reduction by H_2 in the presence of nickel.

This study explores some of the complexities involved in the dechlorination of chlorinated organics using bimetallic systems. There are several apparently contradictory studies in the literature, which may result from differences in the methods of producing the bimetallic phase. For example, previous studies have reported enhanced PCP dechlorination with physically mixed nano-scale Ni and ZVI (Cheng et al., 2010). On the other hand, a comparison of isolated ZVI, with physical mix of nano-scale Pd-ZVI, and Pd coated on ZVI, showed enhanced TCE dechlorination rates only in the Pd coated system (Zhang et al., 1998). Therefore, the catalytic reactivity of bimetals and the dechlorination rate depends on, (1) the properties of target chlorinated compounds, (2) properties and surface characteristics of ZVI used and (3) method of bimetallic preparation.

4. CONCLUSIONS

PCP degradation was studied using different ZVI materials (with and without acid pretreatment) and bimetallic systems with ZVI and Ni. The performance of ZVI and the effect of acid washing were dependent on the surface characteristics of ZVI particles. Acid pretreatment of ZVI removed wustite while increasing magnetite on the surface. In general, the presence of magnetite increased the PCP degradation. Nickel coated ZVI (Ni_C/Fe) prepared with acid washed ZVI-T showed complete PCP degradation. However, the catalytic effect of Ni was

dependent on the surface characteristics of ZVI used. The presence of oxides such as wustite, lepidocrocite, hematite and ferrihydrite was consistent with lower PCP degradation by Ni_C/Fe prepared with ZVI-H (AW). A physical mix of Ni powder with ZVI (Ni_S/Fe) dramatically increased the PCP dechlorination and achieved complete degradation of PCP and intermediate CPs. The amount of Ni added to the system affected the rate of PCP dechlorination and the distribution of intermediate products. Rapid and complete PCP degradation can be achieved by following physical mixing of Ni and ZVI as a method of bimetallic preparation. This can minimize the limitations of ZVI use such as accumulation of less chlorinated byproducts and slower dechlorination rates due to oxide formation and ZVI surface passivation.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Agrawal, A. and Tratnyek, P.G. 1996. Reduction of Nitro Aromatic Compounds by Zero-Valent Iron Metal. Environmental Science & Technology 30(1), 153-160.

Arcand, Y., Hawari, J. and Guiot, S.R. 1995. Solubility of pentachlorophenol in aqueous solutions: The pH effect. Water Research 29(1), 131-136.

ATSDR. 1999. Toxicological Profile for Chlorophenols, p. 260, Agency for Toxic Substances and Disease Registry, U.S Department of Health and Human Services, Atlanta,GA 30333.

Cheng, R., Zhou, W., Wang, J.-L., Qi, D., Guo, L., Zhang, W.-X. and Qian, Y. 2010. Dechlorination of pentachlorophenol using nanoscale Fe/Ni particles: Role of nano-Ni and its size effect. Journal of Hazardous materials 180(1-3), 79-85.

Choi, J.H., Choi, S.J. and Kim, Y.H. 2008. Liquid-liquid extraction methods to determine reductive dechlorination of 2,4,6-trichlorophenol by zero-valent metals and zero-valent bimetals. Separation Science and Technology 43(14), 3624-3636.

Cornell, R.M. and Schwertmann, U. 2003. The iron oxides structure, properties, reactions, occurrences, and uses, Weinheim : Wiley-VCH, 2003., Weinheim.

Farrell, J., Kason, M., Melitas, N. and Li, T. 2000. Investigation of the long-term performance of zero-valent iron for reductive dechlorination of trichloroethylene. Environmental Science and Technology 34(3), 514-521.

Feng, J. and Lim, T.-T. 2005. Pathways and kinetics of carbon tetrachloride and chloroform reductions by nano-scale Fe and Fe/Ni particles: comparison with commercial micro-scale Fe and Zn. Chemosphere 59(9), 1267-1277.

Gotpagar, J., Lyuksyutov, S., Cohn, R., Grulke, E. and Bhattacharyya, D. 1999. Reductive Dehalogenation of Trichloroethylene with Zero-Valent Iron: Surface Profiling Microscopy and Rate Enhancement Studies. Langmuir 15(24), 8412-8420.

Huang, Y.H., Zhang, T.C., Shea, P.J. and Comfort, S.D. 2003. Effects of oxide coating and selected cations on nitrate reduction by iron metal. Journal of Environmental Quality 32(4), 1306-1315.

Jaumot, J., Gargallo, R., De Juan, A. and Tauler, R. 2005. A graphical user-friendly interface for MCR-ALS: A new tool for multivariate curve resolution in MATLAB. Chemometrics and Intelligent Laborary Systems 76(1), 101-110.

Kim, J.S., Shea, P.J., Yang, J.E. and Kim, J.-E. 2007. Halide salts accelerate degradation of high explosives by zerovalent iron. Environmental Pollution 147(3), 634-641.

Kim, Y.H. 1999. Reductive dechlorination of chlorinated aliphatic and aromatic compounds using zero valent metals: Modified metals and electron mediators. PhD, Texas A & M University.

Kim, Y.H. and Carraway, E.R. 2000. Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons. Environmental Science and Technology 34(10), 2014-2017.

Lin, C.J. and Lo, S.L. 2005. Effects of iron surface pretreatment on sorption and reduction kinetics of trichloroethylene in a closed batch system. Water Research 39(6), 1037-1046.

Liu, C.C., Tseng, D.H. and Wang, C.Y. 2006. Effects of ferrous ions on the reductive dechlorination of trichloroethylene by zero-valent iron. Journal of Hazardous materials 136(3), 706-713.

Marshall, W.D., Kubatova, A., Lagadec, A.J.M., Miller, D.J. and Hawthorne, S.B. (2002) Zero-valent metal accelerators for the dechlorination of pentachlorophenol (PCP) in subcritical water. Green Chemistry 4(1), 17-23.

Matheson, L.J. and Tratnyek, P.G. 1994. Reductive dehalogenation of chlorinated methanes by iron metal. Environmental Science and Technology 28(12), 2045-2053.

Morales, J., Hutcheson, R. and Cheng, I.F. 2002. Dechlorination of chlorinated phenols by catalyzed and uncatalyzed Fe(0) and Mg(0) particles. Journal of Hazardous materials 90(1), 97-108.

Ritter, K., Odziemkowski, M.S. and Gillham, R.W. 2002. An in situ study of the role of surface films on granular iron in the permeable iron wall technology. Journal of Contaminant Hydrology 55(1-2), 87-111.

Satapanajaru, T., Comfort, S.D. and Shea, P.J. 2003. Enhancing metolachlor destruction rates with aluminum and iron salts during zerovalent iron treatment. Journal of Environmental Quality 32(5), 1726-1734.

Su, C. and Puls, R.W. 1999. Kinetics of trichloroethene reduction by zerovalent iron and tin: Pretreatment effect, apparent activation energy, and intermediate products. Environmental Science and Technology 33(1), 163-168.

Tanjore, S. and Viraraghavan, T. 1994. Pentachlorophenol - Water pollution impacts and removal technologies. International Journal of Environmental Studies 45(2), 155-164.

USEPA. 2011. Drinking water contaminants [Online]. Available: http://water.epa.gov/drink/contaminants/index.cfm [Accessed 06 June 2011]

USEPA. 2010. Toxicological review of Pentachlorophenol:In Support of Summary Information on the Integrated Risk Information System (IRIS) p. 288.

Zhang, W.X., Wang, C.B. and Lien, H.L. 1998. Treatment of chlorinated organic contaminants with nanoscale bimetallic particles. Catalysis Today 40(4), 387-395.