Kinetics of Chromate Reduction by Ferrous Iron

SCOTT E. FENDORF* AND
GUANGCHAO LI

*Soil Science Division, University of Idaho,
Moscow, Idaho 83844-2339*

Reduction of Cr(VI) to Cr(III) is environmentally favorable as the latter species is not toxic to most living organisms and also has a low mobility and bio-availability. Ferrous iron is one possible reductant implicated as a major contributor to the removal of Cr(VI) from suboxic and anoxic waters and soils. Despite the importance of this redox reaction, no mechanistic or kinetic information are available, which are needed to determine the rate of Cr(VI) reduction and to assess the role of oxygen in limiting this reaction. In this study we used a stopped-flow kinetic technique monitored by UV—VIS spectroscopy and an initial rate method to ascertain the rate constant and the rate dependence of each reactant. We observed that the rate of Cr(VI) removal conformed to $-d[Cr(VI)]/dt = k_{cr}[Fe(II)]^{0.6}[Cr(VI)]^1$ where $k_{cr} = 56.3$ (± 3.7) mmol$^{-0.6}$ min^{-1} L$^{0.6}$. Based on this rate expression and that for the oxygenation of Fe(II), Cr(VI) reduction should be unaffected by oxygen except at pH values in excess of 8 even at micromolar concentrations.

Introduction

Chromium is a metal used in various industrial processes, ultimately making its way into soils and waters through industrial spills or waste deposition. In the surface and near-surface environments, two stable oxidation states of Cr persist, Cr(III) and Cr(VI), which have contrasting toxicities, mobilities, and bioavailabilities. Chromium(VI) is toxic to both plants and animals, being a strong oxidizing agent and a potential carcinogen (*1*). Concentrations as low as 0.5 ppm in solution and 5 ppm in soils can be toxic to plants (*2*); in contrast, the trivalent species is generally only toxic to plants at very high concentrations and is necessary in animal nutrition (*3*). Because of these differences, it is essential to have a knowledge of redox reactions altering the state of Cr in the environment.

Reactions that reduce Cr(VI) to Cr(III) are environmentally beneficial since a hazardous species is transformed into a nonhazardous one that has a low mobility in most soils. Although this alleviates the hazard imposed by Cr(VI), the possibility of Cr(III) oxidation back to Cr(VI) should always be considered. Organic matter (both soluble and

insoluble), Fe(II), and sulfides are capable of reducing hexavalent Cr (*4—8*). Whereas organic reductants of Cr(VI) may form soluble chelated complexes with Cr(III) (*9*), thus enhancing the potential for re-oxidation to Cr(VI) by manganese oxides (*10*), inorganic reductants, e.g., Fe(II), eliminate this possibility by promoting the formation of Cr(III) solids of low solubility (*11*). Moreover, the formation of a solid Cr(III) phase will greatly diminish the potential for transformation back to Cr(VI) (*12*).

The capacity of Fe(II) to reduce Cr(VI) is well demonstrated (*13—16*); Fe(II) is one of the dominant reductants of Cr(VI) used in treating industrial-generated Cr wastes (*13*). Reduction of Cr(VI) by Fe(II)(aq) can be expressed by the following general overall reaction

$$H_xCrO_4{}^{x-2}(aq) + 3Fe^{2+}(aq) + iH_2O \rightleftharpoons$$
$$Cr(OH)_y{}^{3-y}(aq) + 3Fe(OH)_z{}^{3-z}(aq) + jH^+ \quad (1)$$
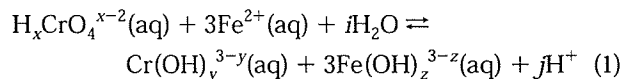
where $i = \{y + 3z\}$ and $j = \{x + y + 3z\}$. Eary and Rai (*13*) observed that Cr(VI) reduction by Fe(II)(aq) was indeed stoichiometric at pH < 10 in simple electrolyte systems. This reaction is rapid with complete reduction occurring within 5 min. Unfortunately, the rapid reaction rate limited obtaining kinetic information on this important process. Further complicating kinetic measurements was the formation of brown precipitates at pH values greater than 4. This precipitate was suspected to form from the reaction

$$xCr(III) + (1 - x)Fe(III) + 3H_2O \rightleftharpoons$$
$$(Cr_xFe_{1-x})(OH)_3 \text{ (s)} + 3H^+ \quad (2)$$
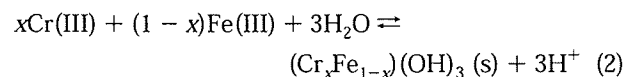
where x can vary from 0 to 1.

Because Fe(II)(aq) concentrations and Fe(II)-bearing solids are prevalent under anoxic conditions, based on reaction 1 Fe(II) should dramatically affect Cr chemistry under such conditions. It is therefore not surprising that Fe(II) was recognized as the dominate reductant of Cr(VI) in a forested wetland soil system at redox levels less than +100 mV (*15*). The role of Fe(II) is especially important when biological activity is limited. Supporting this premise, it was observed that under mildly reducing conditions Fe(II) species were the major reductant of Cr(VI) in sands and gravels of a suboxic aquifer (*16*). Moreover, in acidic soils Fe(II) influenced Cr(VI) at least as much as organic materials (*17*). Even well-crystallized iron oxides such as goethite (α-FeOOH) can have small amounts of Fe(II) that lead to the reduction of Cr(VI) (*18*).

Iron(II) may not have a significant influence on Cr(VI) reduction in oxygenated systems since dissolved O_2 readily oxidizes aqueous Fe(II) to Fe(III) at all but highly acidic pH values (pH < 3) (*19*). However, Eary and Rai (14) have observed that the oxidation of Fe(II)(aq) by Cr(VI) occurred even under well-aerated, high-pH conditions. This finding implies that Fe(II)-bearing minerals undergoing dissolution may significantly impact the reduction of this hazardous form of Cr even in oxygenated systems. In order to determine the extent of Cr(VI) reduction by Fe(II) in oxygenated environments, rate expressions for the oxidation of Fe(II) by Cr(VI) or O_2(g) must be known. The kinetics

* Corresponding author telephone: (208) 885-6767; E-mail address: Fendorf@uidaho.edu.
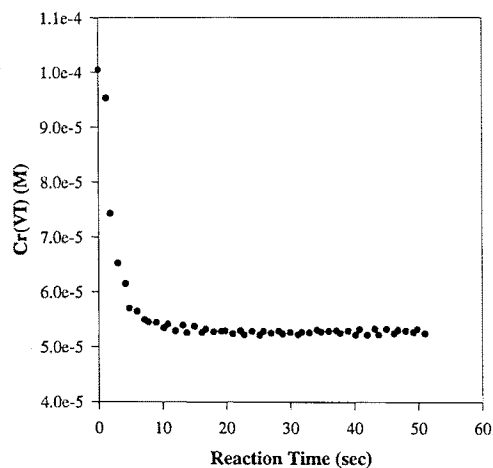
FIGURE 1. Typical UV–VIS monitored stopped-flow kinetic curve for the reduction of Cr(VI) by aqueous Fe(II).
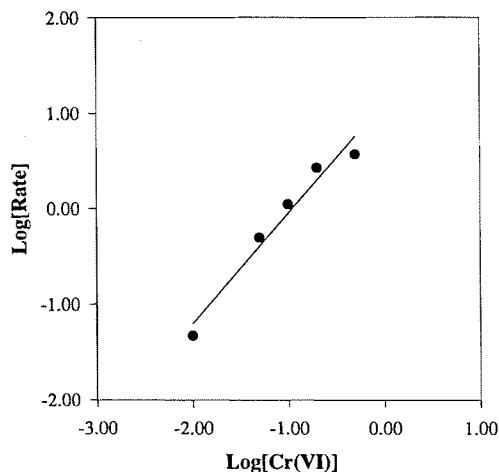

FIGURE 2. Initial rate plot for the dependence of the redox reaction on Cr(VI) concentration. The rate is expressed as mM/min, and the Cr(VI) concentrations are expressed as mM.
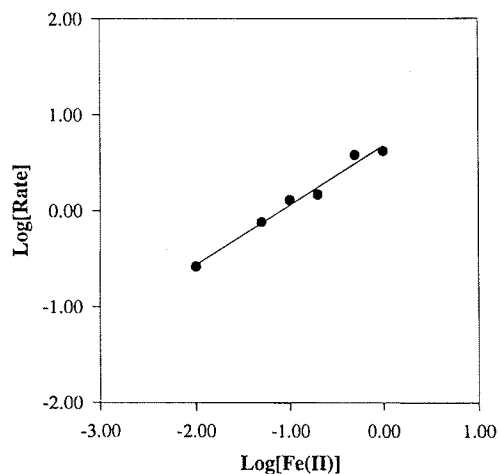

FIGURE 3. Variation of Fe(II) concentration yields an initial rate plot giving the reaction order with respect to this constituent; the rate is in units of mM/min, and the concentration is in mM.

constant over the time of measurement, such as being provided in large excess to the varied reactant. However, because the rate is measured over a very short time period of the reaction, the nonvaried reactant need not necessarily be in excess for this approach (21).

The approach outlined above was used to determine the rate expression for the reduction of Cr(VI). Figure 1 illustrates a typical kinetic curve obtained using the stopped-flow apparatus. By taking the initial linear portion of such curves, the initial reaction rates were obtained. The measured values of the initial reaction rate for various initial conditions are provided in Table 1. The parameters hypothesized to dictate the reaction rate of Cr(VI) removal were Cr(VI) and Fe(II) concentrations. In addition, the reaction rate was also monitored as a function of pH to test for any influences arising from the involvement of H^+ or OH^-, which may enter the reaction directly or influence the hydrolysis or protonation of a reactant.

An initial rate plot with respect to Cr(VI) (Figure 2) resulted in a linear trend ($R^2 = 0.96$) with $n = 1$, indicting a first-order dependence of the reaction rate on [Cr(VI)]. The apparent rate coefficient ($k_{cr}' = k_{cr}[Fe(II)]^n$) was 12.9 min^{-1}, which yields a rate constant of 53.7 $mmol^{-0.6}$ min^{-1} $L^{0.6}$. The initial rate plot of Fe(II) also showed a linear curve ($R^2 = 0.98$) and a 0.6 order dependence on [Fe(II)] (Figure 3). A fractional dependence on Fe(II) in the reduction rate

of Cr(VI) may result from the multistep process described by eq 4. In this reaction sequence, Fe(II) would couple with Cr(VI) as well as reaction intermediates. The rate constant resulting from Fe(II), $k_{cr} = 58.9$ $mmol^{-0.6}$ min^{-1} $L^{0.6}$, is in reasonable agreement with that derived from the variation of Cr(VI). In addition, the initial rate was measured over the pH range of 6.0–8.0 with no significant changes in the reaction rate noted. Therefore, based on this data, the following expression is operational for Cr(VI) reduction by aqueous Fe(II):

$$-\frac{d[(CrVI)]}{dt} = k_{cr}[Fe(II)]^{0.6}[Cr(VI)]^1 \qquad (7)$$

where $k_{cr} = 56.3$ (± 3.7) $mol^{-0.6}$ min^{-1} $L^{0.6}$.

To further validate eq 7, a nonlinear least-squares optimization of the expression in eq 5 was performed for the reaction conditions of 0.1 mM Cr(VI) and Fe(II) with a pH of 6.67. The optimization was performed by varying n_{cr}, n_{fe}, and k, resulting in $n_{cr} = 1$, $n_{fe} = 0.6$, and $k = 64.6$ $mmol^{-0.6}$ min^{-1} $L^{0.6}$. These values are in good agreement with the average values obtained through the measurement of the initial reaction rates. Therefore, based on the measurement of the initial rates and a nonlinear least-squares fitting of the Cr(VI) decay eq 7 seems to be operative with an average rate constant of 56.3 (± 3.7) $mol^{-0.6}$ min^{-1} $L^{0.6}$.

Quantification of the Cr(VI) reduction rate by Fe(II)(aq) permits an evaluation of this process under oxygenated conditions. If the reaction between Cr(VI) and Fe(II) is more rapid than that between Fe(II) and $O_2(g)$, then one may expect appreciable reduction of Cr(VI) by this reductant even in well-aerated systems. Using the rate expressions of eq 3 for the oxygenation of Fe(II) and eq 8 for Cr(VI) reduction, a comparison of the rates was obtained and is presented in Table 2. These calculations were performed assuming atmospheric $O_2(g)$ partial pressures ($pO_2 = 0.20$ atm) and [Fe(II)] = 1×10^{-5} M. It is apparent from Table 2 that even at low concentrations of 10 μM, Cr(VI) will oxidize Fe(II) more rapidly than oxygen at pH values less than 8.0. Furthermore, based on the molecularity of reaction, it may be assumed that the most rapid oxidation of Fe(II) by Cr(VI) would be 3 times the rate of Cr(VI) reduction, leading to the following expression:

$$d[Fe(II)]/dt = 3\ d[Cr(VI)]/dt \qquad (8)$$

TABLE 1

Reaction Parameters Varied in Initial Rate Stopped-Flow Kinetic Studies and Measured Reaction Rate under These Specified Conditions

pH	Fe(II) (M)	Cr(VI) (M)	rate (M min^{-1})
6.67	1.0×10^{-4}	1.0×10^{-5}	4.68×10^{-5}
		5.0×10^{-5}	4.96×10^{-4}
		1.0×10^{-4}	1.11×10^{-3}
		2.0×10^{-4}	2.68×10^{-3}
		5.0×10^{-4}	3.73×10^{-3}
6.67	1.0×10^{-5}	1.0×10^{-4}	2.62×10^{-4}
	5.0×10^{-5}		7.59×10^{-4}
	1.0×10^{-4}		1.29×10^{-3}
	2.0×10^{-4}		1.47×10^{-3}
	5.0×10^{-4}		3.79×10^{-3}
	1.0×10^{-3}		4.17×10^{-3}
6.0	1.0×10^{-4}	1.0×10^{-4}	1.40×10^{-3}
6.67			1.29×10^{-3}
7.5			1.43×10^{-3}
8.2			1.54×10^{-3}

of Fe(II) oxygenation in solution are well-known and conform to

$$-\frac{d[Fe(II)]}{dt} = k_{fe}[Fe(II)][OH^-]^2 pO_2 \qquad (3)$$

where the rate constant k_{fe} equals 8 (±2.5) $\times$ 10^{13} min^{-1} atm^{-1} mol^{-2} L^2 (19). Unfortunately, no rate data are available for the oxidation of Cr(VI) by Fe(II)(aq). Accordingly, it was the objective of this study to determine the rate expression describing the reduction of Cr(VI) by aqueous Fe(II).

Materials and Methods

The rate of Cr(VI) reduction by Fe(II) was measured over the pH range of 6.0–8.0. Many soils and waters are within this pH range, and competition from the oxygenation of Fe(II) is most prevalent at these high-pH values. Redox reaction rates were measured over a range of Cr(VI) and Fe(II) concentrations. Chromium(VI) concentrations ranged from 0.01 to 0.5 mM, and Fe(II) concentrations ranged from 0.01 to 1.0 mM. The specific concentrations and pH values investigated are given in Table 1. All reagents were made from ACS reagent grade materials: Cr(VI) as Na_2CrO_4 and Fe(II) as $FeCl_2$. Stock solutions were made by adding the dried materials to N_2(g) purged distilled deionized water. The solutions were maintained in an O_2(g) limited state by an N_2(g) environment. All reactions were performed in 0.1 mM NaCl to keep a constant ionic strength during the reaction.

To determine the rate constant and reaction orders with respect to both metal ions, an initial rate method (20, 21) and a stopped-flow method monitored by UV–VIS spectrophotometry were used. The reaction rate was monitored by measuring changes in Cr(VI) concentration with time, with Cr(VI) concentrations being recorded by the absorbance at 370 nm. The spectrophotometer was an Aminco DW-2 modified by On-Line Instruments (OLIS) to include a 200-W lamp, a head-on photomultiplier tube, and rapid data acquisition software. The instrumental measurement and mixing times of the reactants were less than 1 s.
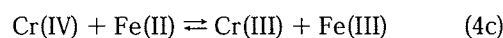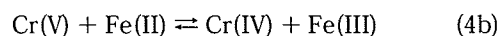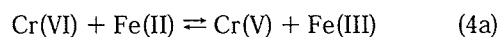
Solutions of each reactant, adjusted to the desired pH, were injected into the mixing cell within the spectrophotometer. The relatively rapid acquisition time of this experimental procedure permitted the initial reaction rate to be monitored. This affords the opportunity to use an initial rate method to determine the reaction order of each constituent and the rate constant for the reaction. An advantage of the method is that the initial reaction rate should be void of complicating reactions imparted from the buildup of reaction products and should be unidirectional (20). Furthermore, the solution pH did not undergo a significant change over this initial reaction period. By varying a single reaction constituent over a range of concentrations while maintaining all other parameters constant, a log–log plot of the reaction rate versus the reactant concentration gives a line with a slope equal to the reaction order and an intercept equal to a rate coefficient. Sequential variation of each reaction parameter thus reveals their order and the rate constant for the reaction.

In addition to the initial rate method, we also deduced the kinetic parameters for reaction 1 using a nonlinear least squares optimization of the reactants order and rate constant. This fitting was conducted using the computer program SAS (22). Analyses were done by allowing the rate constant and the reaction orders with respect to [Cr(VI)] and [Fe(II)] to vary independently.

Results and Discussion

The overall reaction for the reduction of Cr(VI) by Fe(II)-(aq) can be expressed by reaction 1. In the overall reaction, three electrons are transferred to Cr from 3Fe(II). If reaction 1 were an elementary reaction, then the rate expression would be fourth-order, having a first-order dependence on [Cr(VI)] and a third-order dependence on [Fe(II)]. However, redox reactions usually proceed in one electron transfer steps. The reduction of Cr(VI) to Cr(III) would thereby occur in at least three steps as follows:

$$Cr(VI) + Fe(II) \rightleftharpoons Cr(V) + Fe(III) \qquad (4a)$$

$$Cr(V) + Fe(II) \rightleftharpoons Cr(IV) + Fe(III) \qquad (4b)$$

$$Cr(IV) + Fe(II) \rightleftharpoons Cr(III) + Fe(III) \qquad (4c)$$

The production of Cr(III) would be dependent on the concentration of each reactant and a combined rate constant ($k = k_{4a} + k_{4b} + k_{4c}$). Nevertheless, if one measures the removal of Cr(VI) from the system, then the following overall rate expression should result:

$$\frac{d[(CrVI)]}{dt} = k_{cr}[Fe(II)]^m[Cr(VI)]^n \qquad (5)$$

where k_{cr} is the rate constant and m and n are the reaction orders with respect to the given reactants. If either of the reactants in this equation is maintained constant during a reaction series, then the expression simplifies to $R = k_{cr}'$ [V], where R is the reaction rate ($-d[Cr(VI)]/dt$), k_{cr}' is the rate constant multiplied by the concentration of the stationary reactant (in this case either $k_{cr}[Fe(II)]$ or $k_{cr}[Cr(VI)]$), and V is the concentration of the varied reactant. Then, by taking the logarithm of eq 5, a linear equation results:

$$\log R = \log k_{cr}' + n \log [V] \qquad (6)$$

and a plot of this form should yield a slope equal to the reaction order with respect to [V] and an intercept of log k_{cr}'. Optimally the nonvaried reactant should remain

TABLE 2
Reaction Rates for Oxygenation of Fe(II) and Reduction of Cr(VI) as a Function of pH and Chromate Conenctration

pH	oxygenation rate (M min^{-1})[a]	Cr(VI) (M)	Cr(VI) reduction rate (M min^{-1})[a]
4	1.6×10^{-12}	1×10^{-7}	5.6×10^{-6}
5	1.6×10^{-10}	1×10^{-6}	5.6×10^{-5}
6	1.6×10^{-8}	1×10^{-5}	5.6×10^{-4}
7	1.6×10^{-6}	1×10^{-4}	5.6×10^{-3}
8	1.6×10^{-4}	1×10^{-3}	5.6×10^{-2}
9	1.6×10^{-3}		

[a] The values are based on the rate expression of eqs 3 and 7.
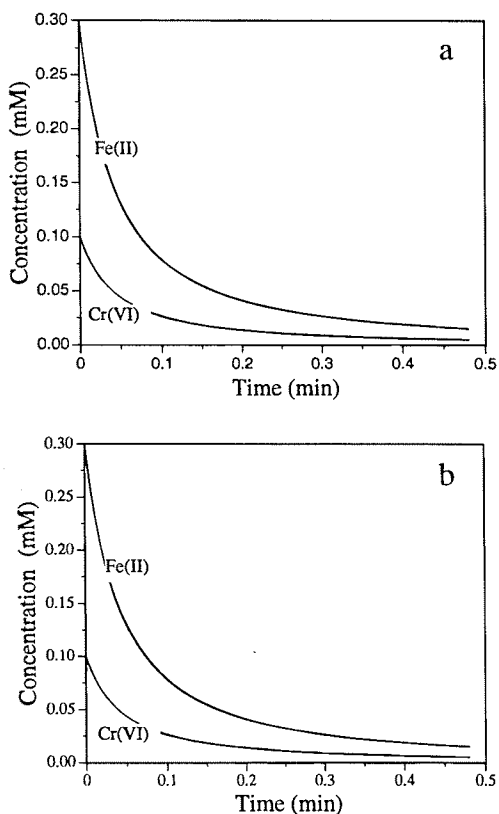

FIGURE 4. Predicted reduction of 0.1 mM Cr(VI) in oxygenated solution by 0.3 mM Fe(II) at (a) pH 6.0 and (b) pH 8.0. The calculated reduction is based on eqs 3, 7, and 8.

Then using eqs 3, 7, and 8, a more quantitative prediction of Cr(VI) reduction by ferrous iron in oxygenated condition can be made.

Figure 4 shows the results of solving these expressions simultaneously using initial concentrations of 0.1 mM for Cr(VI) and 0.3 mM for Fe(II); even at pH 8 the total solution quantity of Cr(VI) was depleted within 0.5 min after reaction. Thus, oxygen would limit Cr(VI) reduction only at very high pH values (pH > 8) or very low Cr(VI) concentrations (Cr-(VI) ≪ 10 μM). As a consequence, Fe(II) should be an effective reductant of Cr(VI) under most soil and water conditions. One should note that in soils or sediments, the oxygenation of Fe(II) may be catalyzed by mineral surfaces (23) and thus decrease the extent of Cr(VI) reduction. In contrast, for sites within soils where oxygen diffusion is limited, creating anaerobic microsites, the oxygenation of Fe(II) would have less of an influence on Cr(VI) reduction. Moreover, despite possible surface effects on the rate of Fe(II) oxygenation, the reduction of Cr(VI) by Fe(II) in aerated systems is verified experimentally (14–17); chromate was reduced by biotite and Fe(II)-bearing hematite under aerated conditions and was dependent on the dissolution of Fe(II) from the minerals (14). This finding has important consequences in that the hazardous form of Cr, Cr(VI), may be transformed to the relatively nontoxic Cr(III) species. In addition, the rate expression for the redox reactions should permit the competitive oxidizing abilities of Cr(VI) and O$_2$(g) for Fe(II) to be determined under various reaction conditions.

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