

**ELECTROCHEMICAL DEPOSITION OF GREEN RUST  
ON ZERO-VALENT IRON**

A Thesis

by

DHANANJAY VIJAY KULKARNI

Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2006

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Bill Batchelor
Committee Members,	Timothy A. Kramer
	Richard H. Loeppert
Head of Department,	David V. Rosowsky

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**ABSTRACT**

Electrochemical Deposition of Green Rust on Zero-Valent Iron.

(May 2006)

Dhananjay Vijay Kulkarni, B.Eng. Civil, Veermata Jijabai Technological Institute, India

Chair of Advisory Committee: Dr. Bill Batchelor

Perchloroethylene (PCE) is a toxic contaminant that has been introduced into the environment over many years through industrial and agricultural wastes. Research has been done in the past to investigate PCE degradation by zero-valent iron (ZVI), green rust (GR) and a mixture of both. The combination of ZVI and green rust has been reported to be more effective for degrading PCE than either of them alone. Forming green rust electrochemically has the potential for depositing GR more effectively on the surface of ZVI where it will be able to more easily transfer electrons from ZVI to contaminants such as PCE. Therefore, the goal of this research was to determine the feasibility of electrochemically depositing green rust on zero-valent iron and to characterize it in terms of its composition, crystal properties and amount produced. XRD analysis was conducted to determine composition and crystal properties and a procedure was developed to measure the amount produced.

Equipment was constructed to deposit green rust electrochemically onto ZVI. A chain of experiments with varying voltage, pH, time and amounts of ZVI were conducted to determine feasible experimental conditions for GR formation. Then, a method was

developed to accurately measure the amount of surface oxides of iron deposited on the zero-valent iron substrate. This method was tested and found useful for measuring iron in:

i) standard solutions of soluble iron with different concentrations of reagents; ii) suspensions with solid iron hydroxides by themselves; and iii) suspensions with solid iron hydroxides and ZVI. Electrochemical experiments were conducted and the amounts of iron hydroxides deposited on the ZVI surface were measured. XRD analysis of the deposits on the surface was conducted and the patterns of XRD-peaks were compared to that of type 2 – sulfate green rust.

## **DEDICATION**

To my loving Mom and Dad

(Sau. Uma Vijay Kulkarni and Hon'ble Vijay D. Kulkarni)

...whose toil in the barren soil of my mind bore this fruit, finally!

## ACKNOWLEDGEMENTS

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I thank my roommates and friends for keeping up my spirit afresh and helping me in non academic sphere of life which helped indirectly to provide me energy to use in the academic life. I very much thank Sachin Mathakari, Sony and Chetan for helping me the way they did.

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## INTRODUCTION

In today's world of increasing pollution, there is a need for a cleaner environment. There is a need for clean air, water and air for a good quality of life. It has been said that the wars of the future would be fought not for land or power, but for water. Clean water is our biological need. Life cannot be supported without water. Unfortunately, such an essential element of our nature is getting polluted daily due to increased industrial and household activities.

A large number of chemicals are produced by different industries for different purposes. Knowingly or unknowingly, those chemicals have become an integral part of our life and are discharged to air, water and soil. Chemicals in surface water and soil can percolate into and pollute groundwater. Groundwater pollution is a major concern. When groundwater is the only source of water, this problem of groundwater pollution is more serious.

Tetrachloroethene is one of the most important chemicals in the environment that contributes to groundwater pollution. It is also known as perchloroethylene (PCE), and the Department of Health and Human Services (DHHS) classifies it as an anticipated carcinogen (1). It enters into the environment through industrial sources where it is widely used for dry cleaning of fabrics and metal degreasing (2). It is also a constituent in some consumer products.

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This thesis follows the style and format of *Environmental Science and Technology*.

Efforts have been made to develop methods to degrade PCE in water and wastewater to non-toxic products. Reductive dechlorination by zero-valent (metallic) iron (ZVI) and green rust (GR) are some of the ways to degrade PCE. ZVI has been shown to degrade PCE in some studies, but the rate of degradation of PCE was too slow to be practically employed for water and wastewater treatment (2). Green rust is a partially oxidized iron hydroxide that has been shown to be effective in degrading PCE (2). Combining ZVI and green rust has been shown to be synergistic for PCE degradation (2).

It may be possible to extend this synergism by increasing the contact between GR and the ZVI surface. One way that this might be done is to directly deposit GR on the surface of ZVI in an electrochemical cell in which ZVI is the anode. GR electrochemically deposited on ZVI possesses the potential to degrade PCE faster and to a greater extent than either reductant alone.

Developing methods for depositing green rust electrochemically and characterizing it are important steps in developing a new method for PCE degradation. Therefore, the overall goal of the research is **to determine the feasibility of electrochemically depositing green rust on zero-valent iron and, to characterize the green rust**. This goal was pursued by completing three objectives:

- a) Develop a technique to deposit green rust on ZVI,
- b) Develop a technique to measure surface oxides and hydroxides of iron,
- c) Characterize the green rust with respect to its composition and crystal properties.

## BACKGROUND

Groundwater contamination by chemicals is a big problem. Tetrachloroethene (PCE) degradation by metallic iron has been studied as a part of efforts to improve technology for groundwater remediation, and it was found that metallic iron is useful to some extent for PCE-degradation (2). Similarly, green rusts were also found to be useful for PCE-degradation (2). Green rusts were first found as corrosion products on iron piles immersed in seawater and on the hulls of large ships (3). Green rusts are compounds with double-layers of mixed Fe(II)-Fe(III) hydroxides surrounding a layer of anions ( $A^{-n}$ ). This structure can be represented by the general formula  $(Fe^{II})_{6-x}(Fe^{III})_x(OH)_{12}A_{x/n} \cdot y H_2O$ . The value of  $x$  is close to 2 when there is an excess of Fe(II) present (4), which results in a  $Fe^{II}/Fe^{III}$  ratio of 2. The value of the stoichiometric coefficient of interlayer water ( $y$ ) is not well known (2).

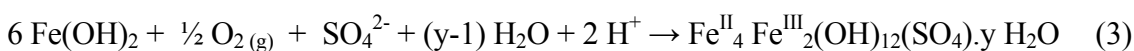
Green rust can be characterized as type 1 or type 2, based on the geometrical arrangement of the anions in the interlayer (5, 6). Each type of green rust can be further identified by the associated anion, e.g. chloride green rust, fluoride green rust, sulfate green rust. For example, type 2 – sulfate green rust can be represented by the general formula for green rust  $((Fe^{II})_{6-x}(Fe^{III})_x(OH)_{12}A_{x/n} \cdot y H_2O)$ , by replacing “A” with  $SO_4$ .

X-ray diffraction (XRD) is often used for qualitative analysis of crystalline solids. The XRD patterns for iron oxy-hydroxides are well documented and these compounds can be distinctly identified by X-ray diffraction (5, 6). Type 2 - sulfate green rust shows three predominant d-spacings, at 1.14, 0.58 and 0.37, during X-ray diffraction analysis (7, 8).

Green rust can be produced by Refait's method (3) in which oxygen in air is used to partially oxidize ferrous hydroxides. The half reactions can be written as follows:



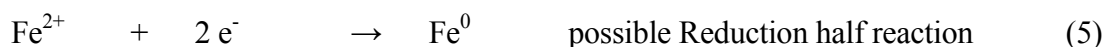
The overall reaction for green rust formation by the air oxidation method can be written as follows:



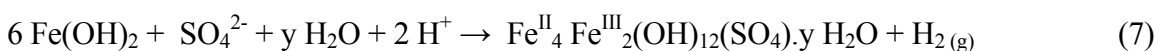
The combination of metallic iron and green rust has been reported to be more effective for degrading PCE than either of them alone (2). Therefore, it is possible that green rust deposited electrochemically on metallic iron might prove to be more effective in degrading PCE than either reductant used alone. There are no reports in the literature of electrochemical deposition of green rust on ZVI. However, Peulon *et al.* (9) reported a technique for electrochemical deposition of thin films of green rusts on inert gold substrate. This technique might be used to electrochemically deposit green rust on ZVI as the next step towards developing new and effective technologies for PCE degradation. Electrochemical deposition offers the potential to produce larger amounts of green rust on the ZVI surface and to produce it with more intimate contact with ZVI. In the method to prepare green rust by partial oxidation of iron hydroxides in open air (4), atmospheric oxygen is used to oxidize Fe(II) to form Fe(III) required to make GR. This oxidation can occur anywhere in solution, not necessarily at the surface of ZVI. Therefore, the normal procedure for producing GR will tend to produce it in the aqueous solution rather than at the surface of ZVI. However, if the

oxidation of Fe(II) were achieved in an electrochemical cell, the chances are good that green rust would form at the anode, where the oxidation occurs. If the anode were constructed of ZVI, it is likely that GR would be formed on the ZVI surface. This combination of ZVI and GR potentially possesses the capability to degrade PCE faster and to a greater extent than either reductant alone (2).

An electrochemical cell consists of a source of electrical potential connected to two electrodes (anode and cathode) that are immersed in an electrolyte. Several redox half-reactions are possible in an electrochemical cell that contains iron electrodes and ferrous sulfate as electrolyte. Either Fe(II) or Fe(0) could be oxidized to form Fe(III) at the anode and the hydrogen ion could be reduced to form hydrogen gas at the cathode.



It is not possible in the experimental set-up to be able to identify exactly which oxidation reaction occurs or to what extent either of the reaction occurs. Similarly there can be some other possible reduction reactions involved but the following overall reaction is based on the assumption that Fe(II) is oxidized to Fe(III), hydrogen ion is reduced to hydrogen gas, and sulfate is the anion in the GR interlayer.



The ferrozine method is commonly used to measure iron in aqueous solution (10, 11). It is a colorimetric technique based on absorption of light of 562 nm wavelength using a

spectrophotometer. This method measures the concentrations of iron in a solution, so the iron oxides and hydroxides must be dissolved before the iron contained in them can be measured.

There are various methods for separating iron oxy-hydroxides from different media and dissolving them. Dilute HCl (0.01 – 0.0001 N HCl) is used to separate iron and iron oxy-hydroxides from clay media (12,13). Heron et al. (14) provides seven methods for extraction and analysis of Fe(II) and Fe(III) including methods for extracting iron/iron-oxy-hydroxides from soil/clay/mica. One such method is the acid ammonium oxalate method and Philips et al. (15) modified it in order to determine the concentrations of oxalate-extractable Fe(III) and Fe(II) in soil sediments. The soil sediment was extracted in acid ammonium oxalate. Fe(II) in the extract was determined directly with the ferrozine method. Fe(III) in the extract was reduced to Fe(II) with  $\text{NH}_2\text{OH} \cdot \text{HCl}$  and total Fe was determined with the ferrozine method. The oxalate-extractable Fe(III) was calculated as the difference between Fe(II) and total Fe. The extraction procedure does not oxidize Fe(II) or reduce Fe(III). This method was able to separately measure Fe(II) and Fe(III) from the soil sediments, but with the limitation that there was no iron substrate present. Ryan used a Ti(III)-citrate-EDTA method (12) for measuring iron oxy-hydroxides that is quite elaborate. Citrate-bicarbonate-dithionite (CBD) is another method used for extraction of iron oxy-hydroxides from soils (13, 14).

None of these methods work well when iron oxy-hydroxides are on the surface of ZVI, because ZVI can be oxidized during the extraction process to produce soluble iron that will



be measured along with iron from the dissolved oxy-hydroxides. Loehberg (16) conducted research on features of ferritic fracture surfaces that examined the fracture mechanisms and strength of steel bars. In doing that, the researcher removed thin oxide-layers on the fractured surfaces using an antioxidant mixture called Endox, but did not measure the iron removed. Endox is a commercial anti-oxidant mixture used in agriculture as “a synergistic anti-oxidant mixture to stabilize vitamins and pigments in premixes, concentrates, and final foods” (17). Endox is a mixture of : butylated hydroxytoluene,  $C_6H_2(OH)(CH_3)[C(CH_3)_3]_2$  (1.3% w/w); tertiary butyl hydroquinone,  $(CH_3)_3CC_6H_3(OH)_2$  (3.5% w/w); phosphoric acid,  $H_3PO_4$  (2.3% w/w), NaOH, cyanide compounds (16, 18 ) in unknown quantities, and sawdust. The concept associated with the use of Endox is that NaOH will react with Fe oxy-hydroxides from the surface of the metallic iron to form soluble compounds of ferrous and ferric ions. After this dissolution, the metal surface will be protected by cathodic polarization and formation of a film of Endox on the iron surface (17).

## EXPERIMENTAL METHODS

An experimental plan was developed to meet the project goals. First, experiments were conducted to develop a technique to deposit green rust on ZVI. This included electrochemical experiments in an anaerobic chamber at various currents, voltages and pH. Then, experiments to develop a technique to measure surface oxy-hydroxides of iron were conducted. These included experiments to determine the suitability of the ferrozine method for measuring soluble Fe(II) in the presence of Endox; the extent to which Endox oxidizes ZVI; and whether or not iron oxy-hydroxides can be accurately measured in the presence of Endox and in the presence of both Endox and ZVI. Finally, experiments were conducted to characterize the iron oxy-hydroxides formed on the surface of ZVI. XRD analysis was used to determine the identity of the solids formed on ZVI by comparison with known patterns of XRD-peaks. The amount of iron oxy-hydroxide deposited on ZVI was measured by extracting iron from the deposits with Endox and analyzing for iron by the ferrozine colorimetric method.

### **Experimental system**

The equipment and reagents used in the experiments are described below.

#### ***Equipment***

Anaerobic chamber: The experimental system includes an anaerobic chamber (Coy Laboratory Products Inc.) for maintaining anaerobic conditions in order to avoid the interference of atmospheric oxygen. The anaerobic chamber is a closed and transparent PVC box with an intermediate chamber for transporting materials into and out of the

chamber. This chamber is maintained in an anaerobic state with a mixture of 95% nitrogen and 5% hydrogen. The anaerobic conditions are maintained all times and monitored with a solution of resazurin, which turns pink in the absence of anaerobic conditions. Details on preparation of this solution are given in Appendix 1. This chamber is equipped with electrical power outlets.

Electrochemical cell: An electrochemical cell was used that was comprised of a glass beaker and two electrodes. Both electrodes were constructed of graphite (Alfa Aesar, model number: AA40791-KN, model descriptor: “rotrode disc”, 99.9995%), but one of them was in contact with particles of zero-valent iron, so it is called the zero-valent iron electrode. Both electrodes are held in position with metal clamps. These metal clamps are connected to the D.C. power supply during the experiments. All experiments were conducted with the electrochemical cell within the anaerobic chamber. The cell was filled with solutions of ferrous sulfate (20 ml, 0.24 M  $\text{FeSO}_4$ ) and sodium hydroxide (20 ml, 0.4 M  $\text{NaOH}$ ). The electrode was immersed in the solutions with the ZVI electrode as the anode and the graphite electrode as the cathode. The anode was connected to the positive terminal of the power supply, and the cathode was connected to the negative terminal. An ammeter was placed in series with the DC supply. A thermometer and pH probe was placed in the cell to measure temperature and pH. The electrons flowed from the anode by oxidation of either  $\text{Fe(II)(aq.)}$  or  $\text{Fe(0)}$  to the positive terminal of the power supply; to the negative terminal of the power supply; to the cathode where they reduced either  $\text{Fe}^{2+}$  to  $\text{Fe}^0$  or  $\text{H}^+$  to  $\text{H}_2$  gas.

DC Power supply: This rectifier (Kenwood USA Corporation, PW18-2) converts A.C. supply to D. C. supply with steady D.C. output. This is used to supply a specific voltage (0 to 18 V) or specific current (0 to 2 A). The voltage can be regulated within 10 mV and the current can be regulated within 10 mA.

pH-meter: This instrument (Thermo Electron Corporation, Orion 420A) was calibrated using 3 standard solutions at pH 4, 7 and 10.

Spectrophotometer: A spectrophotometer (Agilent Technologies, 8453) is used for measuring light absorbance. The relationship between absorbance and concentration of ferrous iron is determined, so that the concentration can be calculated by measuring absorbance. The wavelength used during these measurements was 562 nm.

Centrifuge: A centrifuge (International Equipment Co., CS centrifuge) was used to separate the solids (green rust and ZVI) from the solution. After separation, iron was extracted from the oxy-hydroxides and measured.

Other materials: test tubes (15 ml), pipettes (0.2, 0.5, 1, 5, 10 and 25 ml), oven, thermometer, funnels, syringes, beakers, conical flasks and Whatman filter papers (50 micron pore-size).

### ***Reagents***

The following reagents were prepared according to the procedures described in Appendix 1: 0.24 M FeSO<sub>4</sub>, 0.4 M NaOH, 0.12 N HCl, acid washed zero valent iron, solution of Endox, and solution of resazurin. Reagents used in the ferrozine method were prepared as per standard procedures (10) as described in the Appendix 1. Green rust was prepared by combining solutions of FeSO<sub>4</sub> and NaOH and exposing the mixture to air while constantly stirring and monitoring the pH as described in Appendix 1.

### **Analytical methods**

The Ferrozine method (10) was used for the iron measurements. In this method, a colorimetric reagent produces a colored complex with Fe(II), and its intensity depends upon the concentration of ferrous ions. The absorbance resulting from this color is measured with light of 562 nm wavelength on a spectrophotometer. Total iron (Fe (Tot)) can be measured by reducing all Fe(III) to Fe(II) with a solution of hydroxylamine (10) and then measuring the Fe(II). The absorbances of known concentrations of Fe(II) in water, in full strength Endox and in a 1:10 dilution of Endox were measured and linear regressions were conducted to determine the calibration curves. These three calibration curves were used to calculate concentrations from measured absorbances in the experiments conducted for iron measurements in water, Endox and 1:10 dilution of Endox media respectively.

A multi-step procedure was used to measure iron oxy-hydroxides attached to the surface of ZVI. First, the loosely bound surface deposits were dislodged from the ZVI with a jet of deionized, deaerated water forced through the nozzle of a plastic bottle. Then the

suspension containing high concentrations of soluble and suspended iron was separated from the ZVI and the ZVI was washed multiple times until all loosely attached surface oxy-hydroxides of iron were removed. This was assumed to have occurred, when the washing solution contained less than 10 mg/l Fe(II). The washed ZVI was transferred into a test tube containing Endox solution to dissolve the oxy-hydroxides bound to the surface. A sample of the Endox solution was removed by pipette after 1.5 minutes of contact between Endox and ZVI. It was analyzed for iron concentration using the colorimetric ferrozine method and the standard curve that was prepared in Endox solution.

Following procedure was followed for preparing samples and analyzing them with XRD. All preparation steps occurred in the anaerobic chamber. After each experiment, the ZVI was transferred into a 15-ml sample-bottle and sufficient acetone was added to cover the ZVI. The bottle was capped using a seal with seven layers (polymer septum foil, lead foil, polymer septum foil, rubber disc, polymer septum foil, lead foil, polymer septum foil) and a screw-cap. The bottles were wrapped in a reflective aluminum foil to prevent any exposure to light. These samples were then taken to X-Ray Diffraction Lab at Texas A&M University's Geology & Geophysics Department in Michel T. Halbouty Building room 303. There, the samples were spread over a glass slab (2 cm x 5 cm) that was inserted into the XRD machine.

### **Experimental plan**

A task-wise approach was adopted to develop the experimental plan.

***Task 1: Develop a technique to deposit green rust on ZVI***

A chain of experiments was conducted to determine the set of conditions that allow deposition of green rust on ZVI in an electrochemical cell. These experiments were conducted over ranges of pH (7-10) and voltage (0.5 to 3 V). The amount of iron in the oxy-hydroxides deposited on the ZVI was measured. Results of these experiments were used to develop a feasible set of conditions that resulted in the formation of green rust on the surface of ZVI. First, experiments were conducted to determine the appropriate value for the applied voltage. Then, experiments were conducted with that voltage to determine the standard initial pH. It was anticipated that the initial pH would rise during formation of iron oxy-hydroxides (equation vii) and then fall, because this behavior has been observed during formation of GR by the air-oxidation method (3). The values for voltage and initial pH became part of the standard procedure used in subsequent experiments.

***Task 2: Develop a procedure to separate and measure iron oxy-hydroxides on the surface of zero-valent iron***

There are many well developed techniques for the measurement of different substances in the presence of various possible interferences. However, there are no methods described in the literature that can accurately separate and measure the iron oxy-hydroxides deposited on the surface of zero-valent iron. The problem lies in separating the surface layers of the oxy-hydroxides without oxidizing the iron in the surface layers or in the zero-valent metal. There are no separation methods available to do this and hence a new method was developed. Preliminary work and a literature review indicated the possibility of developing a new separation method using a commercially available reagent called Endox. The method

began by removing any loosely bound surface oxy-hydroxides of iron by washing with water. Then the more strongly attached surface oxy-hydroxides are dissolved in a solution of Endox. Iron is measured in the Endox solution using the ferrozine method with an appropriate standard curve.

Several characteristics of this method were investigated. Possible interferences of Endox with the ferrozine method for measurement of iron in the extracts were evaluated. The claim made by the manufacturer that Endox is an antioxidant was evaluated by determining the extent to which Endox oxidizes ZVI. Experiments were conducted in which the ability of Endox to extract iron from iron oxy-hydroxides was evaluated relative to extraction with 0.12 N HCl. Then the ability of the Endox/ferrozine method to measure iron in iron hydroxides in the presence of ZVI was determined.

Results of these experiments provided a method to separate and quantify the amount of iron oxy-hydroxides that are electrochemically deposited on zero-valent iron. To achieve these objectives following experiments were conducted:

1. Determine if Endox interferes with the analysis of soluble Fe(II) by the ferrozine method.

Experiments were conducted to determine if Fe (II) could be measured with adequate accuracy and precision in the presence of Endox. These experiments were conducted by measuring Fe(II) in multiple samples at neutral pH in deaerated deionized water with different concentrations (0.5 mg/l, 2.5 mg/l, 5.0 mg/l, 7.5 mg/l and 10.0 mg/l). Samples



were prepared in water with one set of replicates and full strength solution of Endox and 1:10 dilution of full strength Endox solution. The details of this experiment are given in Appendix 2.

2. Determine if Endox oxidizes ZVI.

Acid-washed ZVI (2 g) was contacted with Endox and iron was measured as a function of time (5, 30 minutes, 1, 2, 3, 8, 24 hours) using the ferrozine method in the presence of Endox.

3. Determine the ability of Endox/ferrozine method to measure iron oxy-hydroxides on ZVI.

An experiment was conducted to extract iron oxy-hydroxides in the presence of zero-valent iron with Endox and determine the iron concentration in the extract with the ferrozine method. The extraction and analysis was conducted under anaerobic conditions with two replicates at neutral pH. Green rust was used as a representative iron oxy-hydroxide. The composition of green rust was pre-determined by standard ferrozine method. Samples of GR (0.50 ml) by itself and GR in the presence of ZVI (2.0 g) were tested.

***Task 3: Characterize the iron oxy-hydroxides formed on the surface of ZVI***

Iron oxy-hydroxides were formed on the surface of ZVI using the electrochemical method and were characterized in terms of their chemical composition, green rust type, particle-size, and inter-layer separation. This was done by the method of comparison of XRD peaks obtained in the XRD experiments to the known data about the specific types of green rusts.

The Endox/Ferrozine procedure was used to quantify the amount of surface iron oxy-hydroxides deposited on ZVI. The chemical form of the deposits on ZVI was determined by XRD analysis. The diffraction analysis results were provided by the XRD machine. This tested the hypothesis that the solid formed was green rust.

### **Data analysis**

The data obtained in each experiment was recorded and tables and graphs were constructed to compare the data. Linear regressions were made using the data obtained in the experiment that determined the capability of the Endox/Ferrozine method. In the experiment that characterized the reactions of Endox with ZVI, graphs were plotted to observe the effect of time on the reaction. The iron concentrations over time were observed in the experiment that evaluates the ability of the Endox/Ferrozine procedure to extract and quantify iron in oxy-hydroxides on the ZVI surface. In the experiment that characterizes interactions of Endox with iron oxy-hydroxides and zero-valent iron, the iron concentrations over time were observed and compared.

Efficiency of this electrochemical deposition was calculated based on Faraday's basic formulas and an assumption about the time of operation. In calculating the efficiency of an electrochemical process, first, the total charge passed through the system is calculated by the formula  $Q = I t$ ; where  $Q$  is total charge in Coulombs,  $I$  is current through the system in Amperes i.e. Coulombs/seconds and  $t$  is the time in seconds. This charge is converted to total moles of electrons using Faraday's constant (96,485 C/mol). The mass of product is then converted to moles. The moles of electrons consumed per mole of product produced

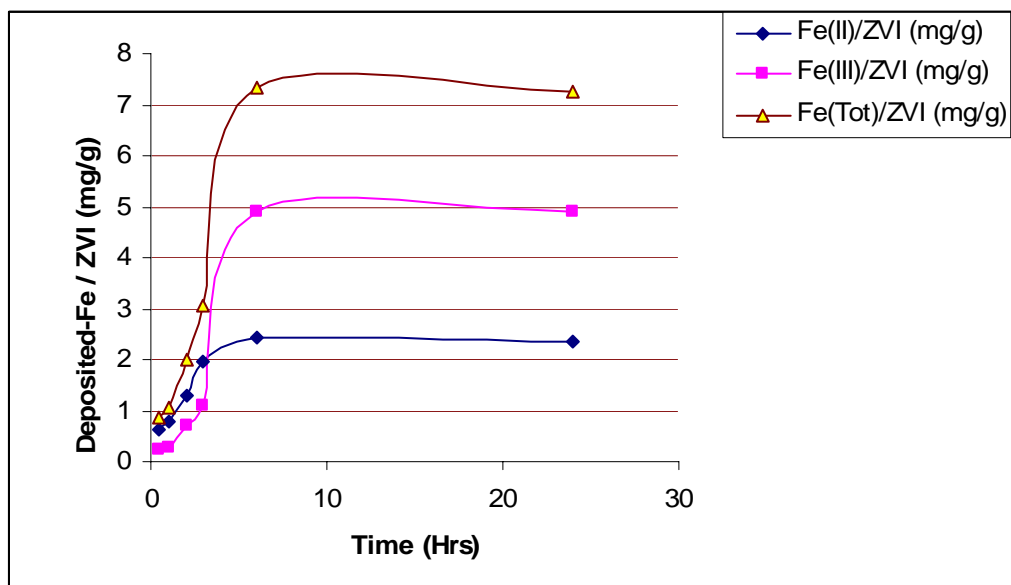
can be found knowing the change in oxidation state that occurs in the reaction that forms the product. For example, when the oxidation state changes by one electron, one mole of electrons will be consumed per mole of product produced. From the total charge supplied, the theoretical amounts of products that could be produced can be calculated. The ratio of actual products produced and the amount of products that could theoretically be produced gives the efficiency of the process. Sample calculations are shown in Appendix 6.

## RESULTS AND DISCUSSION

### **Task 1: Technique to deposit green rust on ZVI**

A series of experiments was conducted to obtain information on electrochemical formation of iron oxy-hydroxides on the surface of ZVI. The working hypothesis of these experiments was that the iron oxy-hydroxide would be green rust. These experiments showed production of a green-colored compound (GCC) on the ZVI.

Figure 1 shows results of an experiment to determine the effect of time on the amount of iron oxy-hydroxides deposited on ZVI by electrochemical processing. The conditions of 1 atm, 25° C, 20 ml each of the FeSO<sub>4</sub> and NaOH reagents, and 2 g of ZVI will be called the “standard conditions” for operation of the electrochemical cell. Figure 1 shows results of an experiment that was conducted at standard conditions and at pH 8 and 3 V. The GCC that had been deposited on ZVI had concentrations of iron as shown in Figure 1.



**Figure 1: Amount of green colored compound deposited on 2 g ZVI in various time durations in the preliminary electrochemical experiments performed to obtain initial estimation for the time of reaction. The conditions of these experiments were: 1 atm, 25° C, 20 ml each of the 0.12 M FeSO<sub>4</sub> and 0.2 M NaOH reagents, 2 g of ZVI, pH 8 and 3 V.**

The figure shows that there is no additional deposition of iron oxy-hydroxides after 6 hours. Hence a time of 6 hours was chosen to be used for the next experiments.

A second set of experiments was conducted to evaluate effects of voltage and pH on production of GCC and the results are shown in Table 1.

**Table 1: Amount of green colored compound deposited on 2 g ZVI in various experimental conditions for estimation of suitable conditions for electrochemical formation of green colored compound resembling green rust on zero valent iron. Conditions of the experiments were: 1 atm, 25° C, 20 ml each of the 0.24 M FeSO<sub>4</sub> and 0.4 M NaOH reagents, 2 g of ZVI and time duration of 6 hours. In case of the 9th and 10th experiments, the time duration was not fixed, but the experiments were stopped when the pH was observed to fall.**

<b>Experiment No.</b>	<b>pH</b>	<b>Voltage (V)</b>	<b>Fe(II) /ZVI (mg/g)</b>	<b>Fe(III) /ZVI (mg/g)</b>	<b>Fe(Tot)/ZVI (mg/g)</b>	<b>Fe(II)/Fe(III)</b>
1	7	3.0	1.8	6.3	8.1	0.30
2	7	3.0	2.4	5.9	8.3	0.40
3	7	3.0	2.3	5.7	8.0	0.40
4	8	3.0	2.45	4.35	6.8	0.60
5	8	1.5	2.9	1.1	4.0	2.6
6	9	3.0	2.8	4.1	6.9	0.70
7	9	1.5	3.82	0.87	4.7	4.4
8	10	1.5	4.55	0.63	5.2	7.2
9	8.11, 8.2, 8.19*	1.5	2.95	1.15	4.1	2.6
10	8.11, 8.2, 8.19*	1.5	3.0	1.2	4.2	2.5

\* pH was not kept constant during these experiments. The values represent the initial, maximum and final pH values.

Results in Table 1 show that at pH 7 there is more Fe(III) in the deposits on ZVI, which indicates greater oxidation of iron. The ratios of Fe(II) to Fe(III) that were measured (0.30 or 0.40) are lower than 2, which is the value normally expected in green rust. The same conclusion applies to other experiments conducted at pH 8 and 9 and at 3 V. Applying a potential of 3 V seems to promote too much oxidation of iron at pH values between 7 and 9 when the potential is applied for six hours. The experiments conducted at pH 10 and 1.5 V does not show appreciable oxidation. At pH 8, the deposits show a Fe(II)/Fe(III) value that

is the closest to that of sulfate green rust. However, when pH is controlled, there is no way to identify the end point. The decrease in pH after a gradual rise can be considered the point at which Fe(II) in the deposits begins to be converted to Fe(III). A decrease in pH has been shown to indicate oxidation of Fe(II) in the green rust that had been produced by oxidation of Fe(II) with air. Certain redox reactions are involved in formation of green rust by oxidation with air (Equations 1, 2, 3) as well as by oxidation with electric current (Equations 4-7). Hence, though it need not be so, it is assumed that the fall in pH gives a similar indication about the end point in the electrochemical experiments. Results from the 9<sup>th</sup> and 10<sup>th</sup> experiments (1.5 V and uncontrolled pH) are particularly important because the Fe(II)/Fe(III) ratios observed in these experiments are close to those expected for sulfate green rust. Conditions of the 9<sup>th</sup> and 10<sup>th</sup> experiments were selected for all the following experiments, except the fixed time of 6 hours. This was done because imposing a potential of 1.5 V did not cause too much oxidation to Fe(III) and because allowing the pH to vary provided a means to identify when the experiment should be stopped. The data in Table 1 show a general trend of more oxidation at lower pH and higher voltage.

## Task 2: Procedure to separate and measure surface oxy-hydroxides of iron

Table 2 presents results of the experiments conducted to determine if Fe(II) can be measured with adequate accuracy and precision in the presence of Endox. Known concentrations of Fe(II) were prepared in water, in a full strength Endox solution, and in a 1:10 dilution of full strength Endox solution. Standard calibration curves were obtained using absorbances recorded for known concentrations of Fe(II) prepared in the three different solutions. The calibration curve obtained for standards prepared in a full strength Endox solution had  $R^2$  of 0.994 and slope of 5.45 mg/l. The calibration curve obtained for standards prepared in a 1:10 dilution of full strength Endox solution had  $R^2$  of 0.999 and slope of 5.56 mg/l. ‘Check samples’ with known concentration of Fe(II) of 6.0 mg/l were measured to have concentration of 6.0 mg/l. These calibration curves were used to measure Fe(II) in the different solutions and the results are shown in Table 2. These were compared were compared to the amounts of Fe(II) added to the solutions (0.5, 2.5, 5, 7.5, 10 mg/l). Samples with a known concentration of Fe(II) in water were analyzed throughout the experiment to check that the calibration remained valid.

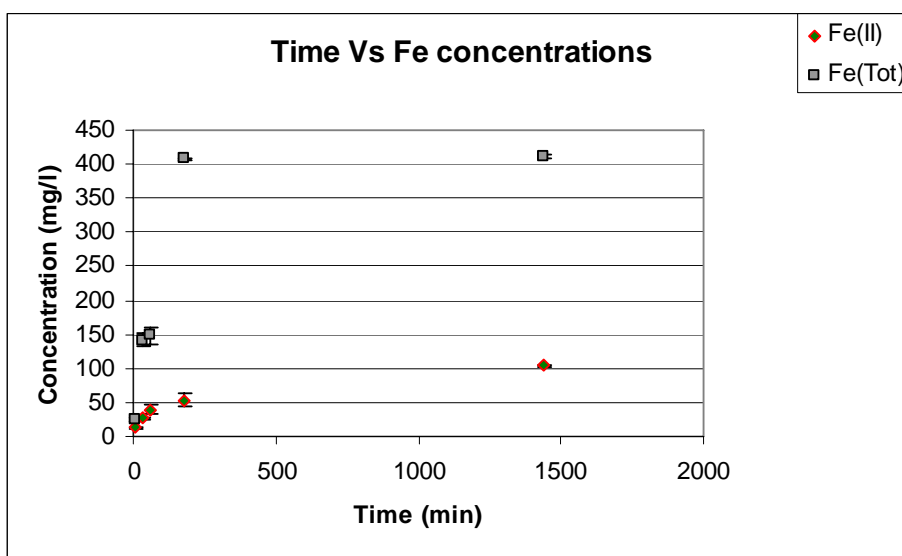
**Table 2: Iron measurement in Endox and 10 times diluted Endox media. The experiments were conducted under the following conditions: 1 atm, 25° C, standard stock solution of Fe(II), deaerated deionized water.**

Fe(II) Added (mg/l)	Fe(II)		Fe(II) (mg/l)	Fe(II)		Fe(II) (mg/l)
	Avg. (mg/l)	Std. Dev. (mg/l)		Avg. (mg/l)	Std. Dev. (mg/l)	
	Endox		Water	1:10 Dilution of Endox		Water
0.5	0.89	0.01	0.57	0.63	0.01	0.58
2.5	2.88	0.02	2.55	2.45	0.03	2.51
5	5.41	0.01	5.21	4.91	0.01	5.02
7.5	7.79	0.14	7.51	7.41	0.06	7.57
10	10.19	0.01	10	9.9	0.07	10



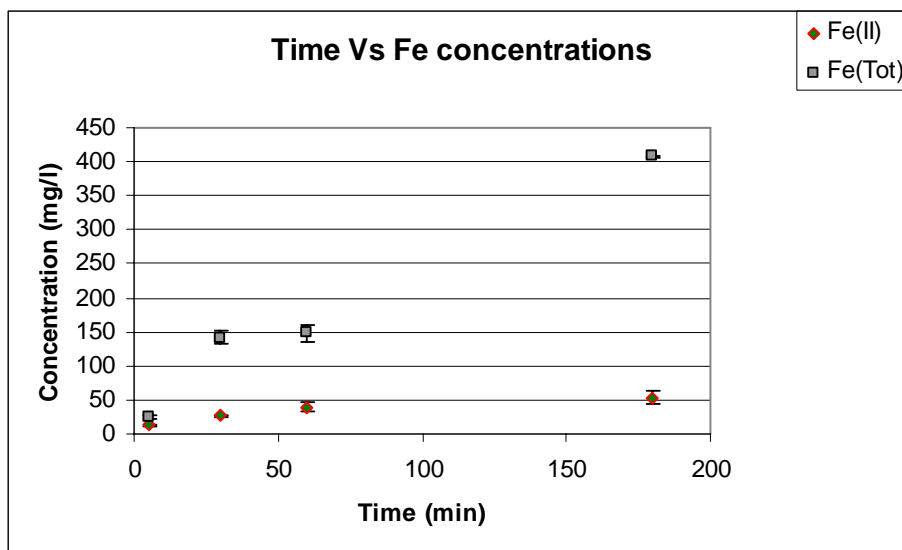
The data in Table 2 show that the measured concentrations of iron in water, full strength Endox solution and 1:10 diluted Endox solution were close to the expected values. Therefore, it can be inferred that the Fe(II) can be measured with acceptable accuracy and precision using the ferrozine method in the presence of Endox.

Figure 2 shows results of the experiment conducted to study the reaction between Endox and ZVI. The data are given in Appendix 4.



**Figure 2: Reaction of Endox with zero valent iron. These experiments were conducted under the following conditions: 1 atm, 25° C, 10 ml of Endox solution and 2 g of ZVI.**

Figure 2 shows that concentrations of Fe(II) and Fe(Tot) increase with time. Behavior at early times is important in developing an analytical procedure, so the data at early times is shown in Figure 3.



**Figure 3: Early part of reaction of Endox with zero valent iron. These experiments were conducted under the following conditions: 1 atm, 25° C, 10 ml of Endox solution and 2 g of ZVI.**

Figure 3 shows that as the time increases the amount of ZVI oxidized is observed to increase. The concentration of Fe (Tot) is less than 25 mg/l after 5 minutes of contact and would be expected to be less at times less than 5 minutes. This level of oxidization at early times provides an estimate of the error that will result when Endox is used to dissolve iron oxy-hydroxides from ZVI, if the extraction occurs in less than 5 minutes.

Table 3 presents results of the experiments conducted to determine if the Endox method can measure iron in iron oxy-hydroxides with adequate accuracy and precision.

**Table 3: Analysis of green rust for content of Fe(II) and Fe(III) after extraction by 0.12 N HCl or Endox. These experiments were conducted with the following conditions: 1 atm, 25° C, 0.5 ml of green rust and 9.5 ml, of 0.12 N HCl or Endox solution.**

<b>Time (Hr)</b>	<b>Fe(II)</b>		<b>Fe(Tot)</b>	
	<b>Avg. (mg/l)</b>	<b>Std. Dev. (mg/l)</b>	<b>Avg. (mg/l)</b>	<b>Std. Dev. (mg/l)</b>
<b><i>GR + HCL</i></b>				
1	295	0	380	0.5
2	293	0.5	378	1.5
3	301	1	376	2.5
8	305	1.5	379	1
24	305	2	382	1
<b><i>GR + Endox</i></b>				
1	278	0.5	375	1
2	279	0	378	1
3	258	0.5	376	0.5
8	259	1	375	2
24	258	2	377	1.5

The relative standard deviations of Fe(II) and Fe(Tot) calculated using measurements at all times were calculated to be 1.9% and 0.6% for GR + HCl and 4.2% and 0.4% for GR + Endox. These small values show that there is little effect of time between 1 and 24 hours on Fe concentrations measured in green rusts, regardless of whether HCl or Endox is used to dissolve the solids. This experiment also shows that the two methods provide similar measurements of Fe(Tot) in the Green Rust. Since the Endox/ferrozine method can measure Fe(II) and Fe(III) in a similar way to that of ferrozine method with 0.12 N HCl the significance of this finding is that this it has an adequate accuracy and precision to be applied to measure iron in green rust deposited on the surface of zero-valent iron and significant problems of metal oxidation during the procedure are not expected. However, Fe(II) measurements in the GR + Endox are lower than those in GR + HCl. This indicates that there is certain discrepancy in the results but still the measured values are close to each

other. The average concentration of 379 mg/l Fe(Tot) obtained using HCl to dissolve the green rust agrees well with the average concentration of 376 mg/l obtained with Endox. Since HCl is often used in standard procedures (10) to dissolve iron hydroxides such as green rust, dissolving them with Endox and analyzing for iron in the presence of Endox appears to be a suitable method.

Table 4 presents results of the experiments conducted to determine the ability of the Endox method to measure iron in iron hydroxides while in the presence of ZVI.

**Table 4: Iron analysis using 0.12 N HCl and Endox in the presence of GR and ZVI. These experiments were conducted under the following conditions: 1 atm, 25° C, 0.5 ml of green rust suspension, 9.5 ml of 0.12 N HCl or Endox solution and 2 g of ZVI.**

Time (Hr)	Fe(II)		Fe(Tot)	
	Avg. (mg/l)	Std. Dev. (mg/l)	Avg. (mg/l)	Std. Dev. (mg/l)
<i>GR+ZVI+HCl</i>				
0.083	1480	16	1870	17
0.5	2680	22	3380	26
1	3290	18	3880	21
2	4290	33	5380	31
3	6300	45	8370	49
8	13300	128	17400	134
24	22300	190	28400	216
<i>GR+ZVI+Endox</i>				
0.083	290	2	398	2.5
0.5	300	2	515	1
1	320	0.5	525	1
2	330	0	610	1
3	315	0.5	780	0.5
8	340	1	780	2
24	365	2	790	1.5

The concentrations of Fe(II) and Fe(Tot) shown in Table 4 can be compared to the concentrations determined for the green rust suspension in the absence of ZVI. These values are 280 mg/l Fe(II) and 375 mg/l Fe(Tot) and were obtained using the standard ferrozine method. The results in Table 4 show large increases in concentrations of dissolved Fe when HCl is added to the mixture of green rust and ZVI. These concentrations steadily increase with time indicating that the ZVI is being oxidized, which can be expected at the low pH resulting from HCl addition, since HCl oxidizes metallic ZVI (19). The mixtures with Endox show much smaller increases in iron concentration. The concentration of Fe(II) measured at 5 minutes represents a 10 mg/l increase over the concentration of the initial green rust suspension. The concentration of Fe(Tot) after 5 minutes of contact with Endox represents an increase of 23 mg/l. These can be compared to corresponding increases of 1200 mg/l Fe(II) and 1495 mg/l for Fe(Tot) observed in the experiments with HCl. These observations signify that iron in green rust cannot be accurately measured in

the presence of ZVI with the traditional method that uses 0.12 N HCl, because of large increase in Fe(II) and Fe(III) due to oxidation, but that is possible if Endox is used instead, since it does not cause oxidation to an appreciable extent.

Experiments were conducted to measure the accuracy and reproducibility of methods for measuring iron oxy-hydroxides in the presence of ZVI. These experiments were carried out in the anaerobic chamber using a contact time with Endox of 2 minutes. Multiple samples were taken from the test tubes containing 0.5 ml GR, 9.5 ml Endox, and 2 g ZVI and the results of the analyses are shown in Appendix 5. Results of these experiments showed a relative standard deviation of about 1% and a relative error of about 0.35%. Hence, the Endox/ferrozine method for extraction and analysis of iron in oxy-hydroxides has acceptable accuracy and precision.

**Task 3: Characterize iron oxy-hydroxides formed on the surface of ZVI**

Results from experiments in task 1 identified convenient conditions for electrochemical deposition of iron oxy-hydroxides on ZVI ( $\text{Fe}^0$ ). These conditions were an imposed electrical potential of 1.5 V and uncontrolled pH. The pH was observed to increase up to a certain value and then to decrease, which was used to indicate the end point for the experiment. The conditions used in this experiment resulted in a measured current of 70 mA at the beginning which gradually increased to 100 mA during the first 5 minutes and then stayed constant until the end of the experiment. This signifies that the rate of consumption of electrons i.e. the rate of reaction stays constant after about 5 minutes. This also means that the reactants were not totally consumed during the course of the experiments.

At the end of each experiment, granular ZVI was coated with a green colored compound. The GCC deposited on the ZVI was dissolved in full strength Endox solution and concentrations of iron in the solution were measured and they are reported in Table 5. This table also shows an electrochemical efficiency of the process. This efficiency is the efficiency for electrons being used for the intended reactions i.e. producing  $\text{Fe(III)}$  needed to form green rust 'on the ZVI-surface'. It is defined as the ratio of electrons utilized in forming green colored compound on the ZVI-surface to the electrons supplied to the cell. Note that this is different from efficiency of the overall reaction which is the ratio of electrons utilized in forming green colored compound anywhere in the cell to the supplied electrons.

A more detailed explanation of how the efficiency was calculated is given in the experimental section and a sample calculation is shown in Appendix 6.

**Table 5: Analysis of green colored compound deposited on ZVI during electrochemical experiments. These experiments were conducted under the following conditions: 1 atm, 25° C, 20 ml each of the 0.24 M FeSO<sub>4</sub> and 0.4 M NaOH reagents, 2 g of ZVI, uncontrolled pH, 1.5V.**

<b>Experiment No.</b>	<b>Fe(II)/ZVI (mg/g)</b>	<b>Fe(III)/ZVI (mg/g)</b>	<b>Fe(Tot)/ZVI (mg/g)</b>	<b>Fe(II)/Fe(III)</b>	<b>Efficiency* of the process %</b>
1	2.91	1.12	4.03	2.6	0.17
2	3.64	0.50	4.14	7.3	0.08
3	2.73	1.32	4.05	2.1	0.20

Note: These are readings for three different and independent experiments done on different days. Results for the first experiment are averages of 6 replicate samples. The other results represent averages of 3 replicate samples.

An average of 3.1 mg/g of Fe(II)/ZVI, 1.0 mg/g of Fe(III) and 4.1 mg/g of Fe(Tot)/ZVI were deposited on ZVI in these experiments. An estimate can be made for how much of



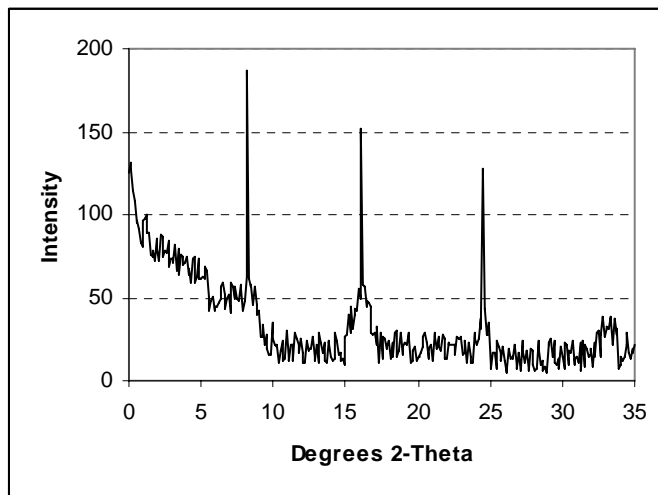
this is the result of oxidation of ZVI during extraction and this estimate can be used to estimate the actual concentration of GCC on the surface of ZVI. The oxidation of ZVI by Endox can be estimated to produce about 5-10 mg/l of Fe (II) and 10-15 mg/l of Fe (Tot). This corresponds to 0.05-0.1 mg/g of Fe(II) and 0.1-0.15 mg/g of Fe(Tot) respectively. This estimate is based on results shown in Figure 3. Therefore, the corrected amount of iron on the surface of ZVI is 3.0 mg/g-ZVI of Fe(II) ( $3.1 - (0.05+0.1)/2 = 3.025$ ) and 4.0 mg/g-ZVI of Fe(Tot) ( $4.1 - (0.1+0.15)/2 = 3.975$ ).

The average Fe(II) to Fe(III) ratio in the GCC is 4, which is not near a value of 2, which might be indicative of the deposits being green rust. However, two of the measured Fe(II)/Fe(III) ratios are close to that expected for sulfate green rust (2.0) and the third value (7.3) is far from the expected value. This might be due to experimental errors like loose-connections between wires and connectors, or wires and clamps or clamps and electrodes or wires and power supply and some other unidentifiable human errors.

The efficiencies were calculated as described in Appendix 6 and they show that the process of deposition is a very inefficient one.

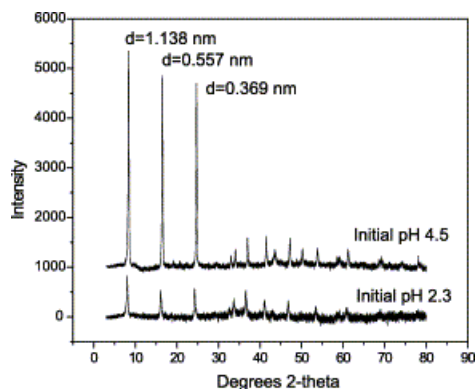
## XRD analysis

Figure 4 presents results of the XRD analysis conducted on the green colored compound deposited on zvi in the electrochemical experiment.



**Figure 4:** The XRD pattern of the green colored compound deposited on ZVI. The compound was produced under the following conditions: 1 atm, 25° C, 20 ml each of the 0.24 M FeSO<sub>4</sub> and 0.4 M NaOH reagents, 2 g of ZVI, uncontrolled pH and 1.5 V. Diffractogram was produced by X-Ray Diffraction Lab at Texas A&M University's Geology & Geophysics Department.

This pattern of XRD peaks is similar to that reported by Wilkin (7) for sulfate green rust, which is shown in Figure 5. This verifies that the deposits are type 2 – sulfate green rust.



**Figure 5: XRD pattern of type 2 – sulfate green rust (7) for comparison with XRD pattern of green colored compound deposited on ZVI.**

The d-spacings can be calculated for each peak in the diffractogram using Bragg's Law and they are presented in Table 6 along with other values from the literature.

$$2 d \sin\Theta = \lambda_0$$

where,  $d$  = lattice interplanar spacing of the crystal,

$\Theta$  = X-ray incidence angle =  $\frac{1}{2}$  (2-theta), and

$\lambda_0$  = wavelength of the X-rays used.

**Table 6: Comparison of XRD analysis**

	Relative intensity (measured)	Relative intensity (literature (7))	3-d spacing (measured) (nm)	3-d spacing (literature (7)) (nm)
Peak 1	100	100	1.1	1.14
Peak 2	84	89	0.55	0.56
Peak 3	67	87	0.36	0.37

X-ray analysis shows that the distance between oxy-hydroxide sheets is about 1.1 nm indicating type 2 – sulfate green rust. The three predominant d-spacings confirm the formation of type 2 – sulfate green rust.

## SUMMARY AND CONCLUSIONS

The degradation of toxic contaminant PCE is a major concern that threatens our environment. The goal of this research was to determine the feasibility of electrochemically depositing green rust on zero-valent iron and to characterize it. This is to be viewed as a pioneering work for possible development of a large scale application of green rusts as a remediation technique for degrading PCE in contaminated waters.

### **Electrochemical deposition of iron oxy-hydroxides on ZVI**

An electrochemical technique was developed for deposition of iron oxy-hydroxides on ZVI. Satisfactory performance of this system was found when operated at an applied electromotive force of 1.5 V at room temperature under anoxic conditions. Monitoring changes in pH affords an easy way to determine the end point for the deposition process. A drop in pH is hypothesized to indicate the beginning of the oxidation of green rust. The electrochemical procedure for depositing iron oxy-hydroxides (Equation vii) on ZVI was found to be an inefficient process for producing Fe(III), with an efficiency of 0.18%. This may not be a major concern when a source of electrons is cheap relative to the potential benefits of contaminant remediation. Furthermore, the oxy-hydroxides deposited on the surface degrade PCE in a redox reaction in which iron in the oxy-hydroxide becomes oxidized. The reduced iron may be able to be regenerated (2) by reaction with electrons obtained from ZVI. In this way, the surface oxy-hydroxides would not be consumed by reactions with chlorinated organics.

### **Technique to measure surface oxy-hydroxides of iron**

Of the several techniques available to separate iron oxy-hydroxides from solid media, none of them were useful to separate surface iron oxy-hydroxides from zero-valent iron (16, 12, 15). A successful method was developed in this research using a commercial mixture called Endox. The principles involved are dissolution of thin layers of iron oxide by Endox, and then measuring the extracted iron using the ferrozine method. This procedure was able to quantify the amount of iron in surface oxy-hydroxides within acceptable errors. In the experiments conducted with Endox, it was seen that Endox in “full-strength” solutions and in solutions diluted by a factor of 10 was a suitable media for iron extraction and that it did not interfere with measurement of iron by the ferrozine method. Although concentrations of Fe (II) and Fe (Tot) increase with time when ZVI is in contact with Endox, only 0.25 mg/g-ZVI was measured after 5 minutes of contact. This is small compared to the range of iron oxy-hydroxides concentrations found on ZVI after electrochemical formation (3.1 to 4.1 mg/g-ZVI). Lower concentrations should be observed at times less than 5 minutes.

The Endox/ferrozine procedure was shown to be able to achieve a relative error of around 0.4% and a relative standard deviation of around 1%. The experiments also showed that iron can be measured with the ferrozine method in systems containing iron hydroxides Endox and ZVI.

### **Characterizing the green rust**

The quantities of Fe (II) and Fe (Tot) deposited on ZVI as oxy-hydroxides are about 3.0 and 4.0 mg Fe/g ZVI, respectively. The ratio  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  for these deposits on the surface of ZVI was found to be near 2 in two out of three cases, which is consistent with the oxy-hydroxides being a form of green rust. XRD analysis of the iron oxy-hydroxides produced on ZVI by the electrochemical process shows that they are type 2 – sulfate green rusts.

### **Suggestions for future research**

Green rust deposition may be possible at other voltages than 1.5 V and this needs to be researched. Research should also be conducted to determine the optimum voltage and other conditions in the electrochemical procedure for producing iron hydroxides on ZVI. Surface oxide measurement is apparently a simple task but in specialized situations it needs rigorous work to be done with utmost care. Endox can be evaluated for its ability to remove surface oxide measurements of other metals. Even after knowing about iron for so many centuries, it poses many challenges and benefits for us. More accurate methods of iron measurement may be developed by studying different compounds. For example, a compound called Rendox exists that belongs to the same class as that of Endox. It is available in a liquid form, which would make it easier to use than Endox, which is only available as a powder. Extensive use of XRD should be made in situations where there is doubt about the identity of a mineral. Since both qualitative and quantitative analysis techniques are very important in any research, quantitative XRD analysis (20) should also be used in study related to electrochemically formed green rusts and other oxy-hydroxides on ZVI.

After the process of electrochemically producing hydroxides on the surface of ZVI is better understood, PCE degradation experiments at various conditions should be conducted to extend the success of this study. Then, the possibility of implementing this research in an economically feasible way in real life should be evaluated.

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## APPENDIX 1

### Reagents

0.24 M ferrous sulfate ( $\text{FeSO}_4$ ) solution:

Accurately weigh 3.33 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in a small tray. Dissolve it in 50 ml deaerated deionized water in a 50-ml volumetric flask. Use magnetic stirrer for complete and homogeneous dissolution. All steps are conducted in the anaerobic chamber.

0.4 M sodium hydroxide ( $\text{NaOH}$ ) solution:

Accurately weigh 0.80 g of  $\text{NaOH}$  in a small tray. Dissolve it in 50 ml deaerated deionized water in a 50-ml volumetric flask. Use magnetic stirrer for complete and homogeneous dissolution. All steps are conducted in the anaerobic chamber.

0.12 N hydrochloric acid ( $\text{HCl}$ ) solution:

Take 100 ml concentrated  $\text{HCl}$ . Add the concentrated acid to 900 ml deaerated deionized water in a jar. Keep this solution in an amber bottle with dispenser.

Acid washed zero valent iron (ZVI):

Take 25 g of ZVI in a beaker with 50 ml 0.12 N  $\text{HCl}$ . After one and two days, replace the  $\text{HCl}$  solution with fresh 0.12 N  $\text{HCl}$ . At the end of the third day, take the beaker into the anaerobic chamber and remove the  $\text{HCl}$ . Wash this ZVI with deaerated, deionized water several times. Remove all the water and soak out the final traces of water using tissue

paper. Place the ZVI on a tray and let it dry. Transfer the ZVI to a small and airtight glass bottle and store in the chamber.

Ferrozine reagents: Prepare the ferrozine reagents as per standard procedures (9).

Endox solution:

Composition of Endox:

Butylated hydroxytoluene ...	$C_6H_2(OH)(CH_3)[C(CH_3)_3]_2$	... 1.3% w/w
Tertiary Butyl Hydroquinone ...	$(CH_3)_3CC_6H_3(OH)_2$	... 3.5% w/w
Phosphoric acid ...	$H_3PO_4$	... 2.3% w/w
Sodium Hydroxide ...	$NaOH$	... undisclosed amount
Sodium Cyanide ...	$NaCN$	... undisclosed amount

The rest is inert matter (sawdust).

Take 25 g of Endox powder, mix it in 100 ml deaerated deionized water, keep it in an oven for 1 hour at a temperature of 105 °C (15). Then filter out the inert particles to obtain a clear Endox solution. Now, make the volume exactly 100 ml. This solution will be identified as 'full strength Endox' solution.

Dilute the full strength Endox solution by a factor of 10 by adding 1 part by volume of the full strength Endox solution to 9 parts by volume of deaerated deionized water.

Resazurin solution (Indicator):

Add 2 g Hydrion<sup>TM</sup> pH buffer powder for pH 9 to 500 ml deaerated deionized water. Add 5 g resazurin ( $C_{12}H_6NO_4Na$ ) (Sigma). Mix well. Add 10 pieces of palladium catalyst. Purge the solution by nitrogen gas for about 1 hour and then transfer the solution into the anaerobic chamber and purge with the chamber atmosphere until the color changes from red-purple to clear. Add 5 ml of this clear solution to a 20-ml clear glass bottle to use as an indicator. If oxygen is present, the clear solution turns purple-red.



Set A samples will be used to calibrate the spectrophotometer.

From Set C, the sample with 0 mg/l Fe (II) in Endox, will serve as a blank for Sets C and D.

Set G samples will serve the purpose of check after the experiment.

In experiment with 10 times diluted Endox:

Set B samples will be used to calibrate the spectrophotometer.

From Set E, the sample with 0 mg/l Fe (II) in 10 times diluted Endox, will serve as a blank for Sets E and F.

Set H samples will serve the purpose of check after the experiment.

### APPENDIX 3

#### Effect of Time on Amounts of iron deposited on ZVI

Table A-2: Amount of green colored compound deposited on 2 g ZVI in various time durations

GCC	Time (Hrs)	Fe(II)/ZVI (mg/g)	SD (mg/g)	Fe(III)/ZVI (mg/g)	SD (mg/g)	Fe(Tot)/ZVI (mg/g)
1	0.5	0.64	0.01	0.23	0.005	0.865
2	1	0.78	0.005	0.28	0	1.055
3	2	1.3	0	0.70	0.015	1.995
4	3	1.95	0.05	1.1	0	3.05
5	6	2.45	0.05	4.9	0	7.35
6	24	2.35	0.05	4.9	0	7.25



**APPENDIX 4****Endox reaction with ZVI****Table A-3: Endox reaction with ZVI**

<b>Reaction Time (Hr)</b>	<b>Fe(II)/ZVI (mg/g)</b>	<b>Std. Dev. (mg/g)</b>	<b>Fe(Tot)/ZVI (mg/g)</b>	<b>Std. Dev. (mg/g)</b>
0.083	0.067	0.015	0.12	0.025
0.5	0.13	0.02	0.71	0.0875
1	0.2	0.081	0.74	0.12
3	0.27	0.089	2.04	0.01
24	0.52	0.02	2.05	0.02

Std. Dev. = Standard deviation

## APPENDIX 5

## Accuracy and precision analysis table

Table A-4: Iron analysis from GR using 0.12 N HCl in standard ferrozine method and iron analysis from GR in Endox in the presence of ZVI

Sample No.	Measured Fe(II) (mg/l)	Measured Fe(Tot) (mg/l)
<i>Iron measured from GR using standard ferrozine method (using 0.12 N HCl)</i>		
1	4720	6730
2	4740	6610
3	4600	6751
4	4660	6614
5	4630	6710
	<b>AVG = 4670</b>	<b>AVG = 6683</b>
	<b>SD = 59.2</b>	<b>SD = 66.4</b>
	<b>%RSD = 1.26</b>	<b>%RSD = 0.99</b>
<i>Iron measured from the same GR when that GR is in Endox in the presence of ZVI using ferrozine method (using Endox to dissolve GR)</i>		
1	4740	6770
2	4770	6710
3	4630	6740
4	4640	6620
5	4740	6770
6	4660	6670
7	4750	6800
8	4630	6630
9	4720	6640
10	4610	6670
11	4630	6750
12	4710	6730
	<b>AVG = 4685</b>	<b>AVG = 6708</b>
	<b>SD = 57.8</b>	<b>SD = 60.9</b>
	<b>%RSD = 1.23</b>	<b>%RSD = 0.91</b>
<b>SD = Standard Deviation</b>		<b>AVG = Average</b>
<b>%RSD = Relative Standard Deviation in percentage</b>		

Average recovery = Measured value / Estimate for true value

So, from the above table:

Average recovery for Fe(II) = 100.3% and

Average recovery for Fe(Tot) = 100.4%

## APPENDIX 6

### Calculations for efficiency of electrochemical process

Efficiency of an electrochemical process should mean the efficiency of electron use. If every electron supplied to the electrochemical cell results in a one unit change in oxidation state of an element, then the efficiency of that conversion process would be 100%. If it takes two electrons supplied to the cell to result in a one unit change (e.g. Fe(III) to Fe(II)), the electron use efficiency is 50%. Therefore, the efficiency is defined as the ratio of the electrons supplied to the electrochemical cell to the electrons participating in a particular redox reaction. The total number of electrons supplied to the electrochemical cell can be calculated as the product of the current times the time applied. Faradays constant is also needed to convert between coulomb and mole. The experiments took 6.17, 6.58 and 6.42 minutes, respectively. Assuming that the experiments all lasted 6 hours, efficiency of the process can be calculated as shown below.

Total number of electrons supplied = 100 mA for 6 Hrs =

$$0.1 \text{ Coulomb/second} \times 3600 \text{ seconds/hr} \times 6 \text{ hr} = 2160 \text{ C}$$

This corresponds to  $2160 \text{ C} / 96485 \text{ C/mol} = 2.2387 \times 10^{-2} \text{ mol e}^{-}$

Moles of product formed =  $1.12 \text{ mg/g of Fe(III)/g-ZVI} \times 2 \text{ g-ZVI} = 2.24 \text{ mg of Fe(III)}$

$$2.24 \times 10^{-3} \text{ mg of Fe(III)} = 2.24 \times 10^{-3} / 55.845 \text{ mol of Fe(III)} = 4.01 \times 10^{-5} \text{ mol of Fe(III)}$$

Now, mole of Fe(III) per mole of electron = Efficiency of the process =

$$4.01 \times 10^{-5} / 2.2387 \times 10^{-2} = 0.001791 = 1.791 \times 10^{-3} = 0.1791\% \approx 0.18\%$$

So, the efficiency of process = 0.18%.

But, for first experiment, using 6.17 hours, instead of 6 hours, we get, total charge passed through the system (Q), = 2220 C and an efficiency of  $4.01 \times 10^{-5} / 2.3009 \times 10^{-2} = 0.175\%$   
~ 0.18%.

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