

REDUCTIVE DECHLORINATION USING MODIFIED GREEN RUSTS IN DEGRADATIVE SOLIDIFICATION/STABILIZATION

Sukil Son (sukil@tamu.edu) and Bill Batchelor
(Texas A&M University, College Station, TX, USA)

ABSTRACT: The goal of this study was to investigate the activity of modified green rusts for chlorinated hydrocarbons degradation to be used in degradative solidification/stabilization (ds/s). Tetrachloroethylene (PCE) was used as a model chlorinated organics to test the activity test of modified green rusts. Chloride green rust was synthesized by partial air oxidation method and modified by 10% Portland cement solution, Portland cement extract and chemical solutions including Al(III), Ca(II), Cu(II), Mg(II), Mn(II), Ni(II), Pt(II) and Zn(II). Green rusts modified by 10% Portland cement and Portland cement extract showed significantly higher PCE reduction rates (~40 and 80 times) than unmodified chloride green rust. Portland cement extract was more efficient modifying agent than 10% Portland cement solution. These techniques may produce green rusts that are complex mixtures of different types of green rust. Modifications by a single element also enhanced the activity of green rust. Cu-modified and Ni-modified green rusts could remove more than 90% of PCE, and Al-modified green rust remove about 65% of PCE for 10 days at room temperature. The activities of single element-modified green rusts were affected by both cation and anion in modifying agents.

INTRODUCTION

Chlorinated compounds are commonly found together with inorganic contaminants in soils and sediments (Riley et al., 1992). Degradative solidification/stabilization (ds/s) is a modification of conventional solidification/stabilization (s/s) that incorporates degradative processes to destroy toxic organic compounds. It is an attractive new technology to remediate soils and sediments contaminated with chlorinated organic contaminants and toxic metals.

Among dechlorination reactions, reductive dechlorination is an attractive degradation process for chlorinated organic contaminants in ds/s systems (Vogel et al., 1987). Various forms of iron that have been reported to enhance the reductive dechlorination of chlorinated hydrocarbons, are attractive reagents to be applied for ds/s processes due to their low cost, low toxicity and general effectiveness.

Green rust is a mixed Fe(II)-Fe(III) hydroxide that may be a potent reductant for chlorinated hydrocarbons in ds/s because it has been found to be able to transform carbon tetrachloride (Erbs et al., 1999), selenate (Myneni et al., 1997, Refait et al., 2000), nitrate and nitrite (Hansen et al., 1994, Koch and Hansen, 1997, Hansen et al., 1996). Green rust has been identified in soil, in high pH environments such as hydrated cements, and in corrosion products (Sagoe-Crentsil and Glasser, 1993a, Sagoe-Crentsil and Glasser, 1993b). Recently, the addition of transition metals such as Cu(II), Ag(I), or Au(III) to green rust has been found to enhance the reductive dechlorination rates of chlorinated ethane and carbon tetrachloride substantially (O'Loughlin and Burris, 2000, O'Loughlin et al., 2001).

This paper evaluates a variety of modified green rusts to be used in ds/s for remediation of soils and sediments contaminated with chlorinated hydrocarbons. Laboratory experiments have been conducted with tetrachloroethylene (PCE) as a model chlorinated hydrocarbon to test the activity of synthesized active reductants for use in ds/s.

MATERIALS AND METHODS

Chemicals. The following chemicals were used as received: tetrachloroethylene (99.9%, HPLC grade, Aldrich), 1,2-dibromopropane (1,2-DBP, 97%, Aldrich), methanol (99.8%, HPLC grade, EM), hexane (98.5%, ACS grade, EM), hydrochloric acid (36.5-38%, ACS grade, EM), sodium hydroxide (97+%, ACS grade, EM), potassium hydroxide (85+%, ACS grade, EM), calcium hydroxide (Fisher), aluminum chloride (hexahydrate, 98+%, Sigma), calcium chloride (dihydrate, 98+%, Aldrich), cupric chloride (dihydrate, 99+%, Aldrich), cupric sulfate (pentahydrate, 98+%, Spectrum Chemical), ferrous chloride (tetrahydrate, 99+%, Sigma), magnesium bromide (hexahydrate, 99%, Aldrich), magnesium chloride (hexahydrate, 99+%, EM), magnesium sulfate (heptahydrate, 98+%, EM), manganous chloride (tetrahydrate, 98+%, Aldrich), manganous sulfate (monohydrate, 98.6%, Fisher), nickel (II) chloride (hexahydrate, Aldrich), nickel sulfate (hexahydrate, Fisher), platinum (IV) chloride (98%, Aldrich), zinc chloride (anhydrous, 98+%, EM) and Portland cement (type I/II, TXI Cement).

Deoxygenated deionized water purified by a Barnstead Nanopure system was prepared by purging for at least 12 hours with the atmosphere of an anaerobic chamber (Coy Laboratory Products) containing 95% N₂ and 5% H₂. Methanolic stock solution of PCE was prepared daily. The base solution of 5 N KOH and the acid solution of 5 N HCl were purged with anaerobic chamber atmosphere for approximately 36 hours and used for pH control of samples.

Experimental Procedure. Chloride green rust (GR_{Cl}) was synthesized by partial air oxidation of a partially neutralized solution of FeCl₂ (Refait et al., 1998). A volume (500 mL) of 0.4 M NaOH solution was slowly added to 500 mL of 0.23 M FeCl₂ solution. The mixture was stirred to precipitate Fe(OH)₂ for several minutes. The solution (1 L) of 0.2 M Fe(OH)₂ was oxidized by stirring with the top of the reactor open to the atmosphere. Reaction was monitored by recording pH. The pH of solution increased during oxidation and the process was stopped when the pH began to clearly decrease. After preparation, GR_{Cl} suspension was stored in an anaerobic chamber. GR_{Cl} suspension was centrifuged and washed with deoxygenated deionized water two times before using. The average concentration of Fe(II) in the GR_{Cl} suspension was 75.4 mM (±2.59%). The average ratio of Fe(II)/Fe(III) was 2.96 (±4.34%).

An amount (100 g) of Portland cement (PC) was added into 1 L of 2.2 N HCl solution in 1 L plastic bottle. The extraction bottle containing the mixture of PC and acid solution was shaken at 250 rpm for 2 days using an orbital shaker at room temperature. The extracted solution was separated into 4 plastic centrifuging bottles (250 mL) and centrifuged at 5000 rpm for 5 min (Beckman model J-6M centrifuge, JS-7.5 rotor). The supernatant of the centrifuged solution was filtered with filter paper (2 μm quantitative filter paper, VWR) to remove suspended solid. The filtered cement extract solution was

purged with anaerobic chamber atmosphere for at least 24 hours in anaerobic chamber. After purging, the Portland cement extract solution (PCX) was stored in an anaerobic chamber. 1 mM chemical solutions were also prepared by dissolving chloride, sulfate or bromide salts of each primary PC component (Al, Ca, Cu, Mg, Mn, Ni, Pt and Zn) into 2.2 N HCl solutions.

GR_{Cl} suspension was centrifuged and the supernatant removed to obtain GR_{Cl} solid. Modified GR_{Cl} was prepared by adding the GR_{Cl} solid and calcium hydroxide to PC, PCX and chemical solutions to obtain a concentration of Fe(II) of 35.0 mM, a concentration of calcium hydroxide of 1.25 M. The mixed solutions were stirred for 3 days at room temperature in an anaerobic chamber.

Clear borosilicate glass vials (nominally 20 mL, Kimble) were used as batch slurry reactors for the activity tests. To minimize the intrusion of oxygen and the loss of PCE, three-layered system containing 2 mil PTFE film (Norton Performance Plastics Co.), lead foil (3M) and a PTFE-lined rubber septum (Kimble) was used for the closure of reactors. After the vials were in the anaerobic chamber for 2 days, the sample solutions containing synthesized reductants were added into the vials. Controls were prepared by adding water and PCE in duplicate and all activity test experiments were conducted in triplicate. Headspace volumes of the vials were minimized (~0.6 mL). The average total volume of sample solution was 24.4 mL in the vials. All samples were prepared in an anaerobic chamber. All pH values of samples were near 11.4.

Reductive dechlorination experiments with each reductant were initiated by spiking 10 μ L of 590 mM PCE methanolic stock solution into each sample. After PCE spiking, the vials were rapidly and tightly capped with the three-layered septum. Then the vials were taken out of the anaerobic chamber and placed on a tumbler to completely mix by end-over-end rotation at 7 rpm at room temperature. PCE concentration in the aqueous phase was measured by GC analysis after extraction.

Analytical Procedures. At each sampling time, reaction vials were taken from the tumbler and centrifuged at 2000 rpm for 15 min (International Equipment Co., model CS centrifuge). Hexane (1 mL) containing 2.6 mg/L of 1,2-DBP as an internal standard was transferred into 1-mL Gas Chromatography (GC) autosampler vials. Aliquots of the supernatant (50 μ L) were added to the GC vials to extract PCE from the aqueous phase. The extraction vials were shaken at 250 rpm for 1 hour using an orbital shaker. The extracted PCE was analyzed by GC (Hewlett-Packard 5890 GC) with an electron captured detector (ECD) and a combination of HP-5 column (30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness, Hewlett-Packard) and SPB-5TM column (30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness, Supelco). Sample injection volume was 1 μ L with split ratio of 30:1. The temperature of injector was set at 220°C and the temperature of the detector was set at 240°C. Helium was used as a carrier gas and nitrogen was used as a makeup gas. Column flow and makeup flow were constant at 1 mL/min and 60 mL/min, respectively. The oven temperature was programmed as follows: held 80°C for 2 min, ramped 5°C/min to 110°C, and held for 2 min.

Iron analysis (Fe(II) and total iron) was conducted by Ferrozine method using UV-VIS spectrophotometer (Hewlett-Packard G1103). The concentration of Fe(III) was obtained by calculating the difference between total iron concentration and Fe(II) concentration.

RESULTS AND DISCUSSION

Figure 1 shows that the kinetics of PCE reduction by chloride green rust (GR_{Cl}), 10% Portland cement-modified green rust (GR_{PC}), PCX-modified green rust (GR_{PCX}) at pH 11.4 and room temperature are described by first-order kinetics. Pseudo first-order rate constants were normalized by ferrous iron concentration ($k_{Fe(II)}$) for systems with GR_{Cl} , GR_{PC} and GR_{PCX} and were found to be 0.000174, 0.00671 and 0.0140 $\text{mM Fe(II)}^{-1}\cdot\text{day}^{-1}$, respectively. The rates of PCE dechlorination by GR_{PC} and GR_{PCX} were approximately 40 and 80 times faster than that of GR_{Cl} , respectively. These results indicate that PC and PCX significantly enhance the activity of GR_{Cl} in reducing PCE. The rate constant of GR_{PC} was about 50% of the rate constant of GR_{PCX} . This result implies the cement extract is more attractive than Portland cement slurry for modifying GR_{Cl} . GR_{PC} and GR_{PCX} may be a combination of different kinds of GRs each modified by different cement components.

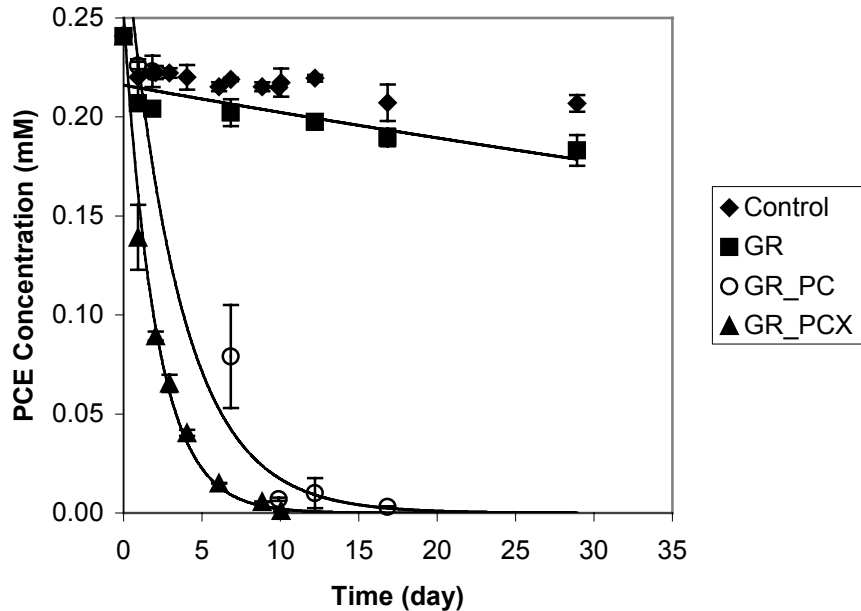


FIGURE 1. Kinetics of PCE reduction by chloride green rust, green rust in 10 % Portland cement slurry and PCX-modified green rust. Error bars are the standard deviations of measured PCE concentrations. Some error bars are smaller than the symbols. Solid lines represent first-order fits. $[Fe(II)]_{GR} = 35.0 \text{ mM}$, $[Fe(II)]_{GR_{PC}} = 35.0 \text{ mM}$, $[Fe(II)]_{GR_{PCX}} = 36.9 \text{ mM}$, $[PCE]_0 = 0.241 \text{ mM}$, $\text{pH} = 11.4$.

The increased activities of GR_{PC} and GR_{PCX} motivated the examination of the effect of selected major and minor cement elements (Al(III), Ca(II), Cu(II), Mg(II), Mn(II), Ni(II), Pt(II) and Zn(II)) in modifying GR_{Cl} . Performances of different modified GRs are presented in terms of PCE removal in 10 days at room temperature. The pHs of all systems were controlled at 11.4. As shown in Figure 2, more than 90% of PCE was removed by Cu-modified GR (GR_{Cu}) and Ni-modified GR (GR_{Ni}). Al-modified GR

removed approximately 65% of PCE. Ca, Mg, Mn, Pt and Zn-modified GR removed a little more PCE (~40%) than GR_{Cl} alone. GRs modified by chloride salts had generally more activity than by sulfate salts except Mn-modification. Mg-modified GR with bromide salt degraded more PCE than those with chloride and sulfate salts. These results indicate that the activities of modified GRs might be affected by both cation and anion.

Research is currently underway to investigate the effects of several factors for the modification of GR_{Cl} and their activities for reductive dechlorination of chlorinated hydrocarbons to be used in ds/s. With the further study for the effect of factors, the dechlorination rate of modified green rust for the ds/s system will be optimized and modified green rusts will be evaluated for application to other processes.

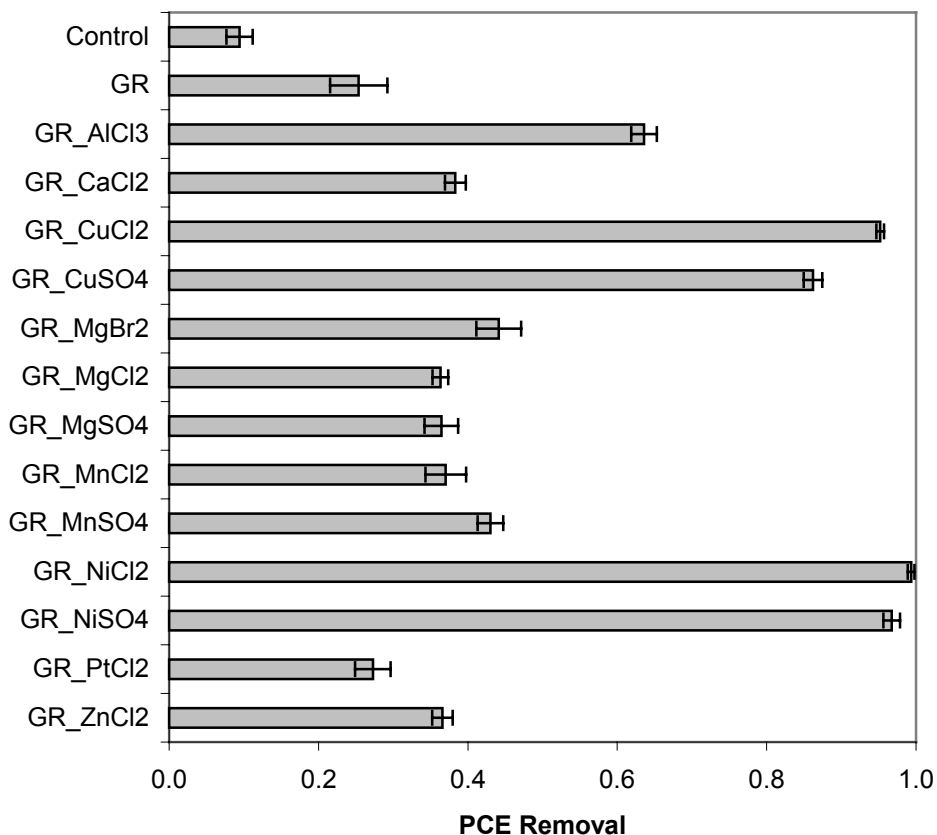


FIGURE 2. PCE removals by single element-modified green rusts. Error bars represent the standard deviations of observed PCE removals. $[\text{Fe(II)}]_{\text{GR}} = 35.0 \text{ mM}$, $[\text{PCE}]_0 = 0.241 \text{ mM}$, $\text{pH} = 11.4$.

ACKNOWLEDGMENTS

This material is based in part upon work supported by the Texas Advanced Technology Program under Grant No. 000512-0215-1999.

REFERENCES

Erbs, M., H.C.B. Hansen, and C.E. Olsen. 1999. "Reductive Dechlorination of Carbon

Tetrachloride Using Iron(II) Iron(III) Hydroxide Sulfate (Green Rust).” *Environmental Science and Technology* 33(2): 307-311.

Hansen, H.C.B., O.K. Borggaard, and J. Sorensen. 1994. “Evaluation of the Free Energy of Formation of Fe(II)-Fe(III) Hydroxide-Sulphate (Green Rust) and Its Reduction of Nitrite.” *Geochimica et Cosmochimica Acta* 58(12): 2599-2608.

Hansen, H.C.B., C.B. Koch, H. Nancke-Krogh, O.K. Borggaard, and J. Sørensen. 1996. “Abiotic Nitrate Reduction to Ammonium: Key Role of Green Rust.” *Environmental Science and Technology* 30(6): 2053-2056.

Koch, C.B., and H.C.B. Hansen. 1997. “Reduction of Nitrate to Ammonium by Sulphate Green Rust.” *Advances in GeoEcology* 30: 373-393.

Myneni, S.C.B., T.K. Tokunaga, and G.E. Brown, Jr. 1997. “Abiotic Selenium Redox Transformations in the Presence of Fe(II,III) Oxides.” *Science* 278(7): 1106-1109.

O’Loughlin, E.J., and D.R. Burris. 2000. “Reductive Transformation of Halogenated Hydrocarbons by Green Rust.” 220th ACS National Meeting; American Chemical Society: Washington D. C., pp. 635-637.

O’Loughlin, E.J., S. Kelly, K. Kemner, and D.R. Burris. 2001. “XAFS Study of the Catalytic Effects of Ag, Au and Cu on the reductive Dechlorination of Carbon Tetrachloride by Green Rust.” 222nd ACS National Meeting; American Chemical Society: Chicago, Illinois, pp. 259-265.

Refait, P.H., M. Abdelmoula, and J.-M.R. Génin. 1998. “Mechanisms of Formation and Structure of Green Rust One in Aqueous Corrosion of Iron in the Presence of Chloride Ions.” *Corrosion Science* 40(9): 1547-1560.

Refait, P., L. Simon, and J.-M.R. Génin. 2000. “Reduction of SeO₄²⁻ Anions and Anoxic Formation of Iron(II)-Iron(III) Hydroxy-Selenate Green Rust.” *Environmental Science and Technology* 34(5): 819-825.

Riley, R.G. et al. 1992. *Chemical Contaminants on DOC Lands Selection of Contaminant Mixtures for Subsurface Science Research*; DOE/ER-0547T; U.S. Department of Energy, Office of Energy Research, Subsurface Science Program: Springfield, Virginia.

Sagoe-Cretnsil, K.K., and F.P. Glasser. 1993a. “Green Rust, Iron Solubility and the Role of Chloride in the Corrosion of Steel at High pH.” *Cement Concrete Res.* 23: 785-791.

Sagoe-Cretnsil, K.K., and F.P. Glasser. 1993b. “Constitution of Green Rust and Its Significance to the Corrosion of Steel in Portland Cement.” *Corrosion* 49(6): 457-463.

Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. “Transformations of Halogenated Aliphatic Compounds.” *Environmental Science and Technology* 21(8): 722-736.