Chromate Removal from Aqueous Wastes by Reduction with Ferrous Ion

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■ Experimental measurements of reaction stoichiometries indicate that optimum conditions for chromate removal from oxygenated, 25 °C aqueous wastes by reduction with ferrous ion occur at pH less than 10.0 in solutions containing the following anions: ClO_4^-, Cl^-, F^-, NO_3^-, and PO_4^{3-}. At pH greater than 10.0 and at lower pH in solutions that contain greater than 10^{-4} M total phosphate, chromate is less efficiently reduced by ferrous ions as evidenced by nonstoichiometric reduction. Nonstoichiometric reduction of the chromate by the ferrous ion is caused by the competitive oxidation of the ferrous ions by dissolved oxygen. Depending on pH and solution composition, the reduction of chromate by ferrous ions causes rapid precipitation of $(Cr_xFe_{1-x})(OH)_3(s)$. The solubility of this solid limits Cr(III) concentrations, between pH 5.0 and pH 11.0, to less than the drinking water limit of 10^{-6} M.

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^{-6} 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 $FeSO_4 \cdot 7H_2O(s)$, 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 (9, 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 O_2 = 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 $K_2Cr_2O_7(s)$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O(s)$ 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 $Na_2SO_4(s)$, $NaCl(s)$, $NaClO_4(s)$, $NaF(s)$, $NaH_2PO_4 \cdot H_2O(s)$, or $NaNO_3(s)$. 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 $HClO_4$ 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 $CO_2(g)$-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 (7.5-8.5 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 $(5.32 \pm 1.56) \times 10^{-6}$ 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-

Table I. 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

ref	reductant	pH of reduction step	pH of pptn step	T, °C	Cr product	effi-ciency[a]	comments
Anderson et al. (5)	magnetite + $FeSO_4 \cdot 7H_2O$	6.0–8.0	6.0–8.0	nr[c]	$Cr(OH)_3$	1–1.2	magnetite is ineffective reductant without $FeSO_4$ but does enhance nucleation of precipitants
Lancy (6)	Fe sulfides	4.5–7	>5.5	nr	$Cr(OH)_3$	nr	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
Butler (7)	magnetized Fe particles	2.7–3.5	>6.3	nr	$Cr(OH)_3$	nr	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(III)
Fournier and Meyer (8)	H_2O_2	<1.5	8–9	25	$Cr(OH)_3$	>1.0 (pH >1.5)	low pH, mixing, and very slow addition of H_2O_2 required to obtain stoichiometric reduction; excess H_2O_2 can reoxidize Cr(III); potential evolution of O_2 gas from H_2O_2 decomposition
Kindl and Atkinson (9)[b]	S^{2-} + Fe(II) salt	7–8.0	1.8–3.0	40–60	$Cr(OH)_3$	1.7–2.7	heating required; sulfide solutions potentially hazardous; lowering pH to 1.8–3.0 will not promote precipitation but will promote dissolution of Cr(III) solids
	ferrous mud of (1 mol of $FeSO_4$ + 1.7 mol of NaOH)	10–12	10–12	40–60	$Cr(OH)_3$	3–5	heating required; at high pH, Fe(II) oxygenation reduces efficiency of Cr(VI) reduction; $Cr(OH)_3$ solubility increases for pH >11.0
Sakakibara et al. (10)	ferrous salt	6–10	7–13	40–95	chromium ferrite	2–100	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.
Hamano (11)	$FeSO_4$	7.5	nr	nr	$Cr(OH)_3$	nr	high molecular weight coagulants used to promote precipitation; Cr concentrations determined by electrochemical methods
Fuji (12)	ferrous salt	4.5–8.5	4.5–8.5	nr	$Cr(OH)_3$	1.0	redox potential controlled to −50 to −150 mV; effects of solution composition not discussed but this appears to be the simplest and effective method
Moring (13)	Fe electrode	4.5–5.8	nr	nr	$Cr(OH)_3$	nr	most effective for narrow pH range; limited lifetime of electrodes; rapid rates of reduction can be achieved
VEB (14)	$FeSO_4$ + electrolytic reduction	<3.0	nr	nr	nr	nr	efficient reduction in acidic solutions because of continuous reduction of Fe(III) to Fe(II); addition of base needed to precipitate Cr(III)

[a] 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). [b] Kindl and Atkinson (9) report two treatment methods. [c] nr indicates quantities not reported.

odically, 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(II), 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 9.6×10^{-6} M, and the added Fe(II) concentration was 19.2×10^{-6} M, giving a ratio of 2.0 mol of Fe(II) to 1.0 mol of Cr(VI). Higher concentrations of 10^{-2} M Cr(VI) and 3.2×10^{-2} 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 Na_2SO_4 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

$$Cr(VI)(aq) + 3Fe(II)(aq) \rightarrow Cr(III)(aq) + 3Fe(III)(aq) \quad (1)$$
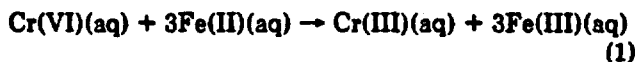
in which the possible complexes of aqueous Cr and Fe have been ignored to focus attention on the reaction stoichiometry. This reaction was observed to be complete within 1–2 min in the experiments. Consequently, results are described here in terms of the reaction stoichiometry, which can be defined by 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 ox-
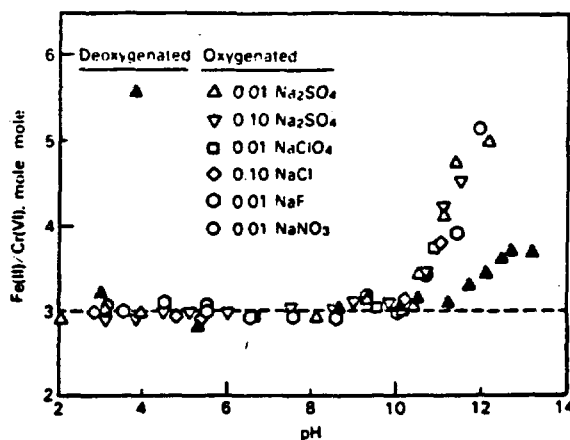

Figure 1. Molar ratios of Fe(II) oxidized to Cr(VI) reduced after 5 min of reaction as a function of pH and ionic composition for oxygenated and deoxygenated solutions at 25 °C.
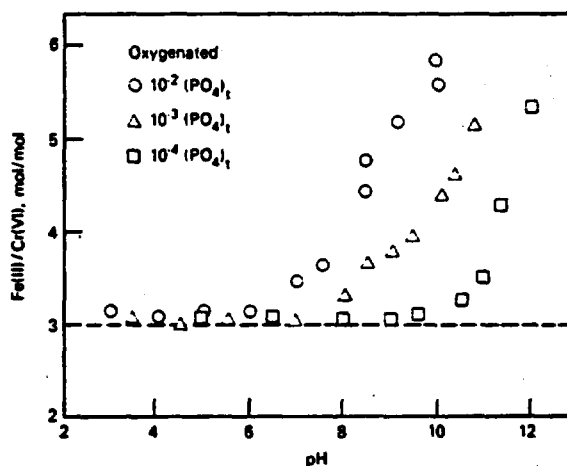

Figure 2. Molar ratios of Fe(II) oxidized to Cr(VI) reduced after 5 min of reaction as a function of pH for three total phosphate concentrations in oxygenated solutions at 25 °C.

ygenated 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_3-$(PO_4)_2 \cdot 2H_2O(s)$ 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 promotes 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 CrO_4^{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

$$Fe(II)(aq) + {}^1/_4 O_2(aq) + H^+ \rightarrow Fe(III)(aq) + {}^1/_2 H_2O$$

(2)
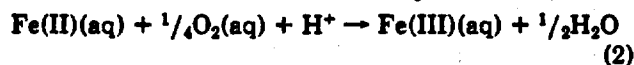
The rate of this reaction is shown in Figure 3 in terms of the decrease in the half-life of aqueous Fe(II) as a function of pH for solutions exposed to air. The rate of Fe(II) oxygenation is directly dependent on the dissolved oxygen concentration (17, 24–27). The rate dependence on pH is reported to 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 $Fe(OH)_3(s)$, 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
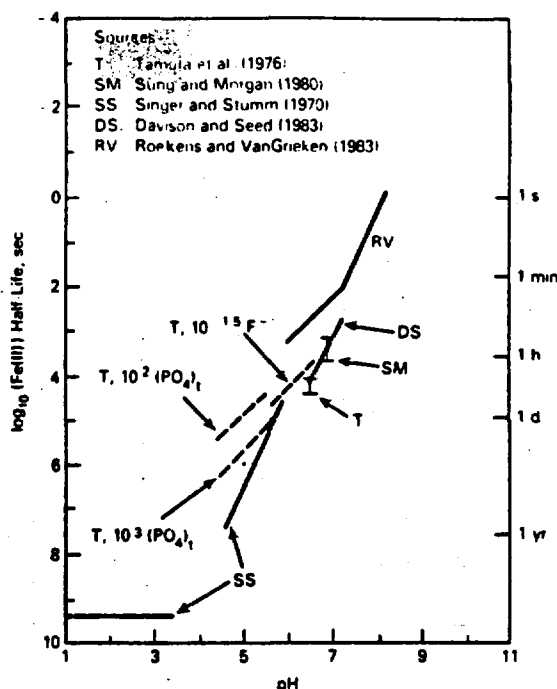

Figure 3. Half-lives for aqueous Fe(II) as a function of pH at 25 °C calculated for oxidation by dissolved oxygen (partial pressure of O_2 = 0.2 atm) using available rate information (17, 25–28). Dashed lines drawn for the one fluoride and the two total phosphate concentrations are from the rate laws of Tamura et al. (17).

by dissolved oxygen. Rates calculated from the rate laws of Tamura et al. (17) for 10^{-2} and 10^{-3} M phosphate and $10^{-1.5}$ 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 reductant 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 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 both 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 19.2×10^{-5} M Fe(II) in Aerated (2.59×10^{-4} M O_2) 9.6×10^{-5} M Cr(VI) Solutions[a]

	mol $\times 10^5$		Fe(II) oxidized		
pH	Cr(VI) reduced	O_2 consumed	obsd	calcd[a]	Fe(II) oxidized/ Cr(VI) reduced
		10^{-2} Sulfate			
3.0	6.34	0.0	19.20	19.02	3.03
10.0	6.34	0.06	19.20	19.02	3.03
11.0	5.28	0.34	19.20	17.20	3.64
12.0	3.90	1.88	19.20	19.20	4.92
		10^{-2} Phosphate			
5.0	6.26	0.0	19.20	18.78	3.07
7.0	5.85	0.38	19.20	17.55	3.28
8.5	4.39	1.31	19.20	18.41	4.37
10.0	3.49	2.19	19.20	19.22	5.50

[a] Calculated from measured amounts of Cr(VI) reduced and O_2 consumed. One mole 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) reduced + $4O_2$ consumed.

Table III. Fe and Cr Contents of Hydroxide Precipitates

	wt %			Fe/Cr,
pH	$Fe(OH)_3(s)$	$Cr(OH)_3(s)$	total	mol/mol
	10^{-1} M Na_2SO_4			
3.91	75.2	27.1	102.3	2.6
4.52	72.3	17.2	89.5	3.9
5.19	69.4	21.6	91.0	3.0
6.19	72.7	24.2	96.7	2.8
7.70	75.2	25.0	100.2	2.8
8.60	74.6	24.6	99.2	2.8
9.72	75.8	25.0	100.8	2.8
	10^{-1} M NaCl			
4.81	74.4	23.8	98.2	2.9
5.41	73.8	25.8	99.6	2.7
10.30	77.3	25.6	102.9	2.8
11.06	80.4	26.3	106.7	2.8

Table II, we can account for 90–100% of the total Fe(II) oxidized in the experimental solutions. As shown in Table II, increased consumptions of dissolved oxygen correspond to decreases in the amounts of Cr(VI) reduced, and consequently, to the conditions of nonstoichiometric Cr(VI) reduction. These mass balance calculations clearly show that the nonstoichiometric reduction of Cr(VI) observed at pH greater than 10.0 and at lower pH in the presence of phosphate is caused by the competitive oxidation of Fe(II) by dissolved oxygen.

The observation that nonstoichiometric reduction also occurred in deoxygenated solutions but at higher pH than in aerated solution (Figure 1) is also consistent with the dependence of the Fe(II) oxygenation rate on pH and on dissolved-oxygen concentration. These solutions were continuously sparged with Ar but still contained an average of 5.31×10^{-6} M (0.17 ppm) dissolved oxygen. Because the rate of Fe(II) oxygenation is directly dependent on dissolved oxygen concentration (17, 24–27), a higher pH is required to offset the effect of the decreased dissolved oxygen concentration on the oxygenation rate. The small amount of oxygen in the sparging gas was sufficient to oxidize some of the aqueous Fe(II) under extremely alkaline conditions. Only a small amount of reaction between Fe(II) and dissolved oxygen is needed to cause measurable changes in the reaction stoichiometry.

Our conclusion that nonstoichiometric reduction of Cr(VI) is caused by an increase in the rate of Fe(II) oxygenation in phosphate solutions is also consistent with the results of Tamura et al. (17). According to the rate law given by these authors, concentrations of phosphate greater than 10^{-4} M are required to produce Fe(II) oxygenation rates that are more rapid than those measured in phosphate-free solutions (Figure 3). In our experiments, concentrations greater than 10^{-4} M phosphate were also required to increase the Fe(II) oxygenation rate enough to cause nonstoichiometric Cr(VI) reduction to occur at lower pH values (<10.0) than that determined for phosphate-free solutions (Figures 1 and 2). In contrast to the phosphate solutions, significant increases in the rates of Fe(II) oxygenation in fluoride solutions were not evident in our experiments (Figure 1). However, very high concentrations of fluoride (at least $10^{-1.5}$ M) are needed to increase the aqueous Fe(II) oxygenation rate to be greater than those calculated for most other slightly acidic solutions according to the rate law of Tamura et al. (17) (Figure 3).

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.

$$xCr(III) + (1 - x)Fe(III) + 3H_2O =$$
$$(Cr_xFe_{1-x})(OH)_3(s) + 3H^+ \quad (3)$$
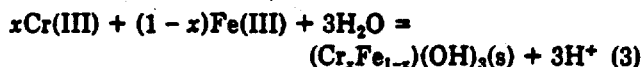
where x can vary between 0 and 1. Chromium(III) hydroxide solids, including $Cr(OH)_3(s)$ and the solid solution $(Cr,Fe)(OH)_3(s)$, have been observed to precipitate rapidly in moderately acidic to alkaline solutions and are expected to be the important solubility-controlling solids for dissolved Cr(III) 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 $(Cr,Fe)(OH)_3(s)$ or of a mixture of $Fe(OH)_3(s)$ and $Cr(OH)_3(s)$. Therefore, a number of reduction experiments with concentrated solutions [10^{-2} M Cr(VI)] were conducted to produce enough Cr(III) precipitates for solubility experiments. These precipitates were equilibrated in 10^{-2} 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
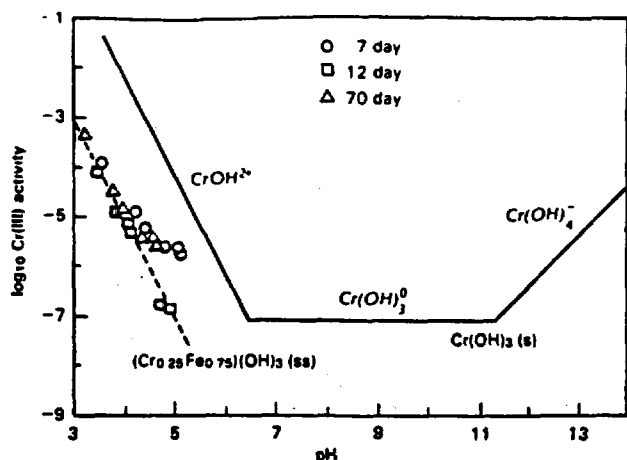
Figure 4. Activities of CrOH^{2+} as a function of pH determined in the solubility experiments compared to the activities predicted from the equilibrium constants of Rai et al. (29) and Sass and Rai (30) for Cr(OH)$_3$(s) and (Cr$_{0.25}$Fe$_{0.75}$)(OH)$_3$(s) solubilities and Cr(III) hydrolysis at 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 (Cr$_{0.25}$Fe$_{0.75}$)(OH)$_3$(s). 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 (Cr$_{0.25}$Fe$_{0.75}$)(OH)$_3$(s) (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 (Cr$_x$Fe$_{1-x}$)(OH)$_3$(s) will generally limit total dissolved Cr concentrations, as Cr(III), to values that are less than the drinking water standard of 10^{-6} 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 phosphate solutions, the competitive oxidation 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 (Cr$_x$Fe$_{1-x}$)(OH)$_3$(s). 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^{-6} M Cr.

Acknowledgments

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