Chromate Removal from Aqueous Wastes by Reduction with Ferrous Ion

L. E. Eary* and Dhanpat Ral
Battelle Pacific Northwest Laboratories, P.O. Box 999, Richland, Washington 99352

Introduction

Chromates are used or generated by a number of industrial processes including electroplating, tanning, cooling with water, pulp producing, and ore and petroleum refining (1). Chromates [Cr(VI)] are strong oxidants and are toxic to plants (2) and animals (3). The present limit for dissolved Cr in drinking water is 10⁻⁴ M (4), a level that requires that some industrial waste solutions be treated to lower Cr(VI) concentrations before discharge to the environment. The existing chemical and electrochemical treatment processes for lowering Cr(VI) concentrations generally involve the aqueous reduction of Cr(VI) to Cr(III) and the subsequent adjustment of the solution pH to near-neutral conditions to precipitate the Cr(III) ions produced (Table I) (5-14). A number of chemical reductants for converting Cr(VI) to Cr(III) are described in the patent and journal literatures (Table I), including ferrous iron [Fe(II)] compounds and iron electrodes (5-7, 9-14), hydrogen peroxide (8), and reduced sulfur compounds (15). Among these reductants, Fe(II) compounds are the most commonly used reagents reported in the patent literature (Table I).

The length of time required to remove aqueous Cr(VI) by various treatment methods (Table I) is largely determined by the reactivity of the Fe(II) source. Methods that use slowly dissolving Fe(II) solids such as magnetite (5), iron sulfides (6), or ferrous iron particles (7, 9) require from 15 min to 6 h, acidic pH, and, in some cases, elevated temperatures to increase the amount and rate of Fe(II) release to solution (Table I). Methods that use highly soluble Fe(II) salts (9-12, 14), such as FeSO₄·7H₂O(s), are reported to produce much more rapid rates of aqueous Cr(VI) reduction, but some of these methods also require that the solutions be heated to 40-90 °C (8, 10), a potentially cumbersome and expensive step for an industrial treatment process. A process described by Fuji (12) that involves the addition of soluble Fe(II) salts is the simplest method and is reported to give rapid and stoichiometric reduction of aqueous Cr(VI) between pH 4.5 and pH 8.5. However, the question of whether Fe(II) ions can efficiently reduce Cr(VI) in oxygenated solutions has not been addressed in previous studies. Aqueous Fe(II) ions are rapidly oxidized by dissolved oxygen in solutions that have been equilibrated with air-oxygen (partial pressure O₂ = 0.2 atm) with pH greater than about 6.5-7.0 (16). Furthermore, the presence of either phosphate or fluoride ions is reported by Tamura et al. (17) to accelerate the rate of aqueous oxygenation (i.e., oxidation by dissolved oxygen) of Fe(II) in acidic solutions. For some of the treatment methods in Table I, from 2 to 100 times the stoichiometric amount of Fe(II) is reportedly needed to accomplish complete Cr(VI) reduction (9, 10). Because it is likely that no significant oxidants other than dissolved oxygen and Cr(VI) were present in the solutions used in the various treatment methods investigated, we suspected that the aqueous oxidation of Fe(II) by dissolved oxygen might be a competitive reaction that could decrease the efficiency of Cr(VI) reduction by Fe(II) under some conditions. The purpose of this work was to determine the optimum conditions for Cr(VI) reduction by aqueous Fe(II) ions by studying reaction stoichiometries as a function of dissolved-oxygen concentration, pH, and ionic composition.

Experimental Section

Materials. The sources of Cr(VI) and Fe(II) ions in the experiments were stock solutions made by dissolving measured amounts of K₂Cr₂O₇(s) and Fe(NH₄)₂(SO₄)₂-6H₂O(s) in deionized water. The water used for the Fe(II) stock solutions was deoxygenated to the extent possible by sparging with 99.99% Ar for at least 12 h. The pH values of the Fe(II) stock solutions were then adjusted to 5.0-5.5 to minimize the addition of hydrogen ions to the experimental solutions. The Fe(II) solutions were analyzed daily, and new solutions were made whenever any Fe(III) was detected.

The ionic compositions of the experimental solutions were adjusted from 10⁻⁴ to 10⁻¹ M by adding measured amounts of sodium salts, either Na₂SO₄(s), NaCl(s), NaClO₄(s), NaF(s), NaH₂PO₄·H₂O(s), or NaNO₃(s). The pH was adjusted by the addition of 1.0 M NaOH or a 1.0 M acid that contained the same anion as that present in the sodium salt used to set the ionic composition. The NaF solutions were an exception in which 1.0 M HClO₄ was used for pH adjustment. Deionized water was used to make all solutions.

Procedures. All rate experiments were conducted at 25 ± 2 °C in 1.0-L plastic bottles. The solutions were rapidly stirred to ensure complete mixing. Experimental solutions were aerated for at least 1 h with CO₂-free and water-saturated air to saturate the solutions with dissolved oxygen before aliquots of the Fe(II) and Cr(VI) stock solutions were added, and the solutions were aerated continuously during the experiments. The aeration resulted in concentrations of 2.34 ± 10⁻⁴ to 2.66 ± 10⁻⁴ M (7.5-8.6 ppm) dissolved oxygen depending on the salt concentration. Also, eight deoxygenated experiments were conducted with solutions that were sparged with 99.99% Ar for 2 h to reduce the dissolved-oxygen concentrations. Dissolved-oxygen concentrations in these experiments averaged 5.32 ± 1.56 × 10⁻⁴ M (0.17 ppm).

The rate experiments were started by the rapid addition of a measured volume of the Fe(II) stock solution to a rapidly stirred solution of known ionic composition, pH, and dissolved-oxygen and Cr(VI) concentrations. Peri-
samples for solubility measurements were periodically resulting in Cr(III) and Fe(III) concentrations that were placed on a shaker tray for solubility studies. Solution observed to precipitate within approximately 1-10 min, values of the resulting suspensions were adjusted to iron(III) hydroxides produced by the redox reactions. For Fe(II) were used in some additional experiments to cause run for 1-2 h, but the collection of samples after the first and in four more conducted at pH 5.0, 7.0, 8.5, and 10.0 addition of the Fe(II) ions. As a result, it was difficult to conducted at pH 3.5, 10.0, 11.0, and 12.0 in 10^-2 M Na_2SO_4 was generally complete within the first 1-2 min after the filtered through 0.22-μm porosity syringe-type filters, were determined.

tween 3.2 and 5.2 with 10^-2 M H_2SO_4 and the bottles were the pH range of about 5.0-11.0, these hydroxides were formation on the precipitation rates of chromium(III) and precipitation of enough solid to allow solubility studies to few minutes merely provided additional data for deter-

Higher concentrations of 10^-5 M Cr(VI) and 3.2 X 10^-5 M, and the added Fe(II) concentration was 19.2 X 10^-5 M, CKVT) reduced and Fe(II) oxidized could be measured and be conducted. The precipitates in these experiments were mining the average ratio of moles Fe(II) oxidized to moles occurring in the experimental solutions. Experiments were

Table 1. Summary of Reductants, Conditions, and Efficiencies of Treatment Processes for Removing Cr(VI) from Various Aqueous Wastes Reported in the U.S. and Foreign Patent Literature

<table>
<thead>
<tr>
<th><em>ref</em></th>
<th>reductant</th>
<th>pH of reduction step</th>
<th>pH of ppm step</th>
<th>T, °C</th>
<th>Cr product</th>
<th>efficiency*</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anderson et al. (5)</td>
<td>magnetite + FeSO_4·7H_2O</td>
<td>6.0-8.0</td>
<td>6.0-8.0</td>
<td>nr</td>
<td>Cr(OH)_3</td>
<td>1-1.2</td>
<td>magnetite is ineffective reductant without FeSO_4, but does enhance nucleation of precipitants</td>
</tr>
<tr>
<td>Lancy (6)</td>
<td>Fe sulfides</td>
<td>4.5-7</td>
<td>&gt;5.5</td>
<td>nr</td>
<td>Cr(OH)_3</td>
<td>nr</td>
<td>Fe sulfides must be continuously abraded; up to 1 h needed to reduce 15 ppm of Cr(VI) by 200 g of pyrite; pH may be lowered significantly by pyrite dissolution</td>
</tr>
<tr>
<td>Butler (7)</td>
<td>magnetized Fe particles</td>
<td>2.7-3.5</td>
<td>&gt;6.3</td>
<td>nr</td>
<td>Cr(OH)_3</td>
<td>nr</td>
<td>high-purity Fe particles, low pH, magnetic field, and mixing needed to obtain reduction of Cr(VI) in 15 min; addition of base required to precipitate Cr(II)</td>
</tr>
<tr>
<td>Fournier and Meyer (8)</td>
<td>H_2O_3</td>
<td>&lt;1.5</td>
<td>8-9</td>
<td>25</td>
<td>Cr(OH)_3</td>
<td>&gt;1.0 (pH &gt;1.5)</td>
<td>low pH, mixing, and very slow addition of H_2O_3 required to obtain stoichiometric reduction; excess H_2O_3 can reoxidize Cr(III); potential evolution of O_2 gas from H_2O_3 decomposition</td>
</tr>
<tr>
<td>Kindl and Atkinson (9)*</td>
<td>S^2+ + Fe(II) salt</td>
<td>7-8.0</td>
<td>1.6-3.0</td>
<td>40-60</td>
<td>Cr(OH)_3</td>
<td>1.7-2.7</td>
<td>heating required; sulfide solutions potentially hazardous; lowering pH to 1.6-3.0 will not promote precipitation but will promote dissolution of Cr(III) solids</td>
</tr>
<tr>
<td></td>
<td>ferrous mud of (1 mol of FeSO_4 + 1.7 mole of NaOH)</td>
<td>10-12</td>
<td>10-12</td>
<td>40-60</td>
<td>Cr(OH)_3</td>
<td>3-5</td>
<td>heating required; at high pH, Fe(II) oxidation reduces efficiency of Cr(VI) reduction; Cr(OH)_3 solubility increases for pH &gt;11.0</td>
</tr>
<tr>
<td>Sakakibara et al. (10)</td>
<td>ferrous salt</td>
<td>6-10</td>
<td>7-13</td>
<td>40-95</td>
<td>Cr(OH)_3</td>
<td>2-100</td>
<td>heating, stirring, and anaerobic conditions are required; up to 6 h are needed to precipitate reaction products; large excesses of Fe(II) over the stoichiometric amount Indicate loss of reductant to competitive reactions is common; high molecular weight coagulants used to promote precipitation; Cr concentrations determined by electrochemical methods redox potential controlled to -0.0 to -0.150 mV; effects of solution composition not discussed but this appears to be the simplest and effective method most effective for narrow pH range; limited lifetime of electrodes; rapid rates of reduction can be achieved efficient reduction in acidic solutions because of continuous reduction of Fe(III) to Fe(II); addition of base needed to precipitate Cr(III)</td>
</tr>
<tr>
<td>Hamano (11)</td>
<td>FeSO_4</td>
<td>7.5</td>
<td>nr</td>
<td>nr</td>
<td>Cr(OH)_3</td>
<td>nr</td>
<td>heating, stirring, and anaerobic conditions are required; up to 6 h are needed to precipitate reaction products; large excesses of Fe(II) over the stoichiometric amount Indicate loss of reductant to competitive reactions is common; high molecular weight coagulants used to promote precipitation; Cr concentrations determined by electrochemical methods redox potential controlled to -0.0 to -0.150 mV; effects of solution composition not discussed but this appears to be the simplest and effective method most effective for narrow pH range; limited lifetime of electrodes; rapid rates of reduction can be achieved efficient reduction in acidic solutions because of continuous reduction of Fe(III) to Fe(II); addition of base needed to precipitate Cr(III)</td>
</tr>
<tr>
<td>Fuji (12)</td>
<td>ferrous salt</td>
<td>4.5-8.5</td>
<td>4.5-5.5</td>
<td>nr</td>
<td>Cr(OH)_3</td>
<td>1.0</td>
<td>heating, stirring, and anaerobic conditions are required; up to 6 h are needed to precipitate reaction products; large excesses of Fe(II) over the stoichiometric amount Indicate loss of reductant to competitive reactions is common; high molecular weight coagulants used to promote precipitation; Cr concentrations determined by electrochemical methods redox potential controlled to -0.0 to -0.150 mV; effects of solution composition not discussed but this appears to be the simplest and effective method most effective for narrow pH range; limited lifetime of electrodes; rapid rates of reduction can be achieved efficient reduction in acidic solutions because of continuous reduction of Fe(III) to Fe(II); addition of base needed to precipitate Cr(III)</td>
</tr>
<tr>
<td>Moring (13)</td>
<td>Fe electrode</td>
<td>4.5-5.8</td>
<td>nr</td>
<td>nr</td>
<td>Cr(OH)_3</td>
<td>nr</td>
<td>heating, stirring, and anaerobic conditions are required; up to 6 h are needed to precipitate reaction products; large excesses of Fe(II) over the stoichiometric amount Indicate loss of reductant to competitive reactions is common; high molecular weight coagulants used to promote precipitation; Cr concentrations determined by electrochemical methods redox potential controlled to -0.0 to -0.150 mV; effects of solution composition not discussed but this appears to be the simplest and effective method most effective for narrow pH range; limited lifetime of electrodes; rapid rates of reduction can be achieved efficient reduction in acidic solutions because of continuous reduction of Fe(III) to Fe(II); addition of base needed to precipitate Cr(III)</td>
</tr>
<tr>
<td>VEB (14)</td>
<td>FeSO_4 + electrolytic reduction</td>
<td>&lt;3.0</td>
<td>nr</td>
<td>nr</td>
<td>Cr(OH)_3</td>
<td>nr</td>
<td>heating, stirring, and anaerobic conditions are required; up to 6 h are needed to precipitate reaction products; large excesses of Fe(II) over the stoichiometric amount Indicate loss of reductant to competitive reactions is common; high molecular weight coagulants used to promote precipitation; Cr concentrations determined by electrochemical methods redox potential controlled to -0.0 to -0.150 mV; effects of solution composition not discussed but this appears to be the simplest and effective method most effective for narrow pH range; limited lifetime of electrodes; rapid rates of reduction can be achieved efficient reduction in acidic solutions because of continuous reduction of Fe(III) to Fe(II); addition of base needed to precipitate Cr(III)</td>
</tr>
</tbody>
</table>

*Efficiency is defined here in terms of the stoichiometric amount of Fe(II) required to produce complete Cr(VI) reduction, i.e., 3 mol of Fe(II) to 1 mol of Cr(VI). *Kindl and Atkinson (9) report two treatment methods. *nr indicates quantities not reported.

dically, a 5-mL aliquot was withdrawn and immediately filtered through 0.22-μm porosity syringe-type filters, acidified, and analyzed for Cr(VI), total Cr, Fe(III), and total Fe concentrations. In additional experiments conducted at pH 3.5, 10.0, 11.0, and 12.0 in 10^-2 M Na_2SO_4 and in four more conducted at pH 5.0, 7.0, 8.5, and 10.0 in 10^-2 M phosphate, unfiltered acidified samples were analyzed for the presence of Fe(II) in precipitates. In most experiments, the initial Cr(VI) concentration was 9.6 X 10^-6 M, and the added Fe(II) concentration was 19.2 X 10^-5 M, giving a ratio of 2.0 mol of Fe(II) to 1.0 mol of Cr(VI). Higher concentrations of 10^-5 M Cr(VI) and 3.2 X 10^-5 M Fe(II) were used in some additional experiments to cause precipitation of enough solid to allow solubility studies to be conducted. The precipitates in these experiments were formed at pH 5.4 in 10^-2 M Na_2SO_4. After complete reduction and precipitation of the dissolved Cr, the pH values of the resulting suspensions were adjusted to between 3.2 and 5.2 with 10^-2 M H_2SO_4, and the bottles were placed on a shaker tray for solubility studies. Solution samples for solubility measurements were periodically removed from the bottles and filtered through 0.018-μm filters before the total dissolved-chromium concentrations were determined.

The observed rates of aqueous Cr(VI) reduction by the aqueous Fe(II) were extremely rapid. Chromate reduction was generally complete within the first 1-2 min after the addition of the Fe(II) ions. As a result, it was difficult to measure accurately the actual progress of the reactions over time by measuring changes in solution concentrations of reactants and products. However, the total amounts of Cr(VI) reduced and Fe(II) oxidized could be measured and used to determine the stoichiometries of the reactions occurring in the experimental solutions. Experiments were run for 1-2 h, but the collection of samples after the first few minutes merely provided additional data for determining the average ratio of moles Fe(II) oxidized to moles Cr(VI) reduced. It also provided some qualitative information on the precipitation rates of chromium(III) and iron(III) hydroxides produced by the redox reactions. For the pH range of about 5.0-11.0, these hydroxides were observed to precipitate within approximately 1-10 min, resulting in Cr(III) and Fe(III) concentrations that were below the analytical detection limits. For these experi-
ments, the molar ratios of Fe(II) oxidized to Cr(VI) reduced were calculated from the initial Fe(II) concentrations divided by the difference between the initial and final Cr(VI) concentrations.

The small hydrogen ion contents of the added Fe(II) stock solutions and the precipitation reactions that took place in the experimental solutions caused decreases in the initial pH values. The decrease in pH was caused predominantly by the precipitation of Fe(III) and Cr(III) products as hydroxides after the reduction reaction had been initiated. This pH decrease was minimized to less than 0.2 pH unit by the continual injection of 1.0 M NaOH. In experiments conducted at initial pH values that were less than 3.5 and greater than 10.5, NaOH was not added because the hydrogen ion contents were buffered well enough to result in decreases in pH that were less than 0.2 unit. In these experiments, the pH drifted downward as the precipitation reactions progressed before stabilizing after 15-45 min. Because the reduction reaction is so rapid, it is the initial pH which is most descriptive of the rate effects of pH, and we report our experimental results here in terms of the initial solution pH.

Analytical Methods. The concentrations of Cr(VI) and total Cr were determined colorimetrically to a detection level of 10-20 ppb according to the diphenylcarbazide method of Skougstad et al. (18). Concentrations of Fe(II) and total Fe were also determined colorimetrically to a detection level of 50 ppb by the ferrozine method of Gibbs (19). Concentrations of Cr(III) and Fe(III) were calculated by differences. The pH was determined with a combination glass-reference electrode, and dissolved-oxygen concentrations were measured with a dissolved-oxygen probe. Precipitates that were collected for elemental analyses were washed in 10-1 M Na2SO4 to displace adsorbed Cr(VI), dried at 90°C for 3 days, and completely dissolved by acid digestion, and then their Cr and Fe contents were determined by inductively coupled plasma (ICP) spectroscopy to a detection level of 2 ppb. The concentrations of total dissolved Cr from the solubility experiments were also determined by ICP spectroscopy.

Results and Discussion

Reaction Stoichiometry. The reduction of aqueous Cr(VI) by aqueous Fe(II) can be described by the overall reaction

$$\text{Cr(VI)}(aq) + 3\text{Fe(II)}(aq) \rightarrow \text{Cr(III)}(aq) + 3\text{Fe(III)}(aq)$$

(1)

in which the possible complexes of aqueous Cr and Fe have been ignored to focus attention on the reaction stoichiometry. This reaction was observed to be complete within 1-2 min in the experiments. Consequently, results are described here in terms of the reaction stoichiometry, which can be defined by the molar ratio of aqueous Fe(II) oxidized to aqueous Cr(VI) reduced. Figure 1 shows molar ratios that were determined after 5 min for experiments conducted in oxygenated sulfate, perchlorate, chloride, fluoride, and nitrate solutions and in deoxygenated sulfate solutions. Given the stoichiometry of reaction 1, a ratio of 3.0 mol of aqueous Fe(II) oxidized to 1.0 mol of aqueous Cr(VI) reduced is predicted, and this ratio is shown as the dashed line in Figure 1 for comparison. A molar ratio of 3.0 was consistently measured for the pH range 2.0-10.0 in the oxygenated solutions and for pH up to about 11.5 in the deoxygenated solutions (Figure 1). At higher pH, the molar ratios deviated from the predicted ratio of 3.0 to significantly higher values, indicating that the reduction of the aqueous Cr(VI) by Fe(II) ions is nonstoichiometric under highly alkaline conditions (Figure 1). In other oxygenated solutions containing 10-4 M phosphate, the change in molar ratios relative to pH was similar to that found for the other anionic media (Figure 2). However, for higher phosphate concentrations, the molar ratios deviated from the predicted value of 3.0 at progressively lower pH, as shown in Figure 2 by the results for the 10-3 and 10-2 M phosphate solutions. The changes in reaction stoichiometry shown in Figures 1 and 2 indicate that aqueous Cr(VI) reduction by aqueous Fe(II) is nonstoichiometric in most all highly alkaline solutions and in moderately alkaline solutions that contain high phosphate concentrations.

The experimental solutions did not contain any oxidants for aqueous Fe(II) other than the added Cr(VI) and dissolved oxygen. Also, the concentrations of Cr(VI) were observed to be stable indefinitely in blank solutions, indicating that other reductants for Cr(VI) were absent. Thus, the increases in the molar ratios to above 3.0 (Figures 1 and 2) under conditions of high pH and high-phosphate concentration can only be caused by one of the following three possibilities: (1) a loss of aqueous Fe(II) because of the precipitation of Fe(II) solids, (2) a decrease in the rate of reaction between aqueous Cr(VI) and aqueous Fe(II), or (3) an acceleration of rate of aqueous Fe(II) oxidation by dissolved oxygen.

Given the starting Fe(II) concentrations, the experiments conducted at pH above about 8.5 were potentially oversaturated with respect to Fe(OH)2(s) solubility (20)
for a short initial period. The precipitation of Fe(PO4)2·2H2O(s) also could have occurred in the experiments conducted in alkaline solutions that contained phosphate. However, analyses of the precipitates from three experiments conducted at pH greater than 10.0 in 10^2 M sulfate solutions and from four experiments that were conducted at pH 5.0–10.0 in 10^2 M phosphate solutions showed that no Fe(II) was present in the precipitated solids. These results show that precipitation of Fe(II) was not the cause of nonstoichiometric Cr(VI) reduction, the first possibility discussed above.

Distinguishing between the other two possible causes of nonstoichiometric reduction is difficult on the basis of our experimental measurements. The measured reaction stoichiometries are indicative only of the relative rates of the two reactions, that is, the rate of the reaction between aqueous Fe(II) and Cr(VI) relative to the rate of the reaction between aqueous Fe(II) and dissolved oxygen but not of the absolute reaction rates. However, reported information on the kinetics of these two reactions is useful for making some conclusions. On the basis of kinetic studies, Espenson and King (21) and Westheimer (22) have characterized the rate-determining step for the aqueous reduction of Cr(VI) by Fe(II) as an inner-sphere reaction. Inner-sphere reactions can generally be expected to increase in rate as pH increases because hydrolysis of the reactants provides the energy for the transfer of electrons through bridging hydroxyl ions (23). Ferrous ions become more hydrolyzed as pH is increased over the pH range at which nonstoichiometric reduction was observed (Figures 1 and 2), but CrO4^{2-} was the dominant Cr(VI) species in all of the experimental solutions with pH greater than 6.5 (20). On the basis of the characterization of the reaction between Cr(VI) and Fe(II) as being an inner-sphere reaction, it is unlikely that an increase in pH, which results in increased hydrolysis of the Fe(II) ions, would cause a decrease in the reaction rate. In fact, the opposite effect is more likely, ruling out the second possibility posed above. Consequently, we expect that the change in relative rates as a function of pH is caused by an increase in the reactivity of Fe(II) ions toward oxidation by dissolved oxygen, the third possibility suggested above.

The rate of aqueous Fe(II) oxidation by dissolved oxygen is known to be increased significantly as pH is increased on the basis of the results of numerous kinetic studies (17, 24–27). This reaction is described by

\[ \text{Fe(II)(aq) + 1/2O}_2(aq) + H^+ \rightarrow \text{Fe(III)(aq) + 1/2H}_2O \]  

(2)

The rate of this reaction is shown in Figure 3 in terms of the decrease in the half-life of aqueous Fe(II) as a function of pH for solutions exposed to air. The rate of Fe(II) oxidation is directly dependent on the dissolved oxygen concentration (17, 24–27). The rate dependence on pH is reported to change transitionally from zero order to inverse first order to inverse second order as solution pH is raised from 2.0 to about 8.5 (17, 28). The increase in rate with pH has been related to increased hydrolysis of Fe(II) ions in near-neutral to alkaline solutions (28). The oxygenation rate is also catalyzed by Fe(OH)2(s), a product of the oxygenation reaction that is rapidly precipitated at slightly acidic to alkaline pH (26). The overall result is a rapid decrease in the half-life of aqueous Fe(II) over the mid-pH range as the oxygenation rate is increased. Rates of Fe(II) oxygenation continue to increase with pH for pH greater than 8.5, but rate data are imprecise because of the rapidity of the reaction (26–28). Also, Tamura et al. (17) have observed that the presence of phosphate and fluoride ions cause an increase in the rate of aqueous Fe(II) oxidation by dissolved oxygen. Rates calculated from the rate laws of Tamura et al. (17) for 10^{-2} and 10^{-3} M phosphate and 10^{-13} M fluoride solutions are shown by the dashed lines in Figure 3 for comparison. On the basis of the available rate data, we conclude that the rate of Fe(II) oxidation by dissolved oxygen becomes rapid enough at pH greater than 10.0 and at lower pH, depending on the phosphate concentration, to cause a decrease in the amount of Fe(II) that reacts with aqueous Cr(VI). The result is observable in our experiments as nonstoichiometric reduction (Figures 1 and 2).

The conclusion that nonstoichiometric reduction results from Fe(II) oxidation by dissolved oxygen is supported by mass balance calculations of the amounts of Fe(II) oxidized by Cr(VI) and by dissolved oxygen. The solutions contained an excess amount of oxidant for Fe(II) as Cr(VI) and dissolved oxygen. The only oxidant for Cr(VI), however, is Fe(II). Thus, by measuring changes in the concentrations of the oxidants, Cr(VI) and dissolved oxygen, we can calculate the mass of Fe(II) that reacts with each oxidant by knowing the pertinent reaction stoichiometries. For example, in the experiments in which produced stoichiometric reduction of Cr(VI), the Cr(VI) concentrations were decreased while the dissolved-oxygen concentrations remained constant at the initial values. The combination of stoichiometric Cr(VI) reduction and no consumption of the dissolved oxygen indicates that Fe(II) reacted only with Cr(VI) in these experiments. However, in experiments which produced nonstoichiometric Cr(VI) reduction, both the Cr(VI) and the dissolved-oxygen concentrations decreased. These decreases are shown in Table II in terms of the amounts of Cr(VI) reduced and dissolved oxygen consumed. The only species that could have rapidly reduced dissolved oxygen in the experiments was Fe(II), indicating that Fe(II) was oxidized by Cr(VI) and by dissolved oxygen in these experiments. Using the stoichiometries of reactions 1 and 2 and the amounts of Cr(VI) reduced and dissolved oxygen consumed given in...
Table II. Oxidation of 19.2 x 10^{-4} M Fe(II) in Aerated (2.59 x 10^{-4} M O_2) 9.6 x 10^{-4} M Cr(VI) Solutions* \\

<table>
<thead>
<tr>
<th>pH</th>
<th>Cr(VI)</th>
<th>Fe(II) oxidized</th>
<th>Fe(II) oxidized/ Cr(VI) reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>6.34</td>
<td>0.0</td>
<td>19.20</td>
</tr>
<tr>
<td>10.0</td>
<td>6.34</td>
<td>0.06</td>
<td>19.20</td>
</tr>
<tr>
<td>11.0</td>
<td>5.28</td>
<td>0.34</td>
<td>19.20</td>
</tr>
<tr>
<td>12.0</td>
<td>3.90</td>
<td>1.88</td>
<td>19.20</td>
</tr>
</tbody>
</table>

*Calculated from measured amounts of Cr(VI) oxidized and O_2 consumed. One mol of Cr(VI) oxidizes 3 mol of Fe(II) (eq 1) and 1 mol of O_2 oxidizes 4 mol of Fe(II) (eq 2). Therefore, total Fe(II) oxidized is calculated from Fe(II) oxidized = 3Cr(VI) oxidized + 4O_2 consumed.

Table III. Fe and Cr Contents of Hydroxide Precipitates

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe(OH)_3(s)</th>
<th>Cr(OH)_3(s)</th>
<th>total</th>
<th>Fe/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.91</td>
<td>75.2</td>
<td>27.1</td>
<td>102.3</td>
<td>2.6</td>
</tr>
<tr>
<td>4.52</td>
<td>72.3</td>
<td>17.2</td>
<td>89.5</td>
<td>3.9</td>
</tr>
<tr>
<td>5.19</td>
<td>69.4</td>
<td>21.6</td>
<td>91.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6.19</td>
<td>72.7</td>
<td>24.2</td>
<td>96.7</td>
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<td>7.70</td>
<td>75.2</td>
<td>25.0</td>
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<tr>
<td>8.60</td>
<td>74.6</td>
<td>24.6</td>
<td>99.2</td>
<td>2.8</td>
</tr>
<tr>
<td>9.72</td>
<td>75.8</td>
<td>25.0</td>
<td>100.8</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Precipitation of Reduced Chromium. The products of the reduction reaction 1 will be precipitated as hydroxide solids in slightly acidic to alkaline solutions depending on their solution concentrations, i.e.,

Cr(III) + (1 - x)Fe(III) + 3H_2O = (Cr_xFe_{1-x})(OH)_3(s) + 3H^+ (3)

where x can vary between 0 and 1. Chromium(III) hydroxide solids, including Cr(OH)_3(s) and the solid solution (Cr_xFe_{1-x})(OH)_3(s), have been observed to precipitate rapidly in moderately acidic to alkaline solutions and are expected to be the important solubility-controlling solids for dissolved Cr(III) for a wide range of pH (29, 30). Brown solids formed rapidly in our reduction experiments, and aqueous Cr(III) that resulted from the reduction of aqueous Cr(VI) by aqueous Fe(II) quickly precipitated except at low pH. The precipitates from 11 of the experiments conducted in 10^{-1} M sulfate and chloride solutions covering a range in pH were collected and analyzed for the Cr and Fe contents (Table III). The measured compositions indicated that the precipitates consisted entirely of iron(III) and chromium(III) hydroxide solids, although two solids gave low total weight percentages, possibly because of incomplete removal of adsorbed water from the solids before analyses (Table III). The molar ratios of Fe(III) to Cr(III) in the solids were consistently near 3.0 (Table III), as would be expected from the stoichiometry of reaction 1.

It is not possible to determine by analytical methods whether the fine-grained precipitates that formed in the reduction experiments consisted of (Cr_xFe_{1-x})(OH)_3(s) or of a mixture of Fe(OH)_3(s) and Cr(OH)_3(s). Therefore, a number of reduction experiments with concentrated solutions (10^{-4} M Cr(VI)) were conducted to produce enough Cr(III) precipitates for solubility experiments. These precipitates were equilibrated in 10^{-4} M Na_2SO_4. Rai et al. (29) and Sass and Rai (30) report that equilibrium concentrations of Cr(III) are generally reached within 6 days in the presence of chromium(III) hydroxides under acidic conditions. The concentrations of Cr(III) measured in our solubility experiments at 12 and 70 days were similar (Figure 4), indicating that equilibrium concentrations were achieved. These measured concentrations, corrected to activities by the Davies equation (16), are shown in Figure 4. These activities are significantly less than those predicted from the solubility of Cr(OH)_3(s) (29). However, Sass and Rai (30) and Rai et al. (31) have shown that when both Cr(III) and Fe(III) are present in acidic solutions that the resulting hydroxide precipitate is a solid solution with the general formula of (Cr_xFe_{1-x})(OH)_3(s). On the basis of the stoichiometry of reaction 1 and the elemental compositions of the precipitates shown in Table III, we can
The reduction of aqueous Cr(VI) by aqueous Fe(II) not only removes the toxic Cr(VI) species from solution but also results in the precipitation of \((\text{Cr}_{0.25}\text{Fe}_{0.75})\text{(OH)}_3\) (Figure 4). Our data on the solubility experiments compared to the activities predicted from the equilibrium constants of Rai et al. (29) and Sass and Rai (30) for \((\text{Cr(OH)}_3)^2\) and \((\text{Cr}_{0.25}\text{Fe}_{0.75})\text{(OH)}_2\) solubilities and Cr(III) hydrolysis at 25 °C. Names in italics refer to aqueous species.

predict that the mole fraction Cr(III) in the hydroxide solid solution formed in acidic solutions should be 0.25, giving a solid solution composition of \((\text{Cr}_{0.25}\text{Fe}_{0.75})\text{(OH)}_2\). Chromium(III) concentrations that are predicted from the solubility data of Sass and Rai (30) for this composition are shown in Figure 4 by the dashed line. The similarity of the observed Cr(III) activities with those predicted from the thermochemical data of Sass and Rai (30) for \((\text{Cr}_{0.25}\text{Fe}_{0.75})\text{(OH)}_2\) (Figure 4) indicates that Cr(III) concentrations are controlled by solubility phenomena. The 0.25 mole fraction of Cr in the solid solution may not always be the product of Cr(VI) reduction by Fe(II), depending on the solution composition, and the mole fraction may change during weathering. However, the solubility of \((\text{Cr}_{0.25}\text{Fe}_{0.75})\text{(OH)}_2\) will generally limit total dissolved Cr concentrations, as Cr(III), to values that are less than the drinking water standard of \(10^{-4}\) M between pH 5.0 and pH 11.0 (Figure 4).

Conclusions

The experimental results presented here and a review of the existing literature indicate that the most efficient method for removing aqueous Cr(VI) from waste waters is by the simple addition of Fe(II) salts. Although this method is similar to that patented by Fuji (12), our data on the stoichiometry of the reduction reaction show that aqueous Fe(II) quantitatively reduces aqueous Cr(VI) over the pH range of 2.0–10.0 even in oxygenated solutions. However, at higher pH and at intermediate to alkaline conditions, the oxidative competition of aqueous Fe(II) by dissolved oxygen produces nonstoichiometric reduction of aqueous Cr(VI).

The reduction of aqueous Cr(VI) by aqueous Fe(II) not only removes the toxic Cr(VI) species from solution but also results in the precipitation of \((\text{Cr}_{0.25}\text{Fe}_{0.75})\text{(OH)}_2\). The solubility of this solid limits Cr(III) concentrations, over the pH range of approximately 5.0–11.0, to less than the drinking water standard of \(10^{-4}\) M Cr.

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