CHROMIUM REDUCTION VIA GREEN RUSTS: A STUDY OF CHARACTERIZATION, REACTION KINETICS AND MECHANISMS

A THESIS
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AUGUST, 2002
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ABSTRACT

Green rusts, ferrous-ferric iron oxides, occur in many anaerobic soil and sediment systems and are highly reactive, making them important in polyvalent contaminant reduction. However, much has yet to be examined with respect to the mechanisms of these environmentally relevant reactions. Formation of Fe(II)Fe(III) hydroxy green rusts from ferrous sulfate, chloride and carbonate solutions was studied at ambient temperature with pH and oxygen flow controlled. The purified products of these reactions were characterized using vibrational spectroscopy, XRD, SEM, BET, and XAS analyses. Variations in interlayer anion as well as structural differences resulting from Fe^{II}/Fe^{III} ratios were evident in the spectral analysis. In addition, SEM images indicate a dual-phase formation process – the first being slow nucleation and the second a rapid precipitation from solution.

Due to the wide spread use and environmental significance of chromium as well as the kinetic favorability of its reduction by ferrous iron, reactions of chromate with green rusts were examined. Green rusts were reacted with chromate, Cr(VI), to determine the reaction kinetics. GRCl is the most effective reductant of Cr(VI) followed GRCO₃ and GRSO₄, with first-order rate coefficients \(k_{\text{obs}}\) (with respect to Cr(VI) concentration) ranging from 1.22 x 10⁻³ to 3.7 x 10⁻² s⁻¹. The rates of reduction are controlled by the concentration of ferrous iron and structure / chemical bonding of the green rust layers. The nature of the oxidation products of these reactions is independent of the anionic class of GR, but their respective concentrations display a dependence on the initial GR. Chromium(III)-bearing iron oxyhydroxides of magnetite and lepidocrocite were identified as the major oxidation products.
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CHAPTER 1.

INTRODUCTION
Environmental Significance of Chromium

Chromium is a pollutant of concern due to its widespread use in industrial applications such as electroplating, metallurgy, and leather tanning, as well as its natural occurrence in ultramafic rocks and volcanic dusts. Chromium, used in iron, steel, and nonferrous alloys, enhances hardness and resistance to corrosion and oxidation. In the environment, chromium exists as Cr(III) or Cr(VI). The concentration of naturally occurring chromium in U.S. soil ranges from 1 to 2,000 mg/kg, with an average concentration of 54 ppm (Environmental Assessment Division, 2001). While chromium is concentrated in soils, air and water levels are generally low. In air, the range is between 0.01 and 0.03 µg/m³, and drinking water levels are generally less than 2 µg/L (ATSDR, 2000). Chromium has been found in at least 1,036 of the 1,591 current or former EPA National Priorities List (NPL) sites (ATSDR, 2000).

In addition to natural and industrial inputs of chromium, a large source of contamination is the result of nuclear waste reserves. Elevated levels of chromium (60 µg/L to 910 µg/L) in the groundwater from the Superfund site in Hanford, WA have poisoned the nearby Columbia River (Fruchter et al., 2002). These nuclear reactor facilities and many other industrial plants, employed chromium, in the form of sodium dichromate, to prevent corrosion in piping, primarily cooling waters, and the resulting contaminants are present in soil (predominantly as the trivalent form) and/or groundwater (as hexavalent chromium). Remediation techniques for this toxin seek to reduce the metal to a more manageable form, Cr(III).

In its fully oxidized state, hexavalent chromium exists as hydrochromate (HCrO₄⁻), chromate (CrO₄²⁻), and dichromate (Cr₂O₇²⁻) anionic species. The proportion
of each ion in solution is pH dependent. Under basic and neutral pH conditions, chromate forms predominate. As the pH is lowered (6.0 to 6.2), the hydrochromate concentration increases. At very low pH, the dichromate species predominate (EPA, 1984). Chromate is a known carcinogen when inhaled, causes kidney tubule necrosis and is an irritant of plant and animal tissue (Klein, 1996; Puls et al., 1994). As the primary form of natural chromium is Cr(III), the presence of hexavalent chromium is often a tracer for anthropogenic environmental input. This tetrahedrally coordinated oxoanion is highly soluble, highly mobile, and thus of major concern in the environment (Weckhuysen et al., 1996). For these reasons, the U.S. EPA Drinking Water Regulations set drinking water standards of 0.1 mg/L or less (EPA, 1994). However, in soils and groundwater aquifers with lower than neutral pH values, these oxoanions have the potential to sorb on iron oxides and (oxy)hydroxides reducing their solubility (Dzombak and Morel, 1990; Eary and Rai, 1991).

Under reducing conditions, Cr(VI) may be converted to Cr(III) which forms hydroxide solids of limited solubility and strongly adsorbs to solid surfaces limiting its transport (Eary and Rai, 1988; Weckhuysen et al., 1996). For example, Cr(III) commonly sorbs on iron oxides and oxyhydroxides at pH values $\geq 4$ forming strongly bound inner-sphere complexes and/or precipitates (Charlet and Manceau, 1992; Dzombak and Morel, 1990). At dilute concentrations, Cr(III) is essential in human glucose, lipid and protein metabolism. In general, chromium(III) is less toxic than chromium(IV). Cr(III) is most often found in nature as the only ore of chromium, chromite - FeCr$_2$O$_4$. The mineral possesses a spinel structure with Cr(III) occupying the octahedral sites and Fe(II) the tetrahedral sites (Klein and Hurlbut, 1993).
Reduction of chromate is often coupled with abiotic electron transfer reactions on the surfaces of Fe(II)-containing solids. In addition, reaction with sulfides (Patterson et al., 1997) and organic complexes (involving microbial catalysis) lead to chromate reduction (Ishibashi et al., 1990; Llovera et al., 1993). While organic reductants can form soluble, chelated complexes with Cr(III) (James and Bartlett, 1983), inorganic reductants enable the precipitation of insoluble Cr(III) solids (Sass and Rai, 1987). As aqueous ferrous iron concentrations and Fe(II)-bearing solids are common in anoxic conditions, reduction of Cr(VI) by Fe(II) is observed in natural soil systems such as wetlands (Masscheleyn et al., 1992) and suboxic aquifers (Anderson et al., 1994) and in permeable reactive barriers (Powell et al., 1995; Pratt et al., 1997).

In anaerobic systems, Fe(II) often dominates the reduction of Cr(VI) (Fendorf et al., 2000) and in acidic soils Fe(II) is as effective a reducer as organic matter (Eary and Rai, 1991). Even under well-aerated conditions, oxidation of aqueous Fe(II) by Cr(VI) occurs (Eary and Rai, 1989). In addition, Fe(II) reduction of chromate is much faster than biological pathways in anoxic conditions, and when biological activity is limited, aerobic abiological oxidation of ferrous iron helps to immobilize chromium (Fendorf et al., 2000). Thus, Fe(II) present in solution and as solids plays an important role in Cr(VI) reduction. The rate of Cr(VI) reduction by ferrous iron in solution has been established as a very rapid reaction – on a timescale of minutes to months in ferrous rich sediments, soils, and waters (Fendorf and Li, 1996; Pettine et al., 1998; Sedlak and Chan, 1997).

Chromate reduction is also possible when aqueous Cr(VI) sorbs on Fe(II)-bearing Fe(III) solids such as maghemite ($\gamma$-Fe(III)$_2$O$_3$), hematite ($\alpha$-Fe(III)$_2$O$_3$), goethite ($\alpha$-
Fe(III)OOH), or hydrous ferrous oxides (Fe(OH)\textsubscript{3}·nH\textsubscript{2}O) provided surface-bound Fe(II) is present (Bidoglio et al., 1993; Eary and Rai, 1989; Peterson et al., 1996). The possibility of ferrous iron associated with these oxidized iron phases is high in natural systems. Magnetite (Fe(II)Fe(III)\textsubscript{2}O\textsubscript{4}) can also reduce Cr(VI) to Cr(III) in both laboratory and field environments (Peterson et al., 1996). However, magnetite is passivated by reaction with high concentrations of aqueous Cr(VI) at circumneutral pH, limiting the ability of magnetite to act as an electron donor for reduction reactions (Peterson et al., 1997).

**Green Ruts**

Another mixed valence iron oxide of importance with respect to chromium reduction is green rust. Green rusts are Fe(II)-Fe(III) oxyhydroxides within the sjögrenite-pyroaurite structural group consisting of brucite-like layers. Initially, they were characterized as corrosion products in steel and iron water distribution pipes (Stampfl, 1969). Trioctahedral layers of ferrous hydroxide, Fe(OH)\textsubscript{2}, substituted with Fe\textsuperscript{3+} produce an overall net positive charge which is then neutralized by the association of negative anions and water in the interlayer. The nature of the interlayer anion directly affects the structure and classification of the green rust. The most common, and well-studied, anions are chloride, carbonate and sulfate. The classification of green rust 1 (GR1) refers to the chloride and carbonate species as they are both planar anions. In contrast, green rust sulfate falls under the designation GR2 as it is a three-dimensional, tetrahedrally-coordinated anion occupying the interlayer.

Gleyed soil horizons and the uppermost layers of some lake and marine sediments exhibiting the characteristic blue-green color are assumed to be a result of the presence of
GRs (Génin et al., 2001; Trolard et al., 1997). Natural occurrence of green rust minerals was not documented until the last decade, however. Initial reference to environmental occurrence was to rusting of man-made iron materials in anoxic conditions (Génin et al., 1993; Olowe et al., 1990; Schwertmann and Fechter, 1994; Stampfl, 1969) or to precipitation in ochre sludge (Koch and Mörup, 1991). Others have suggested the presence of these minerals from studying iron speciation in soil solutions but have not positively identified them (Ponnamperuma et al., 1967). The first evidence for the existence of green rust as a natural mineral, as opposed to the result of anthropogenic interference, was in 1997. Trolard et al. (1997) characterized a forest soil and identified a naturally occurring green rust providing direct evidence for their presence in nature. The site, in the Fougeres region of Brittany France, consisted of a granitic saprolite underlying genetic horizons of a waterlogged soil. A composition of Fe(II)-Fe(III) GR1(OH) forming in the presence of excess hydroxide was suggested, similar to the mechanism proposed by Refait et al. (1994). Later, Génin et al. (2001) identified this as a natural mineral with the name fougerite and assigned a formula of:

\[ [\text{Fe}^{II}_{1-x}\text{Fe}^{III}_{x}(\text{OH})_{2}]^{x}\cdot [x\text{OH}^{-}\cdot (1-x) \text{H}_{2}\text{O}]^{x-} \leftrightarrow \text{Fe(OH)}_{2+x} \cdot (1-x) \text{H}_{2}\text{O}. \]

However, this mineral has yet to be synthesized.

**Environmental Significance of Green Rust**

Green rust compounds exist as intermediates in the formation and reduction of ferric iron oxides such as goethite, lepidocrocite and magnetite (Schwertmann and Fechter, 1994). In addition, green rusts are a product of microbial degradation by dissimilatory iron reducing bacteria (Fredrickson et al., 1998; Parmer et al., 2001) and identified in field-scale permeable reactive barriers containing Fe(0) (Ritter et al., 2002;
Due to their highly reactive surface areas, sensitivity to oxidation, and the resulting potential to reduce polyvalent elements / contaminants, GRs hold significance in controlling the fate of toxins. Redox chemistry is often a controlling factor in solubility, bioavailability, and toxicity of inorganic contaminants in natural environments (Sposito, 1980).

To date, relatively few studies have been conducted on the ability of GRs as potential contaminant remediators. The sulfate form is the most commonly studied, more than likely due to its ease of synthesis. The contaminants evaluated thus far for GRSO₄ are nitrate (Hansen and Koch, 1998; Hansen et al., 1996), nitrite (Hansen et al., 1994), selenate (Myneni et al., 1997), arsenate (Randall et al., 1999), halogenated methanes (Erbs et al., 1999) and chromate (Loyaux-Lawniczak et al., 2000; Loyaux-Lawniczak et al., 1999). Chloride green rust has been studied with respect to nitrate (Hansen et al., 2000), nitrite (Hansen et al., 2000), and chromate (Loyaux-Lawniczak et al., 2000). The least stable form of green rust, GR₁(CO₃), has minimal representation in the literature, with only reactions involving nitrate (Hansen and Koch, 1999) and chromate (Williams and Scherer, 2001).

Despite their importance, there are a limited number of publications on the kinetics of reduction of environmental contaminants by green rusts. The few reaction rates that have been reported reveal pseudo first-order kinetics with respect to contaminant concentration (Hansen et al., 1994; Hansen and Koch, 1998; Hansen et al., 1996; Myneni et al., 1997). In addition, researchers have also seen an increase in reduction rate using GRCl instead of GRSO₄ (Hansen et al., 2001), and an increase in
reduction rate when the contaminant is introduced before green rust precipitates as opposed to addition after nucleation (Hansen et al., 1994; Myneni et al., 1997).

**Cr(VI) Reduction by Green Ruts**

Loyaux *et al.* (1999) provide one of the first reports describing chromate reduction by GRSO₄. GRSO₄ oxidized to amorphous, Cr-substituted, 2-line ferrihydrite with a fraction of the available solution chromate ions substituted for SO₄²⁻ in the GR interlayer prior to reduction. A later study by the same group (Loyaux-Lawniczak et al., 2000) suggests that the oxidation product is the same for both GRSO₄ and GRCl, thereby implying that the nature of the initial GR has no influence on the product. The proposed mechanism, removal of SO₄²⁻ from the crystal structure, insertion of Cr(III), and rearrangement of the iron hydroxide sheets would lead to a disordered form of Fe(III) oxyhydroxide. Of the three previous studies conducted on the interactions of green rusts with chromium, just one deals with the kinetics of reduction. Most recently, Williams and Scherer (2001) published data suggesting a pseudo first-order reduction of chromate to Cr(III) with respect to Cr(VI) concentration via oxidation of GRCO₃, with rate coefficients \(k_{obs}\) ranging from \(1.2 \times 10^{-3} \text{ s}^{-1}\) to \(11.2 \times 10^{-3} \text{ s}^{-1}\).

No study has compared the three main types of green rust and their reactivity in relation to a certain environmental contaminant. Though initial reports have given an overview of mechanisms of reduction by one member of the green rust classification, little has been done to examine the differences within the group that arise due to structural variations. In order to evaluate the role of green rusts under environmental conditions, and the significance of their structural differences in relation to their reactivity, our study examined the interaction of green rusts with chromium. Chromium
was chosen due to its widespread use and presence in the environment and because of its reactivity toward ferrous iron-bearing minerals. The contributions of green rusts in the reduction of chromate were examined through a comparison of reduction rates.

**Research Objectives**

The objectives of this study were to i) synthesize and fully characterize the three main anionic classes of green rust and to ii) examine the reaction between these green rusts and chromate. The formation of green rusts from ferrous sulfate, chloride and carbonate, and their oxidation products, were studied at circumneutral pH and ambient conditions to gain insight into the structural differences between these compounds. Through solid and solution phase analyses performed during the course of, and following, the reduction reactions, details of the chromate reduction mechanism were studied. Kinetics of chromate reduction by green rusts were examined to determine the rate dependence on the chemical and structural make-up of the green rust solids. Additionally, such analyses allowed the nature of the oxidation product and the extent of surface passivation to be evaluated. To our knowledge, an examination of the three major GR anionic classes with respect to chromate reduction kinetics and mechanisms has not previously been undertaken.
REFERENCES


CHAPTER 2.

GREEN RUST SYNTHESIS AND CHARACTERIZATION
INTRODUCTION

Green rusts, layered mixed-valence iron oxyhydroxides with the pyroaurite structure, exist as intermediates in the formation of Fe(III) oxides and byproducts of ferric iron reduction (including microbially mediated reactions) in anoxic environmental conditions. The two main classes of green rust are based on physical configuration of the interlayer anion. Chloride and carbonate, planar anions, are the most common and well studied components of the class known as GR1 while sulfate and selenate, tetrahedral anions, are the only identified members of GR2. These differences in anion structure affect the reactivity of GRs. While their extreme sensitivity to oxidation makes these compounds difficult to isolate, their oxidation potential is ideal for coupling to the reduction of environmental toxins. GRs hold significance in the field of natural attenuation as redox chemistry is often a controlling factor in solubility, bioavailability, and toxicity in natural environments (Sposito, 1980).

The first laboratory synthesis of green rusts was reported by Girard and Chaudron (1935) and then later by Feitknecht and Keller (1950). Initially characterized as corrosion products in steel and iron water distribution pipes (Stampfl, 1969), the name ‘green rust’ was first used to describe crystalline ferrous/ferric hydroxides containing halide or sulfate anions (Bernal et al., 1959). Gleyed soil horizons and the uppermost layers of some lake and marine sediments exhibiting the characteristic blue-green color are assumed to be a result of the presence of GRs (Trolard et al., 1997).
Formula and Structure

Pyroaurite-type compounds have the general composition:

\[ [M_a^{II}(6-x)M_b^{III}x(OH)_{12}]^{x+}[(A)_{x/n}yH_2O]^{y-} \] (0.9 < x < 4.2)

where \( M \) and \( A^{n-} \) are the metal and anion, respectively, and the amount of interlayer water, \( y \), is between 3 and 3.38 at 25°C for the carbonate anion (Hansen et al., 1994).

This formula, when applied to green rusts, gives \([Fe^{II}_{(1-x)}Fe^{III}_x(OH)_{12}]^{x+}[(x/n)A^{n-}(m/n)H_2O]^{y-}\). Even more specifically, the formula of GR2(SO4), GR1(Cl), and GR1(CO3) are as follows (Génin et al., 1998):

\[
\begin{align*}
\text{GR2(SO}_4) & \quad [Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+} \cdot [SO_4 \cdot nH_2O]^{2-} \\
\text{GR1(Cl)} & \quad [Fe^{II}_3Fe^{III}_x(OH)_{8}]^{2+} \cdot [Cl \cdot nH_2O]^{2-} \\
\text{GR1(CO}_3) & \quad [Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+} \cdot [CO_3 \cdot nH_2O]^{2-}
\end{align*}
\]

GR1 compounds have a stacking sequence \( AcBiBaCjCbAkA \ldots \), where \( A-C \) designate OH⁻ planes, \( a-c \) metal cation layers, and \( i-k \) intercalated layers. In contrast, GR2s retain the original hexagonal stacking of the initial ferrous hydroxide \( AcBijA \ldots \) (Bernal et al., 1959; Feitknecht and Keller, 1950). For GR1s, the positions of intercalated anions depend on the species whereas the positions remain the same for each of the known GR2s (sulfate and selenate) (Génin et al., 2001). Rapid oxidation occurs upon exposure to air and the rate of oxidation, type and concentration of the anion, temperature and pH were noted as factors determining the nature of the oxidation products (Solcova et al., 1981). Also, the ratio of ferrous to ferric iron can vary in these compounds under different conditions, thus affecting their properties and oxidation products.
**Synthesis Procedures**

Green rusts can be synthesized by oxidation of Fe(II) solutions by molecular oxygen in aqueous solution at circumneutral pH. These ferrous solutions are prepared by mixing a ferrous hydroxide salt and caustic soda solution with an excess of salt (Génin et al., 1998). In addition, GRs may be obtained when Fe(III) oxyhydroxides, such as ferrihydrite or lepidocrocite, are reductively dissolved at pH ≥ 6.5 (Taylor and McKenzie, 1980). Often, these reactions are carried out in controlled systems with respect to pH and exposure to oxygen. During the formation of GR2(SO4) and GR1(Cl), loss of Fe and SO4^{2-}/Cl^{-} from solution is linearly related to base consumption (Schwertmann and Fechter, 1994). The end products of these oxidation reactions are most often lepidocrocite and magnetite, depending on pH and oxygen flow rates. Slow oxidation leads to magnetite occurring due to complete dehydration and only partial oxidation of Fe. Lepidocrocite is formed by rapid oxidation of green rust resulting from complete oxidation of Fe and only partially dehydration (Génin et al., 1996; Génin et al., 1998; Miyata, 1983). Other oxidation products that arise from different oxidation and dehydration rates include goethite and maghemite (Myneni et al., 1997).

Schwertmann and Fechter (Schwertmann and Fechter, 1994) propose a two-step reaction in the formation of lepidocrocite by oxidation of ferrous chloride and sulfate. The first reaction involves the nucleation of green rust by formation of Fe^{III} ions which hydrolyze and precipitate as 2-line ferrihydrite, immediately reacting with dissolved Fe^{2+} to form GR:

\[
x^n\text{Fe(OH)}_3^n + y\text{FeSO}_4 + 2(y-z)\text{NaOH} \rightarrow \text{FeyFe_x}^{III}(\text{OH})_{3x+2y-2z}(\text{SO}_4)^2 + (y-z)\text{Na}_2\text{SO}_4
\]  

\[2.1\]
With the rate of green rust formation limited by the rate of ferrihydrite formation, the supply rate of O$_2$ becomes the controlling factor. The formation of green rust is found to cease when a certain minimum in [Fe$^{2+}$] is reached. With further decrease in the concentration of ferrous iron, the solution becomes under-saturated with respect to green rust and decomposes to lepidocrocite:

$$Fe_y^{II}Fe_x^{III}(OH)_{3x+2y-2z}(SO_4)_{2y} + 0.25yO_2 + 2zNaOH \rightarrow (x + y)FeOOH + zNa_2SO_4 + (x + 0.5y)H_2O$$

Such reactions require a minimum [Fe(III)] that lies near 25% of the total Fe for the chloride GR1 system and 33% for the sulfate GR2 form.

The most widely used means of identifying GRs is Mössbauer spectroscopy. This nondestructive method is often used for analysis of samples that contain several phases and for investigation of amorphous materials that may be difficult to characterize by other techniques. The isomer-shifts (IS) and quadrupole splitting (QS) are unique to specific ions and, in the case of green rust, allow for the distinction between Fe$^{2+}$ and Fe$^{3+}$. Each green rust spectra present two types of quadrupole doublets. One type corresponds to Fe$^{3+}$ ions with an IS and QS of 0.45 mm s$^{-1}$ and 0.50 mm s$^{-1}$ respectively. The larger IS and QS of 1.25 mm s$^{-1}$ and 2.85 mm s$^{-1}$ are associated with Fe$^{2+}$ ions (Trolard et al., 1997). GR1 and GR2 exhibit different Mössbauer spectra and are easily distinguished by this method. Raman spectroscopy is frequently performed as a confirmation to Mössbauer characterization. These spectra display two sharp peaks corresponding to Fe$^{3+}$-OH (505 cm$^{-1}$) and Fe$^{2+}$-OH (420 cm$^{-1}$) stretching modes (Boucherit and Goff, 1992). Few reports of Fourier transform infrared (FTIR) characterization are available (Legrand et al., 2001; Refait and Génin, 1994; Trolard et
al., 1997) but these spectra are a means of confirming the nature of the interlayer anion and sample purity. The majority of IR bands are a result of H$_2$O and OH stretching and deformation and Fe-O stretching. X-ray diffraction (XRD) is useful in differentiating the two classes of GR as they have different interlayer spacing depending on the nature of the anion, planar or tetrahedral. A strong diffraction peak at low 2$\theta$ values characterizes both types with GR2 having a greater d-spacing than GR1.

**Microbial Interactions**

GRs, while often the result of abiotic reactions, can also form during dissimilatory reduction of hydrous ferric oxide (HFO) by groundwater bacteria (Fredrickson et al., 1998; Zachara et al., 2002a). This is of environmental significance as GR occurs frequently in anoxic soils where Fe(III)-reducing baceria are among the most metabolically active species (Chapelle, 2000; Génin et al., 1998; Lovley and Anderson, 2000; Trolard et al., 1997). In fact, some studies suggest GR exists only in the presence of active bacteria (Chaudhuri et al., 2001; Fredrickson et al., 1998; Ona-Nguema et al., 2002; Zachara et al., 2002b). Rapid transformation to magnetite and siderite occurs after reduction of hydrous ferric oxide (HFO) when bacteria such as *Shewanella putrefaciens* (strain CN32) are inactivated (Fredrickson et al., 1998). Precipitation of GR appears to be advanced by reactions away from the cells as the solid phase is not intimately associated with bacteria. Bioreduction of lepidocrocite ($\gamma$-FeOOH) in batch culture by *S. putrefaciens* (strain CIP 8040) resulted in GR(CO$_3$)$^2^-$ (Ona-Nguema et al., 2002). Again, GR was the major end product when inactivation of bacteria did not inhibit reduction. In addition, *Dechlorosoma suillum*, strain PS, forms GR as a major metabolic product of Fe(II) oxidation with nitrate as the electron acceptor (Chaudhuri et al., 2001). These
studies suggest the presence of GR in natural environments only in active biotic conditions. However, numerous studies have produced green rusts as stable end products under abiotic conditions (Drissi et al., 1995; Hansen et al., 2001; Hansen et al., 1996; Myneni et al., 1997; Ritter et al., 2002; Vins et al., 1987). This implies that green rusts may form by either biotic or abiotic means; however, their existence is the result of numerous pathways including chemical oxidation of ferrous oxides and microbial enzymatic reduction.

**Permeable Reactive Barriers**

More recently, green rust formation as a corrosion product in permeable reactive barriers has been established (Roh et al., 2000). Use of barriers filled with reactive media such as zero-valent iron, to clean contaminant plumes is a new technology emerging for *in situ* and *ex situ* remediation (Matheson and Tratnyek, 1994). In the permeable wall, iron corrosion occurs as a result of oxidation and ensuing precipitation. In reduced environments, oxidation of Fe$^0$ to Fe(OH)$_2$ is favorable; however, the latter is predicted thermodynamically to convert to magnetite or intermediates such as green rust (Schwertmann and Cornell, 1991). Iron metal can be transformed into green rusts chloride, sulfate and carbonate in moderately neutral solutions (6.5 < pH < 8.0) which can then convert to goethite, lepidocrocite, maghemite or magnetite depending on the rate of oxidation and dehydration (Myneni et al., 1997). In processes involving reductive dechloronation of TCE, chlorine is released as chloride ion and can combine with Fe$^{2+}$ to form green rust [Fe$^{II}_3$Fe$^{III}$(OH)$_8$Cl] and amorphous iron hydroxides (Roh et al., 2000). Work to remediate species by reductive dechloronation of organic compounds, especially carbon tetrachloride, could be thwarted by the formation of these iron hydroxides, which
inhibit catalytic hydrogenation, and passivation of iron surfaces. Ritter et al. (2002) state that while green rusts would not hinder processes such as electron transfer and may further react as a reductant, the oxidized forms would be detrimental to these processes.

**Research Objective**

As green rusts are increasingly being discovered in environmental systems, it is vital to have complete physical and structural information on these compounds. Though their existence, in some regard, has been recognized for the last 60 years, only recently have the structural components and environmental significance of green rusts been presented, and there appears much to still be learned. Accordingly, the objectives of this study are to synthesize and fully characterize green rust sulfate, chloride and carbonate. Information gleaned in this chapter should help to further explain the reactivity (and variations therein) of green rusts.
MATERIALS AND METHODS

Chemical Synthesis Procedures

All chemicals were ACS reagent grade and used without further purification. Green rusts (GR) chloride and sulfate were synthesized per the method of Schwertmann and Fechter (1994). All solutions were made anoxic by boiling and cooling distilled, deionized water under O₂-free, N₂ gas. All glassware was equilibrated in the glovebox for at least 24 h prior to use. Reactions were performed in a specially designed chamber that was constructed with inlets for nitrogen, air, acid, base Eh and pH electrodes, and a sampling port. A port on the reaction vessel allowed aliquots to be taken throughout the reaction while maintaining anaerobic conditions; samples were collected by attaching a 20 gauge needle to the sampling tube and inserting it into an N₂ purged, crimp-capped vial outfitted with a syringe.

Reactions were initiated by placing 450 mL solution of 0.8 M FeSO₄·7H₂O or FeCl₂·4H₂O, prepared with anaerobic DI water in an N₂ (95%) / H₂ (5%) filled glovebox (Coy Instruments), into the reaction vessel (Figure 2.1). The solution was uniformly stirred while pH and Eh were monitored using a reference electrode of saturated calomel. The solution pH was then raised to 7.0 ± 0.1 for the sulfate system (6.8 for chloride) with 4 M NaOH and adjusted, as needed, with 1 M HCl. As the pH increased, the color shifted from pale, translucent blue-green to a dark yellowish green and progressed to a dense, deep blue-green shade as the green rust began to precipitate.

Once the desired pH was established, CO₂-free air was introduced in place of the N₂ gas at a rate of 8.4 mL/min while the pH was held constant with the addition of NaOH. As the Eh reading approached a maximum, the airflow was stopped and N₂ was
reintroduced and purged for 15 minutes. Immediately following the N₂-purge, the apparatus was sealed and transferred to an anaerobic glovebox. The solution was then vacuum filtered through a 0.22-µm Millipore filter under N₂, washed three times with anoxic water, and dried. The solids were then stored in the glovebox in N₂ equilibrated glass serum vials and sealed with crimp-capped Teflon-coated rubber septa.

Green rust carbonate was synthesized using the method of Benali et al (2001) that accounts for the low solubility of ferrous carbonate (FeCO₃). A 200 mL solution of NaOH and NaHCO₃ was prepared anaerobically and magnetically stirred under N₂. A 200 mL solution of FeSO₄·7H₂O was added to this basic solution and N₂ replaced with CO₂ free air at a rate of 8.4 mL/min. Solution concentrations were 0.18 M FeSO₄·7H₂O, 0.3 M NaOH, and 0.2 M NaHCO₃. The pH and Eh were monitored but not controlled – due to the presence of carbonate species, the solution was buffered between pH 8 and 9. The reaction was quenched at pH 8.2 to avoid the conversion to other oxidation products such as magnetite or lepidocrocite. Once the reaction was complete, the solid was treated in the same manner described above, being filtered, washed and dried.

**Characterization: Solid Phase Analyses**

The filtered products of the synthesis procedures were analyzed using X-ray diffraction (XRD), micro-Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and X-ray absorption spectroscopy (XAS).

X-ray diffractograms were recorded from 5-65 degrees 2θ using Cu Kα₁ radiation (λ = 1.54056 nm). A Rigaku Geiger-flex Powder Defractometer with generator energy of 35 KeV and a power of 15 mA was employed. Samples were prepared in the glovebox
by admixing with glycerol to form a paste which was smeared onto the sample slide (Hansen and Poulsen, 1999); the glycerol paste was used to limit oxidation during XRD analysis. The glycerol displays itself as an artifact ‘hump’ in the spectra between 15 and 25 degrees 2\(\theta\).

Surface area was determined using a 5-point BET analysis on a Coulter SA 3100. Samples were dried in the glovebox by vacuum dessication for one week prior to analysis. Exposure to air during transfer to the instrument was minimal as evidenced by the lack of color change even in the most sensitive green rust, GR-carbonate.

For SEM imaging, samples were loaded onto carbon stubs in the glovebox and transferred into a vacuum deposition chamber for gold coating. The microscope, JEOL JSM 5600 LV, was run at 15 KeV with magnification from 5,000 to 70,000x and a working distance of 10 mm.

**Vibrational Spectroscopy**

Raman spectra were obtained using a Kaiser HoloLab Series 5000 Raman microscope with a charge coupled device (CCD) detector and motorized X-Y stage. The sample excitation was carried out with an Invictus diode laser (785 nm) with a low light power (less than 0.7 mW average power) to prevent sample degradation caused by heating and photooxidation. Raman spectra were collected through the 100X objective of an optical microscope in order to lower the signal-to-background ratio. A minimum collection time for all samples was 15 s, and 15 spectra were averaged over a Raman shift of 100-3500 cm\(^{-1}\) with no visual indication of sample oxidation. The spectral resolution was 4 cm\(^{-1}\) with a precision of 1 cm\(^{-1}\). Samples were mounted in powder form on a
platinum coated mirror and the sample stage was continuously purged with N₂ gas to prevent oxidation.

Fourier transform infrared spectra were recorded using a Nicolet Nexus 470 FTIR spectrometer with the sample ground and mounted in a KBr pellet. The background spectra (1000 scans) were carried out on a pure KBr pellet. The instrumental resolution was 4 cm⁻¹ with a mirror velocity of 0.6329 cm⁻¹/s.

**X-Ray Absorption Spectroscopy**

X-ray absorption spectra were collected on beamlines 4-1 and 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). The storage ring operates at an energy of 3.0 GeV with currents between 100 and 50 mA. A Si (220) monochromator was used to scan the incident x-ray beam through the K-edge of iron (7111 eV of metallic Fe). The beam was detuned approximately 50 percent to prevent interferences from higher-order harmonics. Internal energy calibration for each sample was accomplished using an iron foil positioned between the second and third in-line ionization chambers with the first inflection point to set to 7111 eV. Incident and transmitted intensities were measured with N₂ purged ionization chambers (I₀ and I₁); fluorescence intensity was measured using a Lytle detector 45 degrees off the sample and orthogonal to the incident beam (Lytle et al., 1984). Each sample was run for 2 to 3 scans and these repetitions were averaged together for data analysis.

XAS data analysis was performed using WinXAS 2.0. Spectra were calibrated and the background subtracted using a two-polynomial fit. Spectrum were then normalized to a unit jump height (atomic cross section) to allow comparison of spectral features on a per-atom basis (Stöhr, 1981).
In order to isolate the scattering contributions of the spectrum, a spline function was fit through the data and subtracted from the experimental curve, taking care to select a spline which followed the envelope of the decaying sine function of the spectrum. Since the amplitude of the wavevector decays with increasing energy, the $\chi(k)$ spectrum is weighted by $k^3$, which gives an approximately equal amplitude across the entire energy range (Fendorf and Sparks, 1996). The spectrum was then Fourier Transformed to produce a radial structure function (RSF) using a k-range of approximately, 3-12 Å⁻¹.

Data analysis for the XANES region was carried using Peak-Fit 4.0 (Jandel Scientific) to determine Fe²⁺ : Fe³⁺ ratios. The first derivative of the XANES spectrum was truncated to contain only the necessary region around the inflection edge. The resulting spectrum was then fit using Gaussian amplitude functions (positive and negative). Using a first derivative Savitzky-Golay method; the spectrum was smoothed (1%) with a Linear D2 baseline of 3%. Peak fitting was based on the nonlinear Marquardt-Levenberg method to adjust fitting parameters for each peak. The higher oxidation state, Fe³⁺, has a larger effective nuclear charge and thus has a slightly larger binding energy. The binding energies of Fe²⁺ and Fe³⁺ are 7122 and 7124 eV, respectively.
RESULTS AND DISCUSSION

Production of Green Rust

Eh and pH data are useful as indicators of the completion of pure green rust precipitation. In the formation of GR chloride, carbonate, and sulfate Eh and pH are inversely related (Figure 2.2). The reaction progress for GRSO₄ synthesis displays an initial pH increase by titration with NaOH to a constant of 7.0 ± 0.1. At t = 1200 s, the addition of air causes a sharp drop in pH as protons are being produced by the oxidation of the iron hydroxide species present in solution. This can be inferred from the Nernst Equation:

\[ Eh(\text{mV}) = E^0 - \frac{59}{n} \log \left( \frac{\text{Red}}{\text{Ox}} \right) + \frac{59}{m} \log \text{pH} \]  \[3\]

where \( n \) is the number of electrons and \( m \) is the number of protons exchanged in a half reaction and the activities of the reduced and oxidized species are represented by parentheses. As the activity of the oxidized species increases with addition of air, the result is an increase in Eh which corresponds to a pH decrease (Sparks, 1995). During oxidation, the pH decreased slowly and reached a pseudo-stabilized state near 6.8. To avoid oxidation products such as magnetite and lepidocrocite, the reaction was stopped before a maximum Eh was reached. Drissi et al. (1995) noted that in reactions without pH control Eh reaches a point where the tangent of the plot of Eh vs. time is zero, corresponding to an equilibrium between green rust and ferric oxyhydroxide. To avoid the ‘amorphous active FeOOH’, we stopped the oxidation before this maximum was reached. Our reactions were quenched at the point of transformation from a nonstoichiometric GR to a stoichiometric GR (Drissi et al., 1995). The sharp drop in Eh noted around 2500 s corresponds to the point at which air addition was ceased and
replaced with \( \text{N}_2 \) purging. As the last of the protons produced from the air oxidation are consumed, the pH increases and stabilizes at pH 7.1 ± 0.1. Both green rust sulfate and chloride were synthesized by this method.

Green rust carbonate synthesis was approached in a slightly different manner. As siderite is sparingly soluble, precipitation of the initial ferrous hydroxide from the corresponding ferrous salt, \( \text{FeCO}_3 \), and caustic soda is not favorable. Thus, \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \) was used as the salt since it gives rise to GR2-SO\(_4\) and would easily be distinguished from GR1 (CO\(_3\)) via XRD (Drissi et al., 1995). The pH was not controlled in this system as it is buffered by carbonate ions and did not deviate from the range of 8-9, the ideal conditions for GR1 (CO\(_3\)) precipitation. As air was introduced to the system at \( t = 1000 \) s, the pH decreased as the Eh increased (Figure 2.2b). The reaction was quenched at pH ~8 to limit the extent of oxidation (Benali et al., 2001). XRD analysis confirmed the purity of the sample; contributions from neither magnetite nor ferrihydrite were present. Benali et al. (2001) found that GR1(CO\(_3\)) rapidly (within a few hours) converted to magnetite when the oxidation product ferrihydrite was present. Also, in the presence of \( \gamma \)-FeOOH, GR is metastable with respect to magnetite just as ferrihydrite is a metastable phase to both goethite and hematite (Cornell and Schwertmann, 1996). As we did not observe this transformation, it speaks to the quality of the sample and is another positive indicator of the purity of GR1 (CO\(_3\)).

**Crystallographic Evaluation**

X-ray diffraction spectra were collected for each of the three green rusts synthesized as well as for their oxidation products. The most distinguishing peak for the green rusts is found at high d-spacing values (Figure 2.3). GR2-SO\(_4\) is characterized by a
d-spacing at 11 Å while GR1-CO$_3$ and GR1-Cl have a smaller d-spacing at 7.9 Å. This difference in d-spacing is a result of the structural variation between GR1 and GR2 type compounds. GR1-Cl and -CO$_3$ incorporate a planar anion into the interlayer while GR2-SO$_4$ has a tetrahedral anion interlayer component. Various stacking sequences arise from these differences. GR2 is characterized by interlayers composed of two consecutive planes of anions and water molecules whereas GR1 have interlayers made of a single plane (Figure 2.4). GR1 has a stacking sequence of the nature $AcBiBaCjCbAkA...$ where $A-C$ designate OH$^-$ planes, $a-c$ metal cation layer and $i-k$ intercalated layers. GR2 compounds follow the original hexagonal stacking of $AcBiija...$ Thus, the distance between hydroxide sheets is larger in GR2 (11 Å) than in GR1 (7.5 Å) (Refait et al., 2000). GRSO$_4$ belongs to the hexagonal system while GRCl and CO$_3$ are part of the rhombohedral system (hexagonal R type). For GR1, the positions of intercalated anions depend on the species (Génin et al., 2001), whereas the positions are all the same for the known GR2s (sulfate and selenate) (Vins et al., 1987). Observed interplanar distances ($d_{hkl}$) and relative intensities ($I/I_1$) are given in Table 2.1. These data are in good agreement with values previously published (Drissi et al., 1995; Génin et al., 2001; Refait et al., 2000; Vins et al., 1987). No other compounds were detected in these diffractograms.

There are significant differences in the diffraction patterns of GR1 and GR2, making this a useful means of differentiation between structural classes. Also, within the same structural classification, GR1, distinction can be made between incorporated interlayer anions. GRCl is more crystalline and exhibits a diffraction doublet with a d-spacing $\approx$ 3.99 Å. This increased crystallinity should make this compound more resistant
to destruction. Upon exposure to air, each green rust exhibits a unique oxidation product (Figure 2.5). GRCO₃ appears to convert to magnetite while GRSO₄ to goethite. The end product of GRCl is more difficult to distinguish and appears to still have slight structural contributions from the original green rust d-spacings of 7.7 Å and 5.4 Å. The oxidation product is composed of a mixture of goethite and lepidocrocite.

The speed at which oxidation takes place impacts the end member. Schwertmann and Fechter (1994), along with others (Solcova et al., 1981), observed that slow oxidation leads to complete dehydration and partial oxidation of green rust to magnetite, whereas fast oxidation of green rust leads to lepidocrocite – a partially hydrated but fully oxidized species. Another important factor which determines the oxidation product is the ratio, R, of [Fe²⁺]/[OH⁻]. Olowe and Genin (1991) studied this factor in depth for GR2-SO₄ and discovered that at low R-values, 0.33, α-FeOOH (goethite) was the end product with an intermediate of amorphous active α-FeOOH. R = 0.5 corresponds to an end product of magnetite while goethite, lepidocrocite and a mixture of the two are observed at R = 0.57, 0.58 and 0.625, respectively. Drissi et al. (1995) report GR1-CO₃ oxidizing to α-FeOOH while GR1-Cl and GR2-SO₄ transform to γ-FeOOH, lepidocrocite, for reactions in which [Fe²⁺]/[OH⁻] = 0.6, corresponding to the stoichiometric conditions of formation of GR1-CO₃. At lower concentrations, goethite formation was accompanied by the appearance of magnetite.

With information from these previous studies, we can infer that the oxidation product observed for GRCO₃ is the result of slow oxidation with a high ratio of [Fe²⁺]/[OH⁻]. The transformation of GRSO₄ to goethite indicates more rapid oxidation with a similar Fe²⁺ to OH⁻ ratio. The fact that GRCl retains some contributions from its
original structure is explained by its crystallinity, and its end products suggest a very rapid oxidation in which some waters of hydration are retained.

We observed that variation in oxidation pathways results in different oxidation products. Upon freeze-drying samples with air, GRCl was converted to lepidocrocite and GRSO₄ to ferrihydrite (Figure 2.6). The end product of GRCO₃ is difficult to distinguish with XRD due to its amorphous nature; however, Raman spectra confirm that it is hematite. The oxidized samples all seem to retain structure from the original green rust – GRCl and GRCO₃ each display a peak at a d-spacing of ~7.5 nm and GRSO₄ at 11 nm. It should be noted that these oxidation products were obtained under specific conditions and oxidation by atmospheric levels of O₂ was rapid.

**Vibrational Characterization of Green Rust**

The synthetic GRs were also identified using Raman spectroscopy. The spectra, shown in Figure 2.7, have peaks at 510 and 433 cm⁻¹ correspond to Fe³⁺-OH stretching and Fe²⁺-OH stretching respectively. These data agree with literature values (Trolard et al., 1997). Theoretically, the energy shifts observed in a Raman spectra should be identical to the energies of its infrared absorption bands, provided that the vibrational modes involved are active toward both IR and Raman scattering. Visual comparison of the Raman spectra (Figure 2.7) and the IR spectra (Figure 2.8) confirm that this is not the case. This is reasonable considering the mechanistic differences between the two methods. Though they are dependent on the same vibrational modes, IR absorption requires that a vibrational mode of the molecule have a change in dipole moment or charge distribution associated with it. Only then can radiation of the same frequency interact with the molecule and promote it to an excited vibrational state. Raman
scattering involves a momentary distortion of the electrons distributed around a bond in a molecule (i.e. change in polarization), followed by reemission of the radiation as the bond returns to its normal state.

Each of the GRs show very weak IR peaks near the same wavelengths as the Fe(II)- and Fe(III)- OH Raman bands (433 and 510 cm\(^{-1}\)). This indicates that GR compounds have a predominantly symmetric Fe-OH stretch that is polarizable. As the bonds lengthen they are easier to distort and are thus Raman active. Since the same peaks are nearly indistinguishable in the IR spectra, we can conclude that the symmetry of the stretch allows for no change in the dipole moment creating an IR inactive mode. A small deviation from perfect symmetrical stretching would yield the small bands noted in the IR. In contrast, the asymmetric Fe-O stretches (650-690 and 790-840 cm\(^{-1}\)) are strong in the IR spectra. This can be explained by the fact that asymmetric stretching would yield a greater dipole moment and allow for an IR active mode whereas the increased polarizability associated with the stretching of one bond would be cancelled out by the decrease associated with shortening of another bond, negating the effect and yielding a Raman inactive mode. The fact that the other IR peaks are not observed in the Raman spectra indicates that those modes are all Raman inactive and not polarizable. Within the IR spectra, each GR exhibits different spectral characteristics indicating structural differences. Carbonate and sulfate peaks were observed in the corresponding spectra. Chloride was not seen, as it exists as a free anion not an oxoanion. The sulfate band split indicates that the T\(_d\) symmetry of SO\(_4\) is disturbed, suggesting that one of the oxygen atoms is bonded differently than the others. This is not observed with CO\(_3\) until it is oxidized, indicating that a change is associated in the sharing of oxygens as a conversion
to hematite ensues. The majority of the rest of the IR bands are a result of different OH stretching and bending modes corresponding to the hydroxide sheets associated with the GR structure.

**Morphological Characteristics**

Scanning electron microscopy images were taken to explore morphology of the GR crystals. Individual crystals were found to be randomly oriented as hexagonal platelets. Within each sieved sample, we observed at least two different crystal sizes that imply two crystal growth stages: one with a length of approximately 1 µm (between 0.5 and 2 µm) per side, and the other being much smaller with a length of approximately 0.2 µm (Figures 2.9 – 2.11). The larger crystals were likely formed via slow oxidation as the pH was raised in the reaction vessel before the addition of air. The small amount of ferric iron present allowed for nucleation and slow growth. On the other hand, the smaller crystals formed rapidly as oxygen was added and ferrous iron was oxidized. While the carbonate system appears amorphous upon inspection of XRD data, SEM images reveals a very small, <0.25 µm, hexagonal edge length (Figure 2.11). It is possible that oxidation occurred during sample transfer resulting in magnetite formation, but data from the kinetics experiment suggest that this was not the case, nor was magnetite observed in the XRD pattern of GR1-CO³.

BET analysis of the vacuum desiccated green rusts reveals an order in surface area of SO⁴ (3.6 m²/g) < Cl (19.0 m²/g) < CO³ (30.1 m²/g) (Figure 2.12). As GRSO⁴ displays very large crystals, its smaller surface area fits accordingly. The more amorphous nature of GRCO³, and its less ordered crystal habit, also agree with the larger
surface area observed. A larger surface area would indicate more reactive sites on the surface of the mineral.

X-ray absorption spectra of were collected and indicate differences in the density of the nearest neighbors to iron atoms within each green rust. However, the similarity in bond distances for the first and second shell of each green rust suggests that these nearest neighbors are not the associated anions. Instead, they are more than likely O and Fe atoms in the octahedral sheets.

Analysis of the XANES region of the spectra reveals the ratio of ferrous to ferric iron. The results (Figure 2.13) agree with proposed formulae indicating a \( \text{Fe}^{2+} : \text{Fe}^{3+} \) ratio of 2:1 for GRSO\(_4\) and GRCO\(_3\), and 3:1 for GRCl. This should result in an increased reactivity of GRCl as it has an increase in ferrous iron and is able to donate electrons more readily.
CONCLUSIONS

The formation of Fe(II)Fe(III) hydroxy-green rusts from ferrous sulfate, chloride and carbonate solutions was studied at ambient temperature with pH and oxygen flow controlled. The purified products of these reactions were characterized using vibrational spectroscopy, XRD, SEM, BET, and XAS analyses. XRD proved a useful means of identification even between GR1s. Each of the green rusts has a different vibrational spectra corresponding to the variation in interlayer anion as well as structural differences resulting from Fe$^{ll}$/Fe$^{III}$. Green rusts sulfate and carbonate have a Fe$^{ll}$/Fe$^{III}$ ratio of 2:1 while GRCI has three times as much ferrous iron than ferric. Surface areas of green rust sulfate, chloride and carbonate are 3.6, 19.0, and 30.1 m$^2$/g respectively. In addition, SEM images indicate a dual-phase formation process – the first being slow nucleation and the second a rapid precipitation. Green rust sulfate has the largest crystal size and most well defined crystal morphology, while green rust chloride has the most crystalline structure. GRCO$_3$, the most amorphous, shows a lesser tendency to form a well-defined hexagonal structure.

The chemical, structural, and morphological characteristics defined in this research are the basis for understanding reactions involving green rusts. The variations noted here will be of importance in the reactivity of these species in natural settings and will define their affinity towards environmental toxins. The potential reactivity towards polyvalent metal contaminants may be defined by the ability of those ions to access interlayer anions, requiring similarities in charge and size for exchange. Since GR occurrence is often associated with microbial activity as the end product of dissimilatory reduction of HFO, within the same microenvironment, iron-oxidizing bacteria may
potentially be able to utilize green rust as an electron donor thereby reoxidizing the substrate and creating an iron cycle. Understanding the chemical structure within these compounds will aid in the examination of mechanisms by which microbes can access the available iron.
REFERENCES


Table 2.1. X-ray diffraction parameters for synthetic green rusts. Values in bold indicate strongest diffraction peak. The interplanar spacings (d) and their relative Miller indices are given

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Figure 2.1. Experimental apparatus for green rust synthesis including titrator, sampling ports, gas inlets and Eh/pH probes.
Figure 2.2. Reaction progress (time) as defined by Eh and pH for (a) GRCl, (b) CO$_3$ and (c) SO$_4$. GRCl and GRSO$_4$ display sharp drops in pH upon addition of air while that of GRCO$_3$ is more gradual due to the synthesis method. Subsequent pH increase indicates cessation of green rust formation and onset of N$_2$ purge.
Figure 2.3. X-ray diffraction pattern of reduced synthetic green rusts. GR2-SO₄ exhibits a distinctive peak at 11 Å due to its increased d-spacing, a result of a tetrahedral interlayer anion.
Figure 2.4. Crystal stacking of GR1-Cl, GR1-CO$_3$, and GR2-SO$_4$. A, B, and C represent hydroxide layers, while a, b, and c are Fe and i, j, and k represent interlayer anions and water.
Figure 2.5. X-ray diffraction patterns of reduced and air-oxidized products of (a) GRCl, (b) GRCO₃, and (c) GRSO₄.
Figure 2.6. X-ray diffractograms of reduced and freeze-drying oxidation products of (a) GRCl, (b) GRCO\textsubscript{3} and (c) GRSO\textsubscript{4}.
Figure 2.7. Raman spectra of synthesized GRSO₄, GRCl, and GRCO₃. The Raman bands at 510 and 433 cm⁻¹ correspond to Fe³⁺-OH stretching and Fe²⁺-OH stretching, respectively.
Figure 2.8. Infrared spectra of synthesized GR1-Cl, GR1-CO$_3$, and GR2-SO$_4$. Carbonate and sulfate peaks are observed in the corresponding spectra. The majority of IR bands are a result of different OH stretching and bending modes corresponding to the hydroxide sheets within the GR structure.
Figure 2.9. SEM images of hexagonal GRSO₄ platelets. In (b), an expanded region of the highlighted area in image (a) is depicted. The two different crystal sizes indicate different precipitation rates.
Figure 2.10. SEM images of well-defined hexagonal GRCl platelets. An expanded region of highlighted region in image (a) is illustrated in (b).
Figure 2.11. SEM images of amorphous hexagonal GRCO₃ platelets; the expanded view shown in (b) displays the smaller crystal size implying faster precipitation.
Figure 2.12. BET Isotherms for synthesized GRC1 (a), GRCO$_3$ (b), and GRSO$_4$ (c). The order of increasing surface area is GRSO$_4$ < GRC1 < GRCO$_3$. 
Figure 2.13. Fe X-ray absorption near edge spectra and resulting spectral deconvolution of synthesized GRCl (a), GRCO₃ (b), and GRSO₄ (c). Ferrous iron has a binding energy of ~7124 eV and that of ferric iron is ~7122 eV.
CHAPTER 3.

CHROMATE REDUCTION BY GREEN RUST
INTRODUCTION

As chromium is widely used in industrial applications, it is often introduced into the environment at high levels. In addition, the presence of chromium in ultramafic rocks contributes to its abundance in nature. In the environment, chromium – a redox active element - exists as Cr(III) or Cr(VI). The release of Cr(VI) from reserves and landfills to surface and subsurface waters is of concern as Cr(VI) is a known toxin, mutagen, teratogen, and carcinogen. The favorable environmental fate of this toxin is reduction of the polyvalent metal to a more manageable form, Cr(III).

Chromium(VI) species are anionic (HCrO$_4^-$ and CrO$_4^{2-}$) and mobile in most neutral to alkaline systems. In acidic conditions, Cr(VI) has the potential to sorb to positively charged sites of iron oxides (Bartlett and James, 1988). Reduction of Cr(VI) species to sparingly soluble Cr(III) hydroxide solids readily occurs by reaction with aqueous ferrous iron (Fendorf and Li, 1996; Pettine et al., 1998; Sedlak and Chan, 1997), H$_2$S (Patterson et al., 1997), and organics (Ishibashi et al., 1990; Llovera et al., 1993). In addition, Fe(II) solids contribute to Cr(III) precipitation (Charlet and Manceau, 1992; Dzombak and Morel, 1990). At dilute concentrations, Cr(III) is essential in human glucidic metabolism and, in general, chromium(III) is less toxic than chromium(VI). Reduction of Cr(VI) by Fe(II) has been observed in natural soil systems such as wetlands (Masscheleyn et al., 1992) and suboxic aquifers (Anderson et al., 1994) and in permeable reactive barriers (Powell et al., 1995; Pratt et al., 1997).
Chromate Reduction by Ferrous Iron

In anaerobic systems, Fe(II) often dominates the reduction of Cr(VI) (Fendorf et al., 2000) and in acidic soils Fe(II) may be just as effective a reducer as organic matter (Eary and Rai, 1991). Even under well-aerated conditions, oxidation of aqueous Fe(II) by Cr(VI) occurs (Eary and Rai, 1989). In addition, Fe(II) reduction of chromate is much faster than biological pathways in anoxic conditions and, when biological activity is limited, aerobic reduction of Cr(VI) by ferrous iron detoxifies and immobilizes chromium (Fendorf et al., 2000). Thus, in both reducing conditions and as iron minerals undergo dissolution via atmospheric oxidation, Fe(II) present in solution and as solids plays an important role in Cr(VI) reduction. The rate of Cr(VI) reduction by ferrous iron in solution has been established with rates of reduction described by:

\[-d[Cr(VI)] / dt = k[Cr(VI)][Fe(II)]\]  \[3.1a\]

where \(k (M^{-1} \text{ min}^{-1})\) is defined as

\[\log k = 6.74 - 1.01 \text{ pH} + 188.5/T\]  \[3.1b\]

for the pH range 1.5-4.5 and

\[\log k = 11.93 + 0.95 \text{ pH} - 4260.1/T - 1.06 \text{ I}^{0.5}\]  \[3.1c\]

for pH 5 to 8.7 from 5 to 40 °C and ionic strength 0.01 to 2 M (Pettine et al., 1998).

Based on these expressions, it was suggested that Cr(VI) reduction is rapid – on a timescale of minutes to months in ferrous rich sediments, soils and waters (Sedlak and Chan, 1997).

Chromate reduction is also possible when aqueous Cr(VI) sorbs on Fe(III) solids such as maghemite (γ-Fe(III)₂O₃), hematite (α-Fe(III)₂O₃), goethite (α-Fe(III)OOH), or hydrous ferrous oxides (Fe(OH)₃·nH₂O) provided surface-bound Fe(II) is present.
The half cell potential range for solid state oxidation \([\text{Fe(II)}] \rightarrow [\text{Fe(III)}]\) is \(-0.34\) to \(-0.65\) V, making structural Fe(II) a stronger reducing agent than aqueous \(\text{Fe}^{2+}\) (-0.77 V) (White and Peterson, 1996). Magnetite \(\text{Fe(II)Fe(III)}_2\text{O}_4\), a mixed valence iron oxide, has been studied for its capacity to reduce Cr(VI) to Cr(III) in both laboratory and field environments (Peterson et al., 1996). Reduction rates for aqueous Cr(VI) reduction by magnetite are linear with time and have a rate constant of \(1.37 \times 10^{-10}\) mol m\(^{-2}\) s\(^{-1}\) at neutral pH (White and Peterson, 1996). Magnetite surfaces are passivated by reaction with aqueous Cr(VI) at circumneutral pH, limiting the ability of magnetite to act as an electron donor for reduction reactions (Peterson et al, 1997).

**Chromate Reduction Mechanisms**

When discussing solid-state ferrous iron oxidation by chromate, there are three potential reaction mechanisms. Cr(VI) reduction can occur by direct electron transfer with structural Fe(II) (White and Peterson, 1996).

\[
9[\text{Fe}^{2+}]_{\text{oxide}} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 6[\text{Fe}^{3+}]_{\text{oxide}} + 3\text{Fe}^{2+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad [3.2]
\]

\[
E = E_{\text{oxide}} + 0.98\ V
\]

Additional chromate can be subsequently, homogeneously reduced in solution by Fe(II) released during the heterogeneous reaction described above.

\[
3\text{Fe}^{2+} + \frac{1}{2} \text{Cr}_2\text{O}_7^{2-} + 7\text{H}^+ \rightarrow 3\text{Fe}^{3+} + \text{Cr}^{3+} + 7/2\ \text{H}_2\text{O} \quad E = 0.423\ V \quad [3.3]
\]

Finally chromate can be reduced by Fe(II) produced independently during dissolution of the ferrous oxide by \(\text{H}^+\) or \(\text{O}_2\). Eary and Ray (1989) proposed that Cr(VI) reduction, in the presence of hematite and biotite, occurs exclusively by homogeneous Fe(II) oxidation in solution. However, White et. al. (1996) suggest Cr(VI) behavior in relation to reaction
with solid Fe(II) is best described by concurrent heterogeneous reaction and homogeneous oxidation of the released Fe(II).

\[ 3[Fe^{2+}]_{\text{oxide}} + \frac{1}{2} \text{Cr}_2\text{O}_7^{2-} + 7\text{H}^+ \rightarrow 2[Fe^{3+}]_{\text{oxide}} + \text{Fe}^{3+} + \text{Cr}^{3+} + \frac{7}{2} \text{H}_2\text{O} \]  

[3.4]

**Green Rust Reactivity**

As ferrous-iron rich solutions and solids are effective reductants of chromate in natural systems, the recent discovery of a green rust mineral in reduced soils offers a new immobilization pathway for chromate. Green rusts, mixed valence iron oxides, have the potential to reduce many environmental contaminants, as they are highly reactive species. Predictions based upon thermodynamics reveal GR to be the most effective of the iron oxides in chromate reduction (Table 3.2). These compounds exist as intermediates in the formation and reduction of ferric iron oxides such as goethite, lepidocrocite and magnetite. In addition, green rusts are the product of microbial degradation by dissimilatory iron reducing bacteria. Due to their highly reactive surfaces, sensitivity to oxidation, and the resulting potential to reduce polyvalent elements / contaminants, GRs hold significance in controlling the fate of toxins and in the field of natural attenuation or remediation techniques.

The ability of green rusts as reductants of environmentally relevant toxins has been examined in the context of some common redox active elements. The contaminants approached thus far for GRSO₄ are nitrate (Hansen and Koch, 1998; Hansen et al., 1996), nitrite (Hansen et al., 1994), selenate (Myneni et al., 1997), arsenate (Randall et al., 1999), halogenated methanes (Erbs et al., 1999) and chromate (Loyaux-Lawniczak et al., 2000; Loyaux-Lawniczak et al., 1999). Chloride green rust has been studied with respect to nitrate (Hansen et al., 2000), nitrite (Hansen et al., 2000), and chromate (Loyaux-
Lawniczak et al., 2000). The least stable form of green rust, GR1(CO₃), has minimal representation in the literature, with only reactions involving nitrate (Hansen and Koch, 1999) and chromate (Williams and Scherer, 2001). Within this body of literature, little work focuses on reaction kinetics. The few reaction rates that have been reported reveal pseudo first-order kinetics with respect to contaminant concentration. In addition, researchers have also seen an increase in reduction rate using GRCl instead of GRSO₄, and an increase in reduction rate when the contaminant is introduced before green rust precipitates as opposed to addition after nucleation.

**Nitrate / Nitrite**

As nitrate reduction by green rust has been studied in the greatest depth, it gives a model by which to base further work with regards to reduction rates and mechanisms. Nitrate, a widely known agricultural pollutant, is often retarded from leaching from soils and sediments under anoxic conditions by denitrification to N₂/NO/ N₂O or reduction to ammonium. Though reduction is most often the result of microbial mediated reactions, GR2-SO₄ and GR1-Cl are also able to induce reductions. Nitrate (NO₃⁻) is stoichiometrically reduced to ammonium (NH₄⁺) by GRSO₄ with the production of magnetite (Fe₃O₄) (Hansen et al., 1996). The reaction is first-order with respect to ferrous iron and nitrate concentrations.

\[
\frac{d[\text{NH}_4^+]}{dt} = k \ [\text{Fe(II)}]_{\text{GR}} \ [\text{NO}_3^-]
\]

where \( k = 4.93 \times 10^{-5} \pm 0.39 \times 10^{-5} \ \text{L mol}^{-1} \ \text{s}^{-1} \)

This rate may be similar or higher than microbial rates of reduction and may be an important abiotic pathway in sediments poor in organic carbon and oxygen and rich in sulfate and carbonate.
Hansen et al. (2001) also show the reduction of nitrate to ammonium via GRCl is governed by first-order kinetics. In contrast with the sulfate system, no dependence with respect to nitrate was observed:

\[
d[NH_4^+] / dt = k [Fe(II)]_{GR} \text{ where } k = 2.0 \pm 0.5 \times 10^{-5} \text{ s}^{-1}
\]  

[3.6]

Note the Fe\(^{2+}\):Fe\(^{3+}\) ratio (3:1) of the GRCl compound can be retained while Cl is exchanged with SO\(_4\) but that the reduction rate decreases six-fold. The more common Fe\(^{2+}\):Fe\(^{3+}\) ratio of 2:1 for GRSO\(_4\) reduces nitrate five times slower than does the 3:1 GRSO\(_4\) form and 30 times slower than GRCl. The high rate of nitrate reduction by GRCl is attributed to the greater ability of chloride than sulfate to exchange with nitrate and the increased amount of ferrous iron in the octahedral layer. The increase in reduction rates at higher Fe\(^{2+}\):Fe\(^{3+}\) ratios is a result of the increase in the reduction capacity.

GRSO\(_4\) is also able to reduce nitrite and results in the formation of goethite and ammonium (Hansen et al., 1994). Estimates of the solubility product and free energy of formation for GRSO\(_4\) are 124.6 ± 0.7 and –4380 ± 4 kJ/mol, respectively. For the reaction of nitrite with GRSO\(_4\):

\[
4.5H_2O + SO_4^{2-}(aq) + 6Fe^{2+}(aq) + NO_2^-(aq) + 9OH^-(aq) \rightleftharpoons \ [Fe^{II}_{4}Fe^{III}_{2}(OH)_{12}][SO_4 \cdot 3H_2O](s) + 0.5N_2O(g)
\]  

[3.7a]

OR:

\[
[Fe^{II}_{4}Fe^{III}_{2}(OH)_{12}][SO_4 \cdot 3H_2O](s) + 2NO_2^-(aq) \rightleftharpoons \ 6\alpha-FeOOH(s) + N_2O(g) + SO_4^{2-}(aq) + 6H_2O
\]  

[3.7b]

Depending on the nitrogen concentration and supply of oxygen, N\(_2\O(g)\) could be further reduced to N\(_2\) (g). The \(\Delta G^0(rxn)\) varies between –590 ± 4 kJ/mol and –527 ± 8 kJ/mol depending on whether the reaction occurs during or after the precipitation of GR. Thus,
if green rust is present, these reactions are thermodynamically favorable in naturally occurring conditions. In addition, the reduction of nitrite to N₂ or NH₄⁺ by GRSO₄ are also thermodynamically feasible.

**Selenium and Halogenated Methane**

Organic acids and microbes often control selenium reduction; however, recent studies suggest that green rust may also play a significant role in this process. GR2-SO₄²⁻ can react in the following manner, forming magnetite as the end product, provided that Fe(III) is present and pH > 4 (Myneni et al., 1997).

\[
\begin{align*}
\text{HSeO}_4^- + 4\text{Fe}^{II}_4\text{Fe}^{III}_2(\text{OH})_{12} \text{SO}_4 \cdot 3\text{H}_2\text{O} & \Leftrightarrow & \text{HSe}^- + 8\text{Fe}_3\text{O}_4 + 4\text{SO}_4^{2-} + 8\text{H}^+ + 32 \text{H}_2\text{O} \\
\end{align*}
\]

This reaction is first-order with respect to selenium concentration having rate constants between 2.08 x 10⁻⁴ s⁻¹ and 4.67 x 10⁻⁶ s⁻¹ (average \(k = 3.19 \pm 1.16 \times 10^{-6} \text{ s}^{-1}\)). Interaction of Se(VI) during GR precipitation increased the kinetics of reduction, yielding average rate constant of 3.64 ± 0.0175 x 10⁻⁴ s⁻¹. However, at low pH, when Fe(II) is present in the form of Fe(H₂O)₆²⁺, Se(VI) is not reduced nor does it complex with iron. Se(VI) may be incorporated in the inner-layers of green rust and then reduced to Se(0), promoting surface Se clusters to form as the green rust is oxidized (Myneni et al., 1997). In contrast, Refait et al. (2000) propose incorporation without conversion to Se(0) as a removal mechanism from solution.

Hypotheses have been made regarding the ability of GRs to reduce organic contaminants as well. Carbon tetrachloride (CCl₄) readily reduces to CHCl₃ and C₂Cl₆ upon exposure to GRSO₄ (Erbs et al., 1999). Again, pseudo first-order kinetics govern this reduction.
\[
\frac{d[Cl^-]}{dt} = -\frac{d[CCl_4]}{dt} = r \cdot k_{obs}[Fe(II)]_{GR} \tag{3.9}
\]

where \(k_{obs}\) is \(0.47 \times 10^{-5} \text{ s}^{-1}\) to \(2.18 \times 10^{-5} \text{ s}^{-1}\)

The rates of reduction are similar to those of nitrate reduction by GRSO_4. It is proposed that nonpolar CCl_4 does not have access to the polar interlayer of GR. As noted previously for inorganic contaminants, reduction of chlorinated aliphatics is often biotically mediated (DiStefano et al., 1991; Semprini et al., 1992); however, GRs may be important in environments where microbial activity is limited such as nonacid and ferrous iron-rich subsoils.

**Arsenic**

Owing to the reactivity of green rust, Randal et al. (1999) explored the reduction of As(V) by GRSO_4. Reduction of As(V) to As(III) is undesirable as the latter species is the more soluble and toxic. Upon reacting with GRSO_4 for 24 h, arsenate remains strongly adsorbed as inner-sphere surface complexes with no reduction observed, forming edge- and double-corner sharing complexes. The same results were obtained whether As(V) was added prior to or after green rust nucleation; it was neither incorporated into the GR structure nor exchanged for SO_4 in the interlayer region. Also, upon oxidation of GRSO_4 to lepidocrocite, arsenate remains preferentially sorbed to GR as a bidentate corner-sharing.

**Cr(VI) Reduction via Green Rusts**

Little work has been carried out to examine reaction kinetics of chromate reduction by green rust. Williams and Scherer (2001) published data proposing a pseudo first-order reaction of chromate by GRCO_3, with rate coefficients \((k_{obs})\) ranging from
1.2 \times 10^{-3} \text{ to } 11.2 \times 10^{-3} \text{ s}^{-1}. \text{ At low Cr(VI) concentrations, first-order rates with respect to Cr(VI) concentration were observed. Whereas, at higher concentrations, rates approach a constant value, theoretically due to the consumption of available Fe(II), were observed.}

Loyaux et al. (1999) provide one of the first reports describing chromate reduction by GRSO₄ giving some mechanistic insight into the reaction. GRSO₄ oxidized to amorphous, Cr-substituted 2-line ferrihydrite, and a fraction of the available solution chromate ions were substituted for SO₄^{2-} in the GR interlayer prior to reduction. This would lead to the removal of SO₄^{2-} from the crystal structure, the destruction of the original stacking sequence of GR, and the presence of Cr(III) in the oxidation product. A later study by the same group (Loyaux-Lawniczak et al., 2000) suggests that the oxidation product is the same for both GRSO₄ and GRCl, thereby implying that the nature of the initial GR has no influence on the product. The proposed mechanism, removal of SO₄^{2-}, insertion of Cr(III), and rearrangement of the iron hydroxide sheets would lead to a disordered form of Fe(III) oxyhydroxide.

\[
15\text{Fe}^{II}_4\text{Fe}^{III}_2(\text{OH})_{12}\text{SO}_4 + 20\text{CrO}_4^{2-} \rightarrow 22\text{Fe}^{45/11}\text{Cr}^{10/11}\text{HO}_8 + 15\text{SO}_4^{2-} + 10\text{OH}^- + 74\text{H}_2\text{O} \tag{3.10a}
\]

for a Fe(II)/Cr(VI) ratio of 3 and

\[
30\text{Fe}^{II}_4\text{Fe}^{III}_2(\text{OH})_{12}\text{SO}_4 + 20\text{CrO}_4^{2-} \rightarrow 22\text{Fe}^{45/11}\text{Cr}^{10/11}\text{HO}_8 + 15\text{SO}_4^{2-} + 10\text{OH}^- + 74\text{H}_2\text{O} + 15\text{Fe}^{II}_4\text{Fe}^{III}_2(\text{OH})_{12}\text{SO}_4 \tag{3.10b}
\]

when Fe(II) / Cr(VI) = 6.

A constant Fe / Cr ratio of 9/2 was reported for the oxidation product independent of the initial Fe(II) / Cr(VI) ratio (Loyaux-Lawniczak et al., 2000).
Research Objective

Ferrous iron bearing minerals are of importance in the reduction of chromate. While the environmental relevance of green rusts and chromate is evident and the thermodynamic favorability of their redox exchange has been shown, their interactions have not been resolved. No study has compared the three main anionic types of green rust and their reactivity in relation to any specific environmental contaminant. In doing so we may glean the importance of each in environmental settings and determine whether there are significant differences in reaction mechanisms within the same mineral class. The objectives of this study were to evaluate the reduction of Cr(VI) by green rust sulfate, chloride and carbonate in order to determine the rates of reduction and the significance of chemical and structural differences with the iron oxides. Using data collected during solid phase analysis of green rusts previously synthesized, as well as solid and solution phase information collected during and following the reduction reactions, details of the chromate reduction mechanism were examined.
MATERIALS AND METHODS

Batch Reduction

In order to determine the rate law governing the reduction of chromium (VI) by each anionic class of green rust, a set of kinetics experiments were conducted. The dried GR samples were sieved through an ASTM standard No. 60 mesh, 250 µm pore-size (0.0098 in) sieve to ensure uniform particle size and surface area. Each reaction was carried out in a 250 mL glass beaker in an N₂–purged glovebox and all were magnetically stirred. Rather than titrating the solution to maintain pH, a buffer was added to each system; MOPS buffer was used to maintain pH 7 and minimize adverse interactions with the Cr(VI) chromophore. Each reaction was performed in duplicate. Keeping initial Cr(VI) concentrations constant and varying the green rust concentration, the solid phase green rust was suspended in a 100 mL volume of 5 mM MOPS. Chromate (as K₂CrO₄) was then introduced to the green rust suspension at a solution concentration of 192 µM. Samples were then taken at various time points during the reaction sequence.

Solution Phase Analysis

Both filtered and unfiltered samples were analyzed colorimetrically by the 1,5-diphenyl carbazide method (Bartlett and James, 1979) with a 5 mM MOPS matrix using a Shimadzu 1601 UV-Visible Spectrophotometer at 540 nm. Total Cr in solution was measured using a Thermo Jarrell Ash IRIS inductively coupled plasma (ICP) spectrometer.
**Solid Phase Analysis**

The filtered products of the synthesis procedures were analyzed using X-ray diffraction (XRD), micro-Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and X-ray absorption spectroscopy (XAS).

X-ray diffractograms were recorded from 5-65 degrees 2θ using Cu Kα₁ radiation (λ = 1.54056 nm). A Rigaku Geiger-flex Powder Defractrometer with generator energy of 35 KeV and a power of 15 mA was employed. Samples were prepared in the glovebox by admixing with glycerol to form a paste which was smeared onto the sample slide (Hansen and Poulsen, 1999); the glycerol paste was used to limit oxidation during XRD analysis. The glycerol displays itself as a ‘hump’ in the spectra between 15 and 25 degrees 2θ.

Surface area was determined using a 5-point BET analysis on a Coulter SA 3100. Samples were dried in the glovebox by vacuum dessication for one week prior to analysis. Exposure to air during transfer to the instrument was minimal as evidenced by the lack of color change even in the most sensitive green rust sample, GR-CO₃. The surface area of green rust phases varies widely. Green rust carbonate has the highest surface area (30.095 m²/g); chloride and sulfate forms follow with surface areas of 18.990 and 3.581 m²/g, respectively.

Raman spectra were obtained using a Kaiser HoloLab Series 5000 Raman microscope with a charge coupled device (CCD) detector and motorized X-Y stage. The sample excitation was carried out with an Invictus diode laser (785 nm) with a low light power (less than 0.7 mW average power) to prevent sample degradation caused by
heating and photooxidation. Raman spectra were collected through the 100X objective of an optical microscope in order to lower the signal-to-background ratio. A minimum collection time for all samples was 15 s, and 15 spectra were averaged over a Raman shift of 100-3500 cm\(^{-1}\) with no visual indication of sample oxidation. The spectral resolution was 4 cm\(^{-1}\) with a precision of 1 cm\(^{-1}\). Samples were mounted in powder form on a platinum coated mirror and the sample stage was continuously purged with N\(_2\) gas to prevent oxidation.

Fourier transform infrared spectra were recorded using a Nicolet Nexus 470 FTIR spectrometer with the sample ground and mounted in a KBr pellet. The background spectra (1000 scans) were carried out on a pure KBr pellet. The instrumental resolution was 4 cm\(^{-1}\) with a mirror velocity of 0.6329 cm\(^{-1}\)/s.

For SEM imaging, samples were loaded onto carbon stubs in the glovebox and transferred into a vacuum deposition chamber for gold coating. The microscope, JEOL JSM 5600 LV, was run at 15 KeV with magnification from 5,000 to 70,000x and a working distance of 10 mm.

X-ray absorption spectra were collected on beamlines 4-1 and 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). The storage ring operates at an energy of 3.0 GeV with currents between 100 and 50 mA. A Si (220) monochromator was used to scan the incident x-ray beam through the K-edge of iron (7111 eV for metallic iron). The beam was detuned approximately 50 percent to prevent interferences from higher-order harmonics. Internal energy calibration for each sample was accomplished using an iron foil positioned between the second and third in-line ionization chambers with the first inflection point to set to 7111 eV. Incident and transmitted intensities were measured.
with N₂ purged ionization chambers (I₀ and I₁); fluorescence intensity was measured using a Lytle detector (Lytle et al., 1984) 45 degrees off the sample and orthogonal to the incident beam. Each sample was run for 2 to 3 scans and these repetitions were averaged together for data analysis.

XAS data analysis was performed using WinXAS 2.0. Spectra were calibrated and the background subtracted using a two-polynomial fit. Spectrum were then normalized to a unit jump height (atomic cross-section) to allow comparison of spectral features on a per-atom basis (Stöhr, 1981).

In order to isolate the scattering contributions of the spectrum, a spline function was fit through the data and subtracted from the experimental curve, taking care to select a spline which followed the envelope of the decaying sine function of the spectrum. Since the amplitude of the wavevector decays with increasing energy, the χ(k) spectrum is weighted by k³, which gives an approximately equal amplitude across the entire energy range (Fendorf and Sparks, 1996). The spectrum was then Fourier transformed to produce a radial structure function (RSF) using a k-range of approximately 3-12 Å⁻¹.

Data analysis for the XANES region was carried using Peak-Fit 4.0 (Jandel Scientific) to determine Fe²⁺: Fe³⁺ ratios. The first derivative of the XANES spectrum was truncated to contain only the necessary region around the inflection edge. The resulting spectrum was then fit using Gaussian amplitude functions (positive and negative). Using a first derivative Savitzky-Golay method, the spectrum was smoothed (1%) with a Linear D2 baseline of 3%. Peak fitting was based on the nonlinear Marquardt-Levenberg method and the AutoFit Peaks I Residuals was used to optimize the fits. The higher oxidation
state, Fe$^{3+}$, has a larger effective nuclear charge and thus has a slightly larger binding energy. The binding energies of Fe$^{2+}$ and Fe$^{3+}$ are 7122 and 7124 eV, respectively.
RESULTS AND DISCUSSION

Reaction Kinetics

The reduction of Cr(VI) by green rusts SO₄, Cl, and CO₃, conducted at three different green rust concentrations (0.125, 0.25, and 0.5 g/L), was carried out in order to ascertain the rate law governing each reaction. Each data set was modeled using a first-order rate expression \( \frac{d[Cr(VI)]}{dt} = -k[Cr(VI)] \) and conformance to the expression is noted (Figure 3.1). At low concentrations of green rust, initial rates were used to avoid complications due to limited Fe(II) availability. The linearity of the observed pseudo first-order rate coefficients with respect to green rust concentration indicates that the reaction is proportional to the suspension density (Figure 3.2). However, as the data do not intercept the y-axis at zero, the reaction is governed by more complicated mechanistics than a simple first-order dependence of green rust. Nevertheless, the reduction of Cr(VI) by green rust can be described by a second-order reaction, dependent on both the concentration of chromate and green rust:

\[
\frac{d[Cr(VI)]}{dt} = -k [Cr(VI)] \{GR\}
\]  

[3.11]

where \( \{GR\} \) is the solution density of green rust.

Based on mass concentrations, green rust chloride proved to be the most facile of the three species in chromate reduction; first-order rate constants \( k_{obs} \) ranged from \( 1.22 \times 10^{-3} \) to \( 3.7 \times 10^{-2} \) s\(^{-1} \). The carbonate system followed with a range of \( k_{obs} \) from \( 1.59 \times 10^{-3} \) to \( 2.39 \times 10^{-2} \) s\(^{-1} \). Finally, green rust sulfate showed the slowest rate of reduction with \( k_{obs} \) of \( 6.83 \times 10^{-4} \) to \( 2.11 \times 10^{-2} \) s\(^{-1} \). The values obtained for the carbonate system are similar to those obtained in a separate study (\( 1.2 \times 10^{-3} \) to \( 1.13 \times 10^{-2} \) s\(^{-1} \); Williams
Using these $k_{obs}$ values, complete rate expressions for each green rust phase were derived:

\[
\text{GRCl: } \frac{d[Cr(VI)]}{dt} = -5.10 \text{ Lmol}^{-1}\text{s}^{-1} [Cr(VI)] \quad [3.12a]
\]

\[
\text{GRCO}_3: \frac{d[Cr(VI)]}{dt} = -3.79 \text{ Lmol}^{-1}\text{s}^{-1} [Cr(VI)] \quad [3.12b]
\]

\[
\text{GRSO}_4: \frac{d[Cr(VI)]}{dt} = -2.45 \text{ Lmol}^{-1}\text{s}^{-1} [Cr(VI)] \quad [3.12c]
\]

The trend observed in rates of reduction is more than likely a direct reflection of the reduction potential of each green rust based on the relative concentration of ferrous iron present. The nature of the anion incorporated in the green rust plays a role in its chemical structure. GR1-Cl has a proposed formula of $\text{[Fe}^{II}_3\text{Fe}^{III}(\text{OH})_8\text{]}^{+} [\text{Cl.nH}_2\text{O}]^{-}$, while GR1-CO$_3$ and GR2-SO$_4$ are thought to be $\text{[Fe}^{II}_4\text{Fe}_2^{III}(\text{OH})_{12}\text{]}^{2+} [\text{CO}_3\text{nH}_2\text{O}]^{2-}$ and $\text{[Fe}^{II}_4\text{Fe}_2^{III}(\text{OH})_{12}\text{]}^{2+} [\text{SO}_4\text{nH}_2\text{O}]^{2-}$, respectively (Génin et al., 1998). Since the ferrous to ferric iron ratio is larger for Cl than CO$_3$ or SO$_4$ (3:1 vs 2:1), a greater proportion of reduced iron is available. Consistent with the fraction of $\text{Fe}^{2+}:\text{Fe}^{3+}$, green rust chloride has more ferrous iron and is able to donate more electrons to chromate thereby reducing Cr(VI) the most rapidly. Even though GRCO$_3$ and SO$_4$ have the same Fe$^{2+}$/Fe$^{3+}$ ratio, GRCO$_3$ has more Fe$^{2+}$ on a per mol basis. It seems plausible that the Fe$^{2+}$ concentration is a primary driving force for electron transfer.

When the data are normalized to ferrous iron concentration, a sequence consistent with mass normalized data is observed Cl > CO$_3$ > SO$_4$ (Figure 3.3). This trend, while not affected by the ratio Fe$^{2+}$ to Fe$_{\text{Total}}$, is influenced by the surface area and nature of the layer structure. GRCO$_3$ with the largest surface area (30.1 m$^2$/g) should react the most rapidly followed by GRCl (S.A. 19.0 m$^2$/g) and GRSO$_4$ (S.A. 3.6 m$^2$/g). The green rust with the most surface available for reaction, GRCO$_3$ is inverted with GRCl because
though they are normalized to total ferrous iron content, the analyses do not normalize to bond strength within the compound. GRCl, having a lower $\Delta G^0_f$ (Refait et al., 1999), has a greater tendency towards reaction and electron transfer than GRCO$_3$ allowing for a more rapid interaction with chromate for the former.

When considering reduction rates normalized to surface area, green rust sulfate has greatest reaction rates followed by chloride and then carbonate (Figure 3.4). Ferrous iron concentration is not able to account for these observations as GR2-SO$_4$ has a Fe$^{2+}$:Fe$^{3+}$ ratio less than that of GR1-Cl. Instead, the crystal stacking structure must be considered. In general, phyllosilicate minerals exhibit terminal bonds due to uncoordinated oxygen or hydroxyl groups on the (100) and (010) faces creating reactive surfaces. Charge satisfied oxygen groups on the (001) plane lead to chemically inert faces. In the case of green rusts, and other layered clay minerals, this should negate the reactivity of interlayer planes. However, isomorphic substitution of Fe$^{3+}$ for Fe$^{2+}$ in the green rust octahedral layers disrupts the charge balance of the (001) surface groups allowing for a potentially reactive surface within the mineral (Figure 3.5). If external reactive sites on the (010) and (100) planes are normalized between the three classes similar rates would be expected if the interlayer were not reactive. However, the observed trend suggests otherwise. GR2-SO$_4$ also hosts a tetrahedrally coordinated interlayer anion which results in a larger d-spacing within the compound than that of the planar anions within GRCl and GRCO$_3$. Chromate, with its tetrahedral structure, should therefore exchange more readily with SO$_4$ than Cl or CO$_3$, allowing for greater access to the structural Fe$^{2+}$ (Figure 3.6). Between GRCl and CO$_3$, the d-spacing is consistent and will not suffice to explain the differences in rate normalized to surface area. However,
continuation of the above argument would imply less access of chromate to the interlayer simply by the nature of its coordination, size and steric hindrances. The available surface sites on chloride are enriched in Fe\(^{2+}\) compared to Fe\(^{3+}\) and this alone is able to reconcile the more rapid rate of reduction observed for GRCl.

The surface area of our carbonate sample is similar to that previously published for green rust, 30 m\(^2\)/g compared to 47 m\(^2\)/g (Williams and Scherer, 2001). Our use of a larger sieve size (0.25 mm vs. 0.15 mm) would lead to a difference in the observed surface area. Moreover, this relatively smaller surface area does not account for the nearly 4-fold increase in our observed Cr(VI) reduction rates by CO\(_3\). It would seem intuitive that a larger surface area would have more reactive sites and thus have higher rates of reduction. Since this is not the case, it is plausible to assume that surface area is not the controlling factor in the variable reactivity of the green rust phases. Another possible explanation could be that the freeze-drying method employed by Williams and Scherer (2001) actually inhibits some surface sites, thereby decreasing the surface reactivity. A mass-based analysis is of greater significance than surface area in natural settings as systems equilibrate to mass not surface area. Thus, rates in natural systems will more than likely follow the trend of Cl > CO\(_3\) > SO\(_4\).

**Fate of Chromate**

Pre-edge features of Cr X-ray absorption near edge structure (XANES) spectra were used to determine contributions from Cr(VI) in the solid phase end product. The 1s to 3d transition that results in the pre-edge is allowed in the tetrahedral Cr(VI)O\(_4\) as it is noncentrosymmetric. However, the octahedral nature of Cr(III)O\(_6\) – having a center of symmetry – forbids the transition. Normalized absorption spectra of the end products
reveals no appreciable contribution from Cr(VI) in the solid phase (Figure 3.7). A control was run with no green rust solid phase present and, as seen in Figure 3.1, Cr(VI) was conserved in the system, indicating that green rust is the only contributor to the reduction of chromate. The effect of filtering the sample was minimal, indicating that all of the Cr(VI) was in solution and little to none was sorbed to the oxidized iron oxide particles. Total chromium is not conserved in solution. Acidification (pH ~2) of samples with 1 M hydrochloric acid did not liberate chromium (Figure 3.8) leading to the conclusion that Cr is being retained by the iron oxides. Cr(III) commonly sorbs on iron oxides and oxyhydroxides at pH values ≥ 4 in the form of strongly bound inner-sphere complexes or precipitates and co-precipitates (Charlet and Manceau, 1992; Dzombak and Morel, 1990; Kendelewicz et al., 1998; Leckie et al., 1984). It is difficult to determine whether the Cr(III) is a surface precipitate or incorporated into the structure of the rapidly converting iron oxides. However, previous studies suggest that Cr is present within the solid phase as substituted ferrihydrite (Hansel et al., 2002; Loyaux-Lawnczak et al., 2000).

**Solid Phase Characteristics**

Upon complete reduction of Cr(VI), each GR was converted to the same end products - magnetite and lepidocrocite (Figure 3.9). Magnetite concentrations increase in the order GRCl < GRSO₄ < GRCO₃. Raman spectra (Figure 3.10) collected on the solid phase product of each reaction confirmed the results of XRD analyses. The two main Raman bands at 667 and 388 cm⁻¹ correspond to the values assigned to lepidocrocite and magnetite (Cornell and Schwertmann, 1996). It appears that each green rust converted completely to these iron oxyhydroxides without retaining the green rust stacking
sequence (Figure 3.11). Green rust oxidation by molecular oxygen produces unique end products for each green rust phase (Chapter 2). Oxidation by chromate is more controlled than that by molecular oxygen and is, therefore, more likely to produce uniform products. It also suggests a reaction mechanism unlike that involved upon exposing a sample to aerobic environments. Loyaux-Lawniczak et al. (1999) note that the kinetics involved in the oxidation of GRSO$_4$ by chromate are not comparable to that observed with dissolved oxygen, the latter being much slower. Active Raman bands are reported for Cr(OH)$_3$ at 525 cm$^{-1}$ and 300, 350, 550, and 610 cm$^{-1}$ for Cr$_2$O$_3$ (Melendres et al., 1992; Zuo et al., 1996). However, these bands are not apparent on the solid phase final product of chromate reduction by green rusts (Figure 3.10). Thus, surface bound Cr(III) oxides and hydroxides are not apparent, again implying that Cr(III) is incorporated within the structure of the iron oxide.

Scanning electron microscopy images verify the complete conversion of green rust to less ordered iron oxides. Instead of well-defined hexagonal platelets, the morphology of the end product of chromate reduction by green rusts suggests an amorphous mass of iron oxyhydroxide particulates (Figures 3.12). In addition, EDX spectra of each sample reveal the chemical composition of these oxides to be purely iron, oxygen and chromium. Also, no sulfate, chloride or carbonate was noted in the spectral analysis implying that these anions are not retained by the green rust as it undergoes oxidation by chromate.

X-ray absorption spectra of the iron K edge were collected for the end product of each GR oxidation. Figure 3.13 compares the background corrected, normalized spectra and the radial structure function obtained by Fourier transformation. In the RSF we see
the first shell of each anionic class at nearly the same distance as the reduced species. However, the second shell of both GRCO₃ and GRSO₄ is shifted to slight greater distance while GRCl retains its atomic shell distance. Each oxyhydroxide now possesses the same Fe²⁺:Fe³⁺ ratio (2:1) (Figure 3.14). If magnetite were the only species controlling Fe²⁺, then we would expect an excess of Fe³⁺. Considering the presence of purely ferric oxides as well, it is curious that the ferrous form of iron is still predominant. This suggests a more complicated end product than our XRD results. Either the green rust has retained some of its structure or another source of ferrous iron must be present. As we did not observe the main diffraction peaks for green rust in any of the samples, the complete conversion of green rust is a valid assumption. It is possible, and likely, that some of the ferrous iron is present as a surface phase on both magnetite and ferric hydroxide.

**Reaction Rates and Mechanisms**

Comparison of rates between green rust phases and a common oxidant has only been considered for GRSO₄ and GRCl with respect to NO₃⁻ previous to this study (Hansen et al., 2001). As was the case for NO₃, results for CrO₄²⁻ indicate a dramatic drop in the rate of reaction for GRSO₄. This is partially the result of the decreased reducing capacity of the GR as the Fe²⁺:Fe³⁺ ratio is lower for GRSO₄ than GRCl. Along with this decrease in Fe²⁺ comes an increase in positive charge on the octahedral sheet thereby increasing the layer charge of GRSO₄. A larger layer charge may limit the accessibility of the inner layer as the sheets are electrostatically attracted. This would decrease exchange of interlayer sulfate with the surrounding solution. Certainly GRCl would be more likely to favor exchange of nitrate for chloride as they are both planar anions and the layer charge is not as great. This may not be the case when considering
exchange of chloride with tetrahedrally coordinated chromate. Although the layer charge would not inhibit exchange, the structure of GR1s prefers planar interlayer anions. Chloride can be exchanged for sulfate without a change in the Fe$^{2+}$:Fe$^{3+}$ ratio indicating a retention of the GR1 structure (Hansen et al., 2001); however, the rates of exchange of sulfate or chromate for chloride within green rust structures are not known. The increased density of ferrous iron in GRCl is more likely to control the rates of reduction in this system of increased complexity.

To address the differences in rates between GRCO$_3$ and GRSO$_4$, we must examine the nature of the interlayer anion. As stated earlier, CO$_3$ is a planar anion while SO$_4$ is tetrahedrally shaped. As noted from the Raman spectra in Chapter 2, GRSO$_4$ seems to have a slight deviation from the usual Td symmetry of the SO$_4$ anion suggesting a different binding mechanism for one of the oxygens. This was not observed for GRCO$_3$. It is possible that one of the sulfate oxygens is shared or interacts with the iron hydroxides layers in green rust. This would make it more difficult for Cr(VI) to break down the layers and attack Fe(II). The thermodynamic constants derived for green rusts suggest this as well, corresponding to the trends noted in reduction rates for mass- and ferrous iron concentration-based analyses. The calculated Gibbs free energy ($\Delta G^o_f$) of anhydrous GRCl, CO$_3$ and SO$_4$ are $-2146 \pm 5$, $-3590 \pm 10$, and $-3795 \pm 15$ kJ/mol, respectively (Refait et al., 1999); water molecules were not considered to intervene in oxidation reactions and thus were not included in these calculations. The most negative value indicates the least favorable reaction; sulfate green rust requires the most energy to break the compound apart and GRCl the least.
The exchange of interlayer anions with the surrounding solution has been previously suggested (Loyaux-Lawniczak et al., 1999) and offers an explanation as to why no chloride, sulfate or carbonate are associated with the oxidized products of green rusts. However, this may occur because the precipitating solids prefer OH\(^-\) or O\(^2-\) to Cl\(^-\), SO\(_4\)\(^2-\), or CO\(_3\)\(^2-\). The incorporation of Cr(III) within the products suggests the occurrence of interlayer exchange with chromate. This would allow for interaction with more reactive sites on the octahedral sheets as suggested earlier. As reduction continues, the well-defined stacking of the GR is disturbed and the result is a poorly ordered oxidation product with chromium associated in the compound. In support of this theory, reduction of chromate by aqueous Fe(II) produces a mixed Cr(III)-Fe(III) hydroxide phase of the form Fe\(_{0.25}\)Cr\(_{0.75}\)(OH)\(_3\)\(_n\)H\(_2\)O (Eary and Rai, 1988; Hansel et al., 2002; Patterson et al., 1997).
CONCLUSIONS AND ENVIRONMENTAL IMPLICATIONS

The rate of chromate reduction by green rusts directly reflects the chemistry, structure, and properties of these minerals. With the abundance of ferrous iron available and the unique stacking of these oxides, chromate reduction is favorable. A proposed mechanism, in which the initial anion is excluded from the structure by exchange with chromate and subsequently followed by electron exchange between structural ferrous iron and aqueous chromate, suggests an explanation of the disordering of the green rust structure to an amorphous ferric oxide incorporating Cr(III).

Chemical reduction rates of chromate by various ferrous iron phases were compared using initial concentrations of \([\text{Cr(VI)}] = 100 \mu\text{M}\) and \([\text{Fe(II)}] = 30 \mu\text{M}\) (Figure 3.15). The rate of reduction of chromium by GR proves to be quite rapid compared to rates of reduction by other solid phase ferrous minerals (magnetite and illmenite). It is unlikely that the formation of magnetite, another mixed valence iron oxyhydroxide, contributes appreciably to the reduction of chromate. The rate of reduction of Cr(VI) by magnetite at pH 7 is approximately \(1.4 \times 10^{-7}\) M/s. This is nearly \(10^3\) times slower than the reaction rates observed by the various forms of green rust. In addition, Cr(III) sorption at the reaction conditions, pH = 7, is quite strong and previous studies (Kendelewicz et al., 1998) have shown a passivating layer on magnetite. Passivation of surface sites is not a contributing factor to the reduction of chromate by green rusts. The complete destruction of parent material to less ordered ferric oxides indicates access of chromium to the entire mineral – not just surface sites.

A much more detailed rate expression is available for aqueous ferrous iron reduction of chromate (Pettine et al., 1998), and at pH 7 green rust rates form an envelope
around the linear trend for Fe\(^{2+}\)\(_{(aq)}\) reduction of Cr(VI). GRCl is an even more effective reducer than ferrous iron while GRCO\(_3\) and GRSO\(_4\) may outcompete Fe(II) at slightly lower pH. In addition, of the previous kinetic studies involving reduction of NH\(_4^+\) (Hansen and Koch, 1999), CCl\(_4\) (Erbs et al., 1999), and Se(VI) (Myneni et al., 1997) by GR, chromium reacts the most rapidly. The free energy of formation of Cr(VI) is much lower than the other ions considered (Table 3.2) (West, 1988), and their reactivity, for the most part, is directly related to the energy required to break the bonds within these compounds. Not only is chromium reduced faster by green rust than all other ions studied, it is also reduced faster by green rust than by microbial interactions. Fendorf et al. (2000) suggest that microbial reduction rates of chromate, at their fastest, do not exceed rates of ~9 \times 10^{-4} \text{ M/h}. This is 10^2 to 10^3 times slower than by GR.

Ferrous iron concentration- and mass-based analyses of reduction rates of chromate by green rusts are more relevant to natural environments. Within this class of minerals, increased rates are observed with the reductant GRCl. This is a result of the increase ratio of ferrous to ferric iron available within the structure increasing the reducing capacity and greater surface area. GRCO\(_3\) and GRSO\(_4\) with their lower Fe\(^{2+}\):Fe\(^{3+}\) ratios are nearly ten times slower in reducing chromate as a result on a per mass basis. Nevertheless, all three anionic classes of green rust appear to be facile reductants of chromate that may impart an important control on the hazard of this ubiquitous toxin.
REFERENCES


transformation of carbon-tetrachloride and other halogenated compounds resulting 


*Emission and Scattering Techniques: Studies of Inorganic Molecules, Solids, and 


Table 3.1. Potential pathways of chromate reduction by ferrous iron-bearing solids and their associated free energies of reaction (calculated for pH 7 and unit activities).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^0$(pH7) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{2+}(\text{aq}) + \frac{1}{3} \text{HCrO}<em>4^- + \frac{8}{3} \text{H}<em>2\text{O} \Leftrightarrow 4/3[\text{Cr}</em>{0.25}\text{Fe}</em>{0.75}]\text{(OH)}_3(\text{s}) + 5/3\text{H}^+$</td>
<td>$-417$</td>
</tr>
<tr>
<td>$\text{FeCO}_3(\text{s})$ (siderite) + $\frac{1}{3} \text{HCrO}<em>4^- + \frac{8}{3}\text{H}<em>2\text{O} \Leftrightarrow 4/3[\text{Cr}</em>{0.25}\text{Fe}</em>{0.75}]\text{(OH)}_3(\text{s}) + 2/3\text{H}^+$ + $\frac{1}{3}\text{HCO}_3^-$</td>
<td>$-256$</td>
</tr>
<tr>
<td>$\text{Fe}^{II}\text{Fe}^{III}_{2}(\text{OH})_4(\text{s})$ (magnetite) + $\frac{1}{3} \text{HCrO}<em>4^- + \frac{14}{3}\text{H}<em>2\text{O} + \frac{1}{3}\text{H}^+$ $\Leftrightarrow$ $4/3[\text{Cr}</em>{0.25}\text{Fe}</em>{0.75}]\text{(OH)}_3(\text{s}) + 2\text{Fe(OH)}_3(\text{s})$</td>
<td>$-167$</td>
</tr>
<tr>
<td>$[\text{Fe}^{II}\text{Fe}^{III}<em>{2}(\text{OH})</em>{12}[\text{SO}_4\cdot8\text{H}<em>2\text{O}]</em>{(\text{s})}$ (GR) + $4/3 \text{HCrO}<em>4^- + 5/3\text{H}<em>2\text{O} \Leftrightarrow$ $16/3[\text{Cr}</em>{0.25}\text{Fe}</em>{0.75}]\text{(OH)}_3(\text{s}) +2/3\text{H}^+$ + $\text{SO}_4^{2-}$ + $2\text{Fe(OH)}_3(\text{s})$</td>
<td>$-1706$</td>
</tr>
</tbody>
</table>
Table 3.2. Gibbs Free Energy of formation for ions reduced by GR (West, 1988).

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Delta G_f^o$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO$_4^{2-}$ (aq)</td>
<td>-173.96</td>
</tr>
<tr>
<td>Se$_2^-$ (aq)</td>
<td>30.9</td>
</tr>
<tr>
<td>NO$_2^-$ (aq)</td>
<td>-7.7</td>
</tr>
<tr>
<td>NH$_4^+$ (aq)</td>
<td>-18.97</td>
</tr>
<tr>
<td>CCl$_4$ (aq)</td>
<td>-15.60</td>
</tr>
</tbody>
</table>
Figure 3.1. Chromate reduction rates upon reaction with (a) GRCI, (b) GRCO₃, and (c) GRSO₄ at various suspension densities. Batch reactors were maintained at pH 7 with 5 mM MOPS buffer. Initial Cr(VI) concentration was 192 µM. Solid lines represent first-order kinetics model. Error bars are based on duplicate reactors.
Figure 3.2. Effect of green rust concentration on first-order rate coefficients for Cr(VI) reduction for GRCI (◊), GRCO₃ (□), and GRSO₄ (Δ). Previously published data for GRCO₃ (○) are also compared (Williams et. al 2002). Reactors contained 192 µM Cr(VI) and pH 7 was maintained with MOPS buffer.
Figure 3.3. Effect of Fe\textsuperscript{2+} / Fe\textsubscript{total} concentration on first-order rate coefficients for Cr(VI) reduction by GRCI (◊), GRCO\textsubscript{3} (□), and GRSO\textsubscript{4} (△). Previously published data for GRCO\textsubscript{3} (○) is also compared (Williams et. al 2002). Reactors contained 192 µM Cr(VI) and pH 7 was maintained with MOPS buffer.
Figure 3.4. Effect of green rust surface area on first-order rate coefficients for Cr(VI) reduction by GRCl (◊), GRCO₃ (□), and GRSO₄ (Δ). Previously published data for GRCO₃ (○) are also compared (Williams et. al 2002). Reactors contained 192 µM Cr(VI) and pH 7 was maintained with MOPS buffer.
Figure 3.5. (a) Phyllosilicate ferrous iron octahedral layer with reactive sites on the (010) (Site 1) and (100) (out of page) planes. (b) Isomorphic substitution of Fe$^{III}$ creates a reactive surface on the (001) (Site 2) plane allowing for interaction of Cr(VI) with the interlayer.
Figure 3.6. Structural characteristics of GRs (a) SO$_4$, (b) CO$_3$, and (c) Cl. GR2-SO$_4$ with its tetrahedrally coordinated interlayer anion and larger d-spacing is more able to exchange with solution chromate. Planar chloride and carbonate create smaller d-spacings, limiting exchange with tetrahedral chromate thereby affecting reduction rates.
Figure 3.7. Chromium X-ray absorption spectra windowed to illustrate the pre-edge region (~5993.5 eV) for solid phase products in the reaction between synthesized GRCO$_3$, GRCl, and GRSO$_4$ and chromate. Each spectra shows minimal contribution from Cr(VI).
Figure 3.8. Temporal comparison of Cr\textsubscript{Total} concentration within batch reactor initially containing 192 $\mu$M Cr(VI)(aq) and 0.125g/L GRSO\textsubscript{4}, GRCO\textsubscript{3}, and GRCl. The pH was maintained at 7 with MOPS buffer. Samples were acidified for analyses to pH 2 with 1 M HCl.
Figure 3.9. X-ray diffractograms of final solid phase product after reaction of Cr(VI) with GRSO₄, GRCl, and GRCO₃. Peaks correspond to lepidocrocite and magnetite.
Figure 3.10. Raman spectra of solids resulting from GRCl, GRCO$_3$, and GRSO$_4$ reacted with Cr(VI).
Figure 3.11. X-ray diffraction patterns for (a) GRCl, (b) GRCO₃, and (c) GRSO₄ reacted with Cr(VI). Reactors were run at ambient conditions with pH = 7 controlled by MOPS buffer.
Figure 3.12. Scanning electron microscopy images of solid phase product resulting from the reaction of Cr(VI) with green rust (a) SO$_4$, (b) Cl, and (c) CO$_3$.
Figure 3.13. Iron X-ray absorption spectroscopy (a) and Fourier transforms (b) of solid phase products of Cr(VI) batch reduction by GRCO$_3$, GRCI, and GRSO$_4$. 
Figure 3.14. Peak fitting of Fe X-ray absorption near edge spectra of GR oxidized by Cr(VI) for (a) GRCl, (b) GRCO₃ and (c) GRSO₄. Ferrous iron has a binding energy of ~7124 eV while that of ferric iron is ~7122.
Figure 3.15. Rate comparison of contaminant reduction by ferrous iron phases (solid and solution). Initial concentrations of [Fe(II)] = 30 µM and [X] = 100 µM where X = Cr(VI), NH₄⁺, Se(VI) and CCl₄. Rate expression for ferrous iron is from Pettine et al. (1998); for magnetite and illmenite from Peterson et al. (1997); for Cr(VI) by GRCO₃⁺ from Williams and Scherer (2001); for NH₄⁺ by GRCI and GRSO₄ from Hansen et al. (2001); CCl₄ from Erbs et al. (1999); and for Se(VI) from Myneni et al. (1999). Dotted lines indicate the minimal effect of pH on reaction rate in GR systems (Williams et al., 2001).
CHAPTER 4. SIGNIFICANCE OF Cr(VI) REDUCTION VIA GREEN RUSTS

The widespread use of chromium in industrial applications and its subsequent deposition in the environment leads to concern over its fate and transport. The human health threat of mobile chromate in soils and groundwater systems increases the severity of contamination. Remediation techniques which can immobilize chromate by reduction to Cr(III) are desirable. Ferrous iron-bearing solids and solutions have the potential to facilitate these reactions with rapid rates in a number of chemically and biologically varied conditions.

Equilibrium with mixed Fe(II)-Fe(III) oxides, specifically green rusts, controls iron concentration in water-logged soil solutions (Bourrie et al., 1999) and the discovery of the green rust mineral fougerite as an active compound in reduced soil environments (Génin et al., 2001; Trolard et al., 1997) highlights the importance of such oxides on soil reactivity. Such phases may have a controlling influence on the fate of strong oxidant contaminants such as chromate. Chromate is in fact reduced to Cr(III) by synthetic GR1-CO3, GR1-Cl, and GR2-SO4 which can be described by a second-order kinetic expression dependent on chromium and green rust concentration. Chromate reduction rates by GRCl are ~10 times faster than those of GRCO3 and GRSO4 on a per mass basis. Rates of reduction are dependent on the external and internal (inter-layer) surfaces. When normalized to external surface area, the structural class (GR1 or GR2) appears to have a controlling factor on the reaction rate—the Fe(II):Fe(III) ratio has a secondary impact within a structural class. Nevertheless, the reactivity of the external surface has an overriding impact on reduction rate leading to both GRCl and GRCO3 having greater
reduction rates (per mass) than GRSO₄. The combined influence of external surface area and Fe(II):Fe(III) ratio results in GRCI having the greatest reduction rate.

The reduction of Cr(VI) by green rusts is a kinetically favorable reaction which proceeds at rates faster than those reported for reduction via other mixed valence iron oxides (e.g., magnetite) and microbial enzymatic reactions. These rates rival those of aqueous ferrous iron implying that under specific conditions green rusts are more efficient in chromate reduction. Chromium concentrations in the groundwater of industrial sites can be similar or much greater than those chosen for this experiment (Environmental Assessment Division, 2001; Fruchter et al., 2002) and the nature of the green rust mineral also differs in anionic components and crystallinity than those explored (Génin et al., 1998). Nevertheless, it is clear that reactions with these mixed valence iron oxides are of importance in controlling the fate of chromium. Finally, not only do the reactions occur at exceedingly rapid rates, they also produce end products which can incorporate Cr(III).

Green rusts hold significance in anaerobic environments such as waterlogged soils and groundwater aquifers. Sites that are high in chromium, nitrates, and other toxins (i.e. Superfund sites and areas of heavy agricultural activity) as well as those laden with iron-reducing bacteria exhibit geologically and chemically advantageous niches for green rusts to contribute to pollutant reduction.
REFERENCES


