

# CHROMATE REDUCTION BY HYDROXYCARBONATE GREEN RUST

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## ABSTRACT

To address the potential for abiotic natural attenuation of chromate, we have studied the kinetics and mechanism of chromate removal in the presence of hydroxycarbonate green rust. The kinetics of chromate removal were studied in batch systems to evaluate the effect of green rust surface area and pH. The rate of chromate removal was dependent on the green rust surface area concentration, and a surface area normalized rate constant ( $k_{sA} = 0.044 \text{ L m}^{-2} \text{ min}^{-1}$ ) was determined. The rate of chromate removal increased with decreased pH. The effect of pH, however, was modest, with only a five-fold increase in rate observed over five pH values (from pH 9.0 to 5.0). Of the three potential pathways hypothesized for chromate removal (reduction, adsorption, or interlayer exchange), reduction was found to be the dominant pathway controlling chromate loss from solution. Negligible adsorption or interlayer exchange of chromate ions was found to occur independently of reduction. The rapid reduction of chromate appears to result in precipitation of Cr(III) phases, such as  $\text{Cr}(\text{OH})_3$  or  $[\text{Fe,Cr}](\text{OH})_3$ .

**Key words:** mineral/water interface, reduced Fe minerals, natural attenuation

## INTRODUCTION

Reduction by reduced iron minerals has recently received a great deal of attention as a potential pathway for the degradation of oxidized environmental contaminants, such as chlorinated solvents, nitroaromatics, and heavy metals. The ubiquitous presence of iron in the environment as both dissolved species and mineral-bearing phases (e.g. magnetite, iron silicates, and green rusts) suggests that reduction by iron may be a significant abiotic pathway in the natural attenuation of environmental contaminants. Of these reduced iron minerals, green rust compounds are some of the strongest reductants, presumably due to their high Fe(II) content. Green rust compounds are composed of positively charged Fe(II)-Fe(III) octahedral sheets and interlayers containing water and anions such as  $\text{CO}_3^{-2}$ ,  $\text{SO}_4^{-2}$ , and  $\text{Cl}^-$ . An Fe(II)-Fe(III) ratio of approximately 2:1 has been found for divalent interlayer anions and 3:1

for monovalent interlayer anions (Refait et al., 1997). Green rust compounds are divided into two types based on the interlayer anion. Type I contains monotonic ions (e.g.,  $\text{Cl}^-$  and  $\text{Br}^-$ ) and planar molecules (e.g.,  $\text{CO}_3^{-2}$ ). Type II contains three-dimensional molecules (e.g.,  $\text{SO}_4^{-2}$ ). The presence of the interlayer anions is necessary to maintain electroneutrality in the green rust structure. For hydroxycarbonate green rust, the proposed chemical formula is  $[\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}] \cdot [\text{CO}_3^{-2} \cdot 2\text{H}_2\text{O}]$  (Hansen, 1989).

Although there is little data available on the reactivity of carbonate green rust, both organic and inorganic contaminants have been shown to react with sulfate green rust. Chlorinated solvents, such as carbon tetrachloride ( $\text{CCl}_4$ ) and chloroform ( $\text{CHCl}_3$ ), were reduced by sulfate green rust in batch reactors containing saturated concentrations of  $\text{CCl}_4$  (Erbs et al., 1999). The two major end products were  $\text{CHCl}_3$  and

hexachloroethane ( $C_2Cl_6$ ), indicating that complete dechlorination did not occur. Sulfate green rust has also been shown to reduce inorganic compounds, such as nitrate (Hansen et al., 1996; Hansen and Koch, 1998), selenium (Myneni et al., 1997), and chromate (Loyaux-Lawniczak et al., 2000). Sulfate green rust was found to reduce chromate to Cr(III), which precipitated as a poorly crystalline Cr(III)-Fe(III) oxyhydroxide. Unlike chromate reduction, which resulted in a completely oxidized iron oxide, the end product of sulfate green rust and  $CCl_4$ , selenate, and nitrate was magnetite (a partially oxidized iron oxide). Nitrate was completely reduced to ammonium at rates similar in magnitude to those observed for biotic degradation (Hansen and Koch, 1998). The expected stoichiometry of eight Fe(II) consumed for every nitrate reduced was observed (Hansen and Koch, 1998). Selenium was reduced from Se(VI) to Se(O), and similar to nitrate, the degradation rates were comparable to those found in sediments where biological activity was presumed to mediate the degradation of selenium (Myneni et al., 1997). Despite these findings, the relative importance of abiotic reactions mediated by green rusts compared to biotic reactions in natural systems is still unresolved (Oremland et al., 1998).

The most likely environment for green rust compounds to form is where Fe(II) and Fe(III) can coexist. Examples of environments that may support these conditions include reductomorphic soils and anoxic groundwater systems. Previous studies have identified green rust compounds in both natural systems (Taylor,

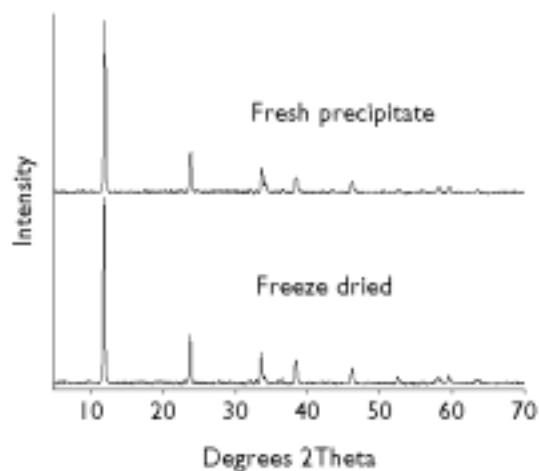
1980; Abdelmoula et al., 1988; Koch and Morup, 1991; Genin et al., 1998) and field-scale permeable reactive barriers (PRBs) containing iron metal ( $Fe^0$ ) (Vogan et al., 1998). To evaluate the role of green rust compounds in these systems, we have studied the transformation of chromate ( $HCrO_4^-$  and  $CrO_4^{2-}$ ) in the presence of hydroxycarbonate green rust. The objective of this work is to develop an understanding of both the pathway and kinetics of chromate removal by hydroxycarbonate green rust. The ability to assess the significance of this transformation pathway relative to other pathways, such as biotic transformation, is limited by (i) a lack of kinetic data for the transformation of contaminants, and (ii) a lack of understanding of the mechanisms controlling the reactivity of green rusts. The kinetic data derived from this work provides the first set of rate constants for the transformation of chromate by hydroxycarbonate green rust. The insight derived will provide an improved basis for predicting the fate of chromate in anoxic soils, sediments, and aquifers and improving the design and implementation of remediation technologies based on  $Fe^0$ .

## EXPERIMENTAL

Hydroxycarbonate green rust was synthesized in an anoxic chamber with a nitrogen and hydrogen atmosphere (95%-5%). All solutions were prepared in nitrogen-purged 18 MW-cm deionized water and were magnetically stirred at all times. Separate solutions of anhydrous  $FeCl_2$  (125 mM) and  $FeCl_3 \cdot 7H_2O$  (25 mM) were prepared in the anoxic chamber. Both solutions

were maintained at a pH of 7.0 with a Metrohm 736 GP Titrino by automatic addition of 1 M  $\text{Na}_2\text{CO}_3$ . The iron salt solutions were prepared to give a ferrous to ferric iron ratio of 5:1 (Hansen, 1989). The ferric iron solution was added to the ferrous iron solution and maintained at pH 8.0 by titration with 1 M  $\text{Na}_2\text{CO}_3$ . The solution was magnetically stirred for approximately two hours until a blue-green precipitate formed and consumption of the 1 M  $\text{Na}_2\text{CO}_3$  ceased. The blue-green precipitate was vacuum filtered under anoxic conditions and rinsed with nitrogen-purged deionized water. The amassed precipitate was freeze dried with a custom vacuum valve to ensure no exposure to the atmosphere during the freeze-drying process. The freeze-dried hydroxycarbonate green rust was sieved (0.15 mm) to obtain a uniform particle size.

To ensure purity and crystallinity of the synthesized hydroxycarbonate green rust, x-ray diffraction (XRD) analysis was performed on a Siemens Diffractometer utilizing  $\text{CuK}\alpha$  radiation. Samples for XRD analysis were prepared by admixing with glycerol to prevent oxidation during measurement (Hansen, 1989). The blue-green color of hydroxycarbonate green rust was maintained for the duration of the XRD analysis and no oxidation was observed. In addition, an XRD pattern of freeze-dried hydroxycarbonate green rust was compared to freshly precipitated hydroxycarbonate green rust to ensure that the freeze-drying process had no effect on the crystal structure (Figure 1). Surface area was analyzed anoxically by nitrogen Brunauer-Emmett-Teller (BET) analysis with a



**Figure 1.** Comparison of XRD patterns for freshly precipitated and freeze-dried hydroxycarbonate green rust. XRD scans were made between  $5^\circ$  and  $80^\circ$  with a step of  $0.02^\circ$  per second.

Quantachrome cell-seal assembly (to prevent the oxidation of green rust) on a Quantachrome Nova analyzer. BET analysis of a freeze-dried hydroxycarbonate green rust sample yields a surface area of  $33.3 \text{ m}^2\text{g}^{-1}$ .

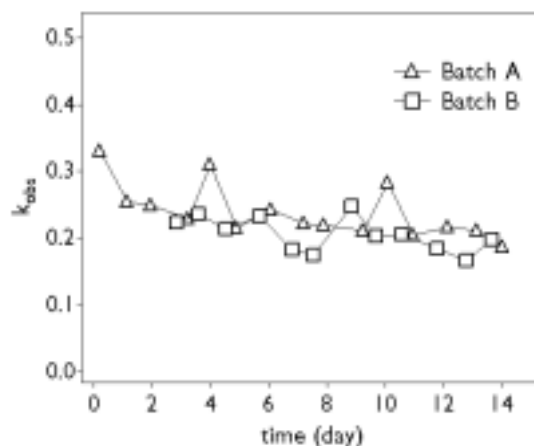
Batch experiments were conducted in an anoxic chamber, with an  $\text{N}_2/\text{H}_2$  atmosphere to prevent the rapid oxidation of green rust. Batch reactors were performed by addition of specific amounts of freeze-dried hydroxycarbonate green rust to nitrogen-purged deionized water, adjusted to desired pH with 0.2 M HCl or 0.1 M NaOH, and spiked with potassium chromate ( $\text{K}_2\text{CrO}_4$ ) to achieve a specific initial concentration of Cr(VI). To avoid possible buffer interactions, all batch experiments were performed individually with pH control achieved by addition of 0.2 M HCl with a Metrohm 736 GP Titrino. Samples for chromium analysis were withdrawn from the reactor and filtered through a Gelman 0.22 mm PTFE filter for dissolved

Cr(VI) measurements. For total chromium measurements ( $Cr(TOT)_{soln,GR}$ ), the sample was not filtered. Total chromium,  $Cr(TOT)$ , is the sum of both Cr(III) and Cr(VI). Hexavalent chromium was measured colorimetrically by the diphenylcarbazide method at 540 nm by either a Dionex HPLC, Dionex method TN24, or with a Spectronic Genesys 5 spectrophotometer according to the method outlined in Standard Methods (AWWA, 1995). Total chromium was measured by oxidation of Cr(III) by potassium permanganate and measured colorimetrically by diphenylcarbazide as outlined by Standard Methods (AWWA, 1995). Dissolved iron was measured colorimetrically with the 1,10-Phenanthroline method (AWWA, 1995).

## RESULTS AND DISCUSSION

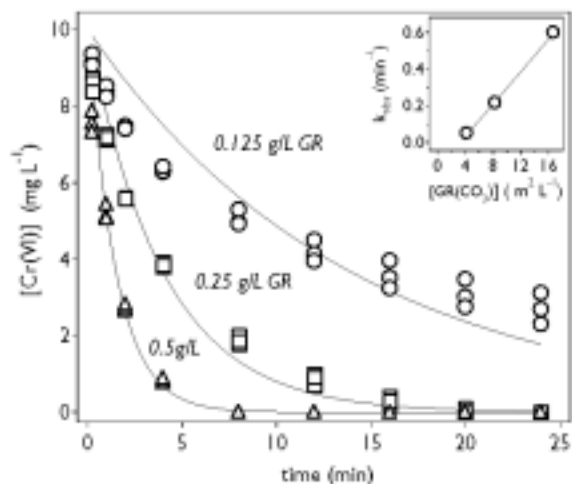
A preliminary set of experiments was performed with the freeze-dried hydroxycarbonate green rust to determine if (i) the green rust synthesis was reproducible and (ii) the reactivity of the freeze-dried green rust was stable over the time period needed to conduct experiments. Figure 2 shows that the first-order reaction rate constant ( $k_{obs}$ ) for chromate reduction by freeze-dried hydroxycarbonate green rust was reasonably reproducible between separate batches of synthesized green rust (average  $k_{obs}$ : batch A =  $0.24 \text{ min}^{-1}$ , batch B =  $0.21 \text{ min}^{-1}$ ). In addition,  $k_{obs}$  remained relatively consistent over a two-week period with a relative standard deviation of less than 40 percent ( $k_{obs} = 0.25 \pm 0.1$ ) among 27 experiments.

The removal of chromate in the presence of different concentrations of hydroxycarbonate



**Figure 2.** Effect of aging on the rate of chromate reduction by two separate batches of freeze-dried hydroxycarbonate green rust. All reactors contained  $0.25 \text{ g L}^{-1}$  ( $8.3 \text{ m}^2 \text{ L}^{-1}$ ) of green rust and an initial concentration of  $10 \text{ mg L}^{-1}$  as chromate.

green rust is shown in Figure 3. Chromate disappears rapidly in the presence of hydroxycarbonate green rust with half-lives ( $t_{1/2}$ ) of less than four minutes. The rate of removal is directly related to the concentration of green rust in the reactor, with about a four-fold faster removal rate observed for a two-fold increase in green rust concentration. The rate of chromate removal is significantly faster than removal rates observed for carbon tetrachloride ( $t_{1/2} > 10$  hours) (Erbs et al., 1999), nitrate ( $t_{1/2} = 3.9 \pm 0.3$  hours) (Hansen et al., 1996), and selenate ( $t_{1/2} = 60.3 \pm 16.2$  hours) (Myneni et al., 1997) in the presence of sulfate green rust. A direct comparison among these rates, however, is not possible because the specific surface area of green rust used in these studies is not known. A plot of  $k_{obs}$  versus green rust surface area concentration reveals a linear relationship (Figure 3 inset). A surface area normalized rate constant ( $k_{SA}$ ) of  $0.044 \text{ L m}^{-2} \text{ min}^{-1}$  for the



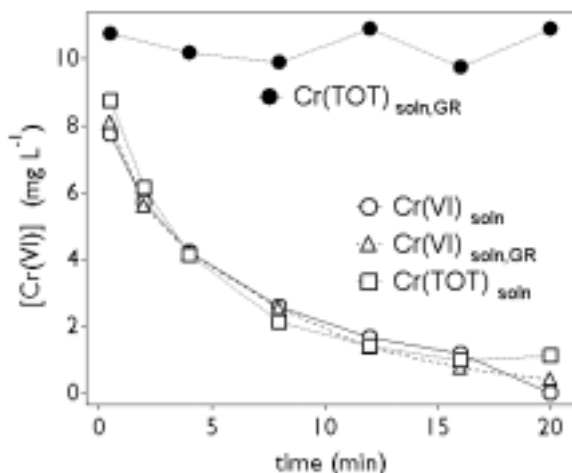
**Figure 3.** Effect of hydroxycarbonate green rust surface area concentration on the rate of chromate removal. All experiments were performed in triplicate. Batch reactors were maintained at pH 7.0 with a pH-STAT by addition of hydrochloric acid (0.2 M). Initial chromate concentration was  $10 \text{ mg L}^{-1}$  as chromate. Solid lines represent a first-order kinetic model. *Inset:* Effect of hydroxycarbonate green rust surface area concentration on first-order rate constants for chromate disappearance. Points represent the average observed rate constant, and error bars represent one standard deviation based on triplicate experiments.

reduction of chromate by hydroxycarbonate green rust was determined from the slope of this line.

At higher green rust surface area concentrations ( $8.3 \text{ m}^2 \text{ L}^{-1}$  and  $16.7 \text{ m}^2 \text{ L}^{-1}$ ), there is a strong adherence to first-order kinetics with respect to the chromate concentration. At a lower green rust surface area concentration ( $4.2 \text{ m}^2 \text{ L}^{-1}$ ), however, a shift from first-order kinetics to zero-order kinetics is observed. This phenomena is typical of heterogeneous systems and may be due to surface-site saturation (Zepp and Wolfe, 1987) of the hydroxycarbonate green rust with chromate or surface passivation by

accumulation of precipitates on the green rust surface. Surface passivation occurs due to the oxidized precipitate physically covering otherwise available Fe(II) sites on the green rust surface. Surface passivation has previously been shown to limit heterogeneous reactions involving the reduction of chromate by magnetite surfaces (Peterson et al., 1997).

Based on the properties of chromate (i.e., oxyanion and strong oxidant), we hypothesize three potential pathways for chromate removal in the presence of green rust: (i) reduction of chromate to Cr(III), (ii) adsorption of chromate to the green rust surface, and (iii) interlayer exchange of chromate with the interlayer anion ( $\text{CO}_3^{2-}$ ) in hydroxycarbonate green rust. Previous studies have identified the nature of the end product to be a solid-solution precipitate of reduced chromium and oxidized iron, resulting in a solid-solution precipitate of  $[\text{Fe,Cr}](\text{OH})_3$  (Loyaux-Lawniczak et al., 2000). A mass balance on chromate, however, was not determined, making it difficult to determine if all of the chromate was reduced. To quantify the loss of chromate to each pathway, a series of four measurements were made at each sampling time to determine the phase (i.e., aqueous or solid) and oxidation state (i.e., III or VI) of chromium. The four measurements include (i) chromate in a filtered sample ( $\text{Cr(VI)}_{\text{soln}}$ ), (ii) chromate in an unfiltered sample that is dissolved with sulfuric acid ( $\text{Cr(VI)}_{\text{soln,GR}}$ ), (iii) total chromium in a filtered sample ( $\text{Cr(TOT)}_{\text{soln}}$ ), and (iv) total chromium in an unfiltered sample dissolved in sulfuric acid ( $\text{Cr(TOT)}_{\text{soln,GR}}$ ). The filtered samples provide information on aqueous con-



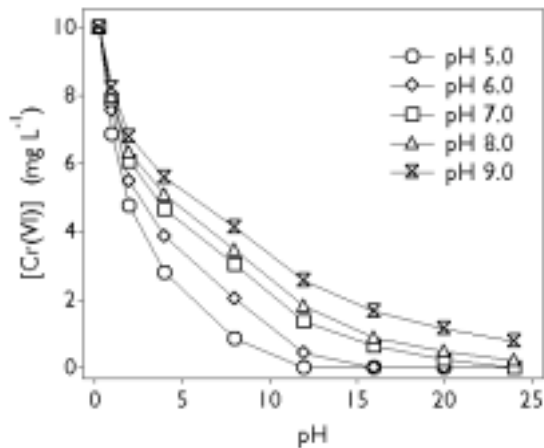
**Figure 4.** Disappearance of Cr(VI) and total chromium from solution and hydroxycarbonate green rust with time. Reactor contained 0.25 g L<sup>-1</sup> green rust and an initial concentration of 10 mg L<sup>-1</sup> as chromate.

centrations of chromium, whereas the unfiltered samples include both aqueous chromium and adsorbed, precipitated, or exchanged chromium. From the difference between the filtered and unfiltered samples, the amount of chromium bound to the surface (i.e., adsorbed, precipitated, or exchanged) can be calculated.

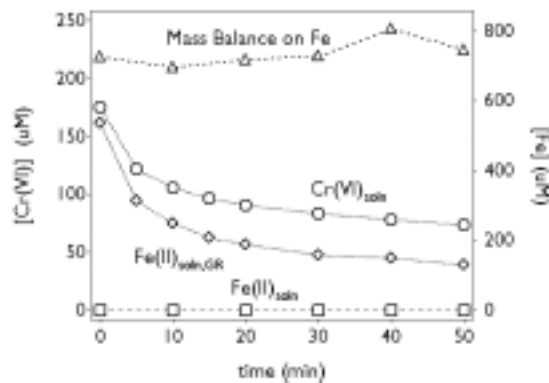
Based on a series of these measurements taken over time, it is clear that chromate is not conserved in the system (Figure 4). The measured quantities of chromium, as  $Cr(VI)_{soln}$  and  $Cr(VI)_{soln,GR}$ , are almost identical, indicating that chromate is being transformed and that adsorption or interlayer exchange are not significant removal pathways on their own. If chromate was conserved in the system by either adsorption or interlayer exchange, the measurement for  $Cr(VI)_{soln,GR}$  would be greater than  $Cr(VI)_{soln}$ . The total chromium in the unfiltered sample ( $Cr(TOT)_{soln,GR}$ ) remains constant throughout the experiment showing that chromium mass is conserved and that chromate is reduced by

hydroxycarbonate green rust. It is important to note that the processes of adsorption or interlayer exchange may be occurring; however, as the chromate ion adsorbs to the surface or exchanges with the interlayer carbonate ion, it is quickly reduced. The similarity between  $Cr(VI)_{soln}$  and  $Cr(TOT)_{soln}$  measurements shown in Figure 4 suggests that the reduced chromium is not remaining in solution. If Cr(III) remained in solution,  $Cr(TOT)_{soln}$  would be greater than  $Cr(VI)_{soln}$ . The loss of Cr(III) from solution is most likely due to the low solubility of  $Cr(OH)_3$  and  $[Fe,Cr](OH)_3$  at near-neutral pH values.  $[Fe,Cr](OH)_3$  has been shown to limit the solubility of Cr(III) in systems with ferric hydroxides (Sass and Rai, 1986), removing chromium to levels below the U.S. EPA Maximum Contaminant Level of 100 parts per billion (U.S. EPA, 2000).

The solubility of  $[Fe,Cr](OH)_3$ , however, is dependent on solution pH, suggesting that removal of chromate in the presence of hydroxycarbonate green rust may be dependent on the solution pH. The reaction of chromate and hydroxycarbonate green rust was studied at five different pH values ranging from 5.0 to 9.0 (Figure 5). The rate of chromate reduction increases as pH decreases, with about a five-fold increase in  $k_{obs}$  as the pH is decreased from 9.0 to 5.0 ( $k_{obs}$  range = 0.1 to 0.55 min<sup>-1</sup>). The increase in the  $k_{obs}$  at lower pH values may be due to an increase in affinity of the negatively charged chromate oxyanion for the hydroxycarbonate green rust surface. Typically at lower pH values, oxide surfaces become protonated and the surface charge becomes



**Figure 5.** Effect of pH on the reduction of chromate by hydroxycarbonate green rust. All reactors contained  $0.25 \text{ g L}^{-1}$  hydroxycarbonate green rust and an initial chromate concentration of  $10 \text{ mg L}^{-1}$ . Reactors were maintained at specified pH value by automatic addition of  $0.2 \text{ M HCl}$ .



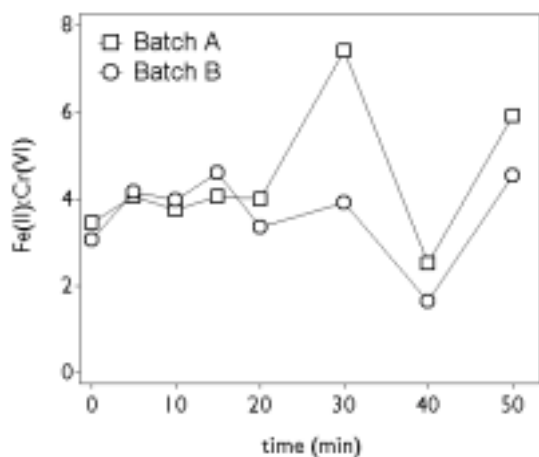
**Figure 6.** Disappearance of Cr(VI) and Fe(II) in the presence of hydroxycarbonate green rust. Reactors contained  $10 \text{ mg L}^{-1}$  chromate and  $3.33 \text{ m}^2 \text{ L}^{-1}$  hydroxycarbonate green rust and were maintained at pH 7.0 by automatic addition of  $0.2 \text{ M HCl}$ .

positive, increasing the electrostatic attraction between the hydroxycarbonate green rust and the chromate oxyanion (Schindler, 1990).

The effect of pH is based on the premise that the reductant in the batch reactor is Fe(II) associated with the hydroxycarbonate green rust. Figure 6 shows that Fe(II) associated with the hydroxycarbonate green rust was lost at a rate proportional to chromate loss. The measurements for total Fe(II) ( $Fe(II)_{soln,GR}$ ) in the reactor sample decreased as chromate was removed. Fe(II) in solution ( $Fe(II)_{soln}$ ) was found to be below measurable detection limits and is not a significant factor contributing to the reduction of chromate. This indicates that Fe(II) associated with the green rust structure is the active reductant. Structural Fe(II) within the green rust has previously been shown to be the reductant of nitrate (Hansen and Koch, 1998) and carbon tetrachloride (Erbs et al., 1999).

Theoretically the change in total Fe(II) to

chromate reduced should be 3:1. The overall stoichiometric ratio of Fe(II) oxidized to chromate reduced in Figure 6 was found to be approximately 4:1 (Figure 7). The average ratio of Fe(II):Cr(VI) for Trial A was  $4.3 \pm 1.54$  and for Trial B,  $4.0 \pm 0.97$ . These ratios are not consistent with the expected result of 3:1, based on the requirement of three Fe(II) atoms oxidized to Fe(III) for every chromate reduced to Cr(III). A potential explanation for the excessive Fe(II) loss is the possible presence of other oxidants (e.g., aqueous  $O_2$  and  $CO_2$ ). It has been demonstrated that iron metal can reduce  $CO_2$  to small chain hydrocarbons (Hardy and Gillham, 1995), suggesting that it may be possible that the  $CO_3^{2-}$  interlayer ion could be reduced by the Fe(II) associated with hydroxycarbonate green rust. A consistent ratio of approximately 4:1 is observed for both trials in Figure 7 for the first 20 minutes of the reaction; however, at times beyond 20 minutes, the



**Figure 7.** Stoichiometric ratio of Fe(II) removal to Cr(VI) reduced over time. Trial A and Trial B were performed from separate synthesized batches of hydroxycarbonate green rust. Batch reactors contained  $0.1 \text{ g L}^{-1}$  carbonate green rust and an initial chromate concentration of  $10 \text{ mg L}^{-1}$ .

system behaved erratically. The unusual behavior at later data points ( $>20 \text{ min}$ ) may be due to a decrease in the rate of chromate reduction while the Fe(II) continues to oxidize at variable rates, possibly by one of the aforementioned reactions.

## CONCLUSION

The results of this study show that chromate is rapidly reduced by hydroxycarbonate green rust, and that there is negligible adsorption to the green rust surface or interlayer exchange occurring independently of reduction. At low surface area concentrations, the rate of chromate reduction by hydroxycarbonate green rust appears to be limited by availability of Fe(II) sites by either a finite number of Fe(II) sites or surface blockage by  $[\text{Fe,Cr}](\text{OH})_3$  precipitating on the hydroxycarbonate green rust. The disappearance of structural Fe(II) in the carbonate green rust suggests that Fe(II) is responsible for the chromate reduction. The rapid reduction

of chromate and subsequent precipitation of Cr(III) phases, such as  $\text{Cr}(\text{OH})_3$  or  $[\text{Fe,Cr}](\text{OH})_3$ , suggests that abiotic reduction of chromate may be an important transformation process in natural systems and engineered remediation technologies based on iron metal ( $\text{Fe}^0$ ).

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