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# Oxidation Kinetics of Co(II)—EDTA in Aqueous and Semi-Aqueous Goethite Suspensions

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The co-disposal of trace metals (e.g., Co), synthetic chelates (e.g., ethylenediaminetetraacetic acid, H<sub>4</sub>EDTA), and water-miscible organic solvents has occurred at some contamination sites. The present study examines the reactions of Co(II)—EDTA<sup>2-</sup> with a redox reactive naturally occurring solid, goethite, in aqueous and semi-aqueous (methanol—water, acetone—water) suspensions. UV—vis spectroscopy indicated that goethite catalyzed oxidation of Co(II)—EDTA<sup>2-</sup> to Co(III)—EDTA<sup>-</sup> by dissolved O<sub>2</sub>. The aerobic reaction was described by a pseudo-first-order rate constant, *k*, of  $0.0078 \pm 0.0002 \text{ h}^{-1}$  at p[H] 5.0 and a goethite concentration of  $3.09 \text{ g L}^{-1}$ . A decreased oxidation rate under N<sub>2</sub>(g) purge was caused by an accumulation of Fe(II) in the goethite suspensions. The addition of acetone monotonically increased *k*. In contrast, methanol additions up to 20 wt % decreased *k*. Further additions of methanol raised *k* in excess of that observed for fully aqueous suspensions. These reactions have important implications on the fate of the redox-sensitive metal in complex, mixed waste environments.

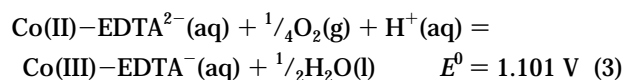
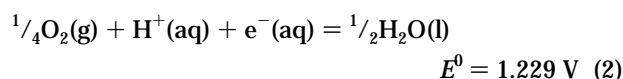
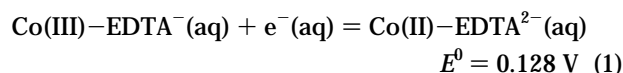
## Introduction

The contamination of soils, surface waters and groundwaters with mixtures of metal ions and complexing organic ligands has received considerable attention (1–3). These mixed contaminant systems are associated with industrial and municipal landfills and with past production of materials for the nuclear power and weapons industries. Complexing agents, organic acids, toxic metals, and radionuclides have been identified as soil/sediment and groundwater contaminants at a number of facilities operated by the U.S. Department of Energy (DOE) (4). Ketones and other organic cosolvents are also present as co-contaminants at several of these sites, and co-contamination by metals/radionuclides, complexing ligands, and organic cosolvents has occurred (4). Predictions of the behavior and fate of any one of these contaminants in soils and sediments is difficult due to a myriad of simultaneous

sorption/desorption, complexation, and oxidation/reduction reactions. This problem is confounded when these substances are present as complex mixtures. The effects of complexing organic ligands on the sorption of metals have been examined by a number of investigators (see reviews in refs 5 and 6), but much less is known about redox transformations in these mixed systems, and little to no information is available on the effects of organic cosolvents on sorption or redox chemistry. Nevertheless, this information is needed to better understand the behavior of these contaminants at many DOE sites. Riley et al. (4) indicated that mixed systems comprised of metals/radionuclides—organic acids/complexing agents—ketones/chlorinated hydrocarbons are ones for which there is a moderate probability of co-contaminant interactions and a significant lack of scientific knowledge.

The environmental behavior of metals complexed by ethylenediaminetetraacetic acid (H<sub>4</sub>EDTA) has been examined by many investigators (1–3, 7). EDTA is resistant to decomposition by ionizing radiation, thermally stable, and very slowly biodegradable. Thus, it is extremely persistent in the environment (1). Particular attention has been paid to Co(II)—EDTA<sup>2-</sup> since the subsurface migration of <sup>60</sup>Co at Oak Ridge National Laboratory and at Chalk River Nuclear Labs has been attributed to the presence of EDTA in soils and groundwater (1, 2).

The oxidation state of Co in Co—EDTA complexes can be either II or III. The thermodynamics of the Co(III)—EDTA<sup>-</sup> and Co(II)—EDTA<sup>2-</sup> in aerobic and acid solutions can be described by the following standard state reactions (8, 9):

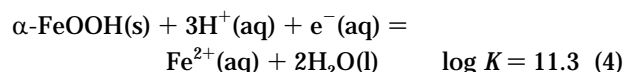


Hence, the equilibrium ratio between Co(III)—EDTA<sup>-</sup> and Co(II)—EDTA<sup>2-</sup> at pH 5, 0.21 atm of O<sub>2</sub>(g), and 25 °C can be calculated as  $>10^{13}$ . However, there is evidence that the homogeneous oxidation reaction is kinetically unfavorable. Adamson and Gonick (10) reported that the oxidation of Co(II)—EDTA<sup>2-</sup> by atmospheric oxygen was noticeable overnight in acidic ferric sulfate solutions. Jardine et al. (11) observed much slower oxidation by O<sub>2</sub> in aqueous CaCl<sub>2</sub> solutions. This discrepancy may have been due to the differences in these experimental systems.

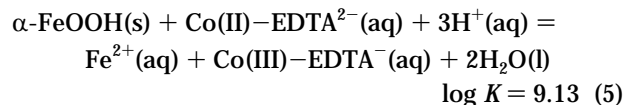
It has been well established that naturally occurring manganese oxides rapidly oxidize Co(II)—EDTA<sup>2-</sup> into Co(III)—EDTA<sup>-</sup> (11). Moreover, Huchital and Wilkins (12) found that Fe(CN)<sub>6</sub><sup>3-</sup> also oxidizes Co(II)—EDTA<sup>2-</sup> to Co(III)—EDTA<sup>-</sup> in minutes. Nonetheless, there has been little information on the redox couple between naturally occurring iron oxides and Co(II)—EDTA<sup>2-</sup> complexes.

Goethite (α-FeOOH) is a common, naturally occurring iron oxide. Its reductive—dissolution reaction can be written as follows (13):

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One can derive the redox reaction for Co(II)–EDTA<sup>2-</sup> and goethite as



At equilibrium conditions of pH 5 and 25 °C, the ratio of Co(III)–EDTA<sup>-</sup> to Co(II)–EDTA<sup>2-</sup> is given as 10<sup>-5.87</sup>/(Fe<sup>2+</sup>). As a result, the redox reaction will be thermodynamically favorable under aerobic conditions when the solution activity of Fe<sup>2+</sup> is low but unfavorable in anoxic environments when free Fe(II) exists.

The Co(III)–EDTA<sup>-</sup> ion is an extremely strong complex, with a log *K* value of 41.4, while that of Co(II)–EDTA<sup>2-</sup> is 16.45. The log *K* values for Fe(III)–EDTA<sup>-</sup> and Fe(II)–EDTA<sup>2-</sup> are 25.1 and 14.3, respectively (14). As stated above, the migration of <sup>60</sup>Co away from waste disposal pits and trenches has been attributed to ligand-facilitated metal transport (1). Without complexation, Co(II) is easily retarded by subsurface solid materials through adsorption, ion exchange, and precipitation reactions. After being oxidized to Co(III)–EDTA<sup>-</sup>, virtually no other common cations in the environment can displace Co from the Co(III)–EDTA<sup>-</sup> complex because of its overwhelming stability. Oxidation of Co(II)–EDTA<sup>2-</sup> to Co(III)–EDTA<sup>-</sup> affects the transport and fate of Co in surface and subsurface environments (3), and information on the role of iron oxides on this reaction is needed. Furthermore, the presence of organic cosolvents in many DOE sites warrants the examination of these redox reactions in semi-aqueous media. It is anticipated that the cosolvents inducing changes in the dielectric constant of the solution and/or specific solvent interactions with the solutes and the goethite surface will affect the oxidation of Co(II)–EDTA<sup>2-</sup> in these environments.

The present study employed UV–vis spectroscopy to examine the dynamics of Co–EDTA reactions with goethite in aqueous and semi-aqueous solutions. Methanol (MeOH)–water and acetone–water mixtures were chosen as model cosolvent systems. The resulting information should prove useful in assessing the potential significance of the oxidation of Co(II)–EDTA<sup>2-</sup> in complex waste environments and in contaminated soils, sediments, and groundwaters.

## Experimental Section

**Materials.** All chemicals used in this investigation were ACS reagent grade unless otherwise indicated. Goethite was prepared in plastic bottles with Fe(NO<sub>3</sub>)<sub>3</sub> (Baker Analyzed reagent) (15, 16), and the resulting suspension was dialyzed with distilled-deionized water until the solution conductivity dropped below 10<sup>-4</sup> S m<sup>-1</sup>. The suspension was then freeze-dried. An X-ray diffraction (XRD) pattern, obtained with Cu Kα radiation (Philips XRG 3100 X-ray generator) (for detailed XRD procedures, see ref 17), was found to be identical to that of a standard reported in the literature (17). The synthesized goethite was crystalline, and no XRD detectable impurities were present. Inductively coupled plasma (ICP) emission spectroscopy analyses of the acid-digested goethite indicated a stoichio-

metric Fe content. The concentrations of Co, Cd, Cu, Na, and Pb were <1.0, 10.0, 31.1, 783, and 12.8 mg kg<sup>-1</sup>, respectively. The specific surface area determined by the N<sub>2</sub>-BET method was 64.3 ± 0.8 m<sup>2</sup> g<sup>-1</sup>.

Co(III)–EDTA<sup>-</sup> was prepared after ref 8, and Co(II)–EDTA<sup>2-</sup> was prepared by mixing Na<sub>2</sub>H<sub>2</sub>EDTA with Co(NO<sub>3</sub>)<sub>2</sub>. The purity of the complexes was checked (≥98%), and the concentrations of the complexes in the stock solutions were standardized by UV-vis spectroscopy based on the molar absorptivity values reported in refs 10 and 18. The 3d electron transfers in Co–EDTA complexes are quantum mechanically forbidden, so the molar absorptance values are small and in the order of 10–100 M<sup>-1</sup> cm<sup>-1</sup> in the wavelength range of 300–800 nm.

**Kinetic Experiments.** Batch experiments were carried out to study the kinetics of Co(II)–EDTA<sup>2-</sup> oxidation by goethite. Goethite powder was suspended in the solvents (~3 g L<sup>-1</sup>) and dispersed by sonification. The suspensions were stirred during the reaction. All experiments were conducted at room temperature (23 ± 2 °C). A constant p[H] was maintained throughout each experiment by adding small amounts of concentrated HCl or KOH solutions. In all experiments, the total Co concentration was about 1 mmol L<sup>-1</sup>. The total EDTA concentration was 1.2× the total Co concentration to ensure that virtually all Co was complexed in the iron oxide suspension. A background electrolyte of 0.1 M (CH<sub>3</sub>)<sub>4</sub>NCl (Me<sub>4</sub>NCl) (Aldrich, Milwaukee, WI) was used in all experiments. Me<sub>4</sub>NCl<sup>+</sup> is a very inert electrolytic cation because of its small ionic potential. HPLC-grade acetone and MeOH (Fisher Optima, Fairlawn, NJ) were used in the semi-aqueous kinetic experiments.

In the beginning of the kinetic experiments, previously prepared Co(II)–EDTA<sup>2-</sup> was mixed with the goethite suspensions. Aliquots of the suspensions were periodically removed and rapidly filtered through 0.2-μm membrane filters (Supor-200, 25 mm, Gelman Sciences, Ann Arbor, MI) to separate the solid phase from the dissolved phase (operationally defined here as particles < 0.2 μm). Spectra of the dissolved Co–EDTA were measured from the filtrates with a UV–vis spectrophotometer (Cary-3, Varian, Australia) equipped with 1-cm quartz cuvettes. Total concentrations of dissolved Co and Fe were measured by atomic absorption spectrophotometry (AAS) using a Perkin-Elmer Model 3030B AAS equipped with flame atomization. Dissolved O<sub>2</sub> concentrations were varied by continuously purging the samples with either air, pure O<sub>2</sub> (denoted as “aerobic”), or N<sub>2</sub> gas (denoted as “anoxic”). Gas purging in the semi-aqueous experiments was limited to flushing of the head space in the reaction vessel. In some cases, aluminum foil was used to wrap the reaction vessel to explore the effect of light on the kinetics.

Solution p[H] measurements were made in both aqueous and semi-aqueous solutions. The glass electrode was calibrated by strong acid and strong base solutions to measure proton concentration [H]; details of the calibration procedure are presented elsewhere (19). Ross Sure-flow pH glass electrodes designed for use in suspensions (Orion, Boston, MA) were utilized to measure p[H] in both the aqueous and semi-aqueous suspensions.

## Results and Discussion

**Evidence of Oxidation and Oxidation Kinetics.** The UV–vis spectra of Co(III)–EDTA<sup>-</sup> and Co(II)–EDTA<sup>2-</sup> measured in this study (Figure 1) were identical to those reported in

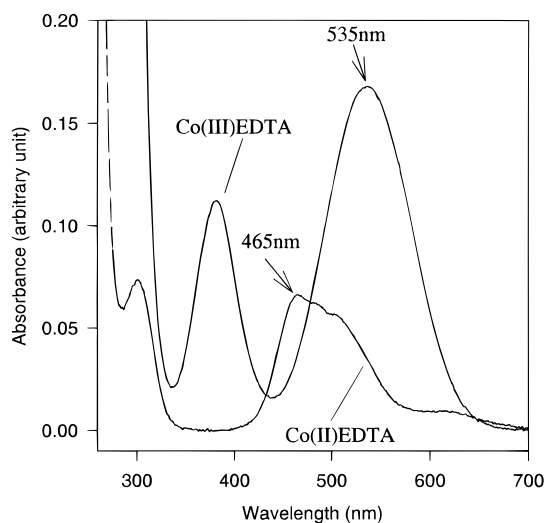


FIGURE 1. UV-vis spectra of Co(II)-EDTA ( $5 \times 10^{-3}$  M) and Co(III)-EDTA ( $5.11 \times 10^{-3}$  M) complexes in water, p[H] 5.6.

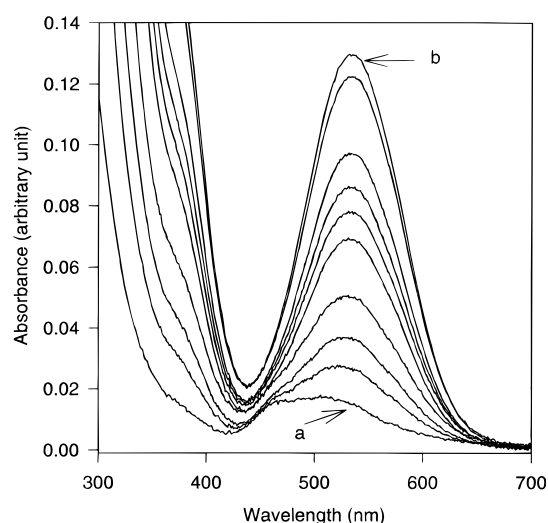


FIGURE 2. Oxidation of Co(II)-EDTA to Co(III)-EDTA as seen by UV-vis spectra. Absorbance increased with increasing reaction time from spectra a to spectra b.  $23 (\pm 2)^\circ\text{C}$ , 0.1 M  $\text{Me}_4\text{NCl}$  as electrolyte.

the literature (10). Both Co(II)-EDTA<sup>2-</sup> and Co(III)-EDTA<sup>-</sup> show multiple peaks in the wavelength range of 250–700 nm but at different absorption maxima. The molar absorbance for Co(II)-EDTA<sup>2-</sup> was  $13.3 \text{ M}^{-1} \text{ cm}^{-1}$  at 465.27 nm,  $25^\circ\text{C}$ , 0.1 M  $\text{Me}_4\text{NCl}$ , and p[H] 4.1, and the molar absorbance of Co(III)-EDTA<sup>-</sup> was  $331 \text{ M}^{-1} \text{ cm}^{-1}$ , under the same solution conditions, at a wavelength of 535 nm. Figure 2 shows a series of spectra acquired at different times during a kinetic experiment. Only Co(II)-EDTA<sup>2-</sup> is present in the solution at the beginning of the experiment. Increased reaction time caused a red shift in the peak position and an increase in peak amplitude, consistent with the formation of Co(III)-EDTA<sup>-</sup>.

The absorbance at 535 nm was used to quantify the Co(III)-EDTA<sup>-</sup> formation rate. The values of  $\epsilon_{535}$  in aqueous solutions for Co(III)-EDTA<sup>-</sup> and Co(II)-EDTA<sup>2-</sup> were measured as 331 and  $7.30 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively, and remained constant for the p[H] range of 4.1–6.0, with or without 0.1 M  $\text{Me}_4\text{NCl}$ . The concentration of dissolved Co(II)-EDTA<sup>2-</sup> was calculated by

$$\text{Co(II)-EDTA} = C_0 - [A - 0.6 \times C_0 \times \epsilon_{\text{II}}] / \epsilon_{\text{III}} \quad (6)$$

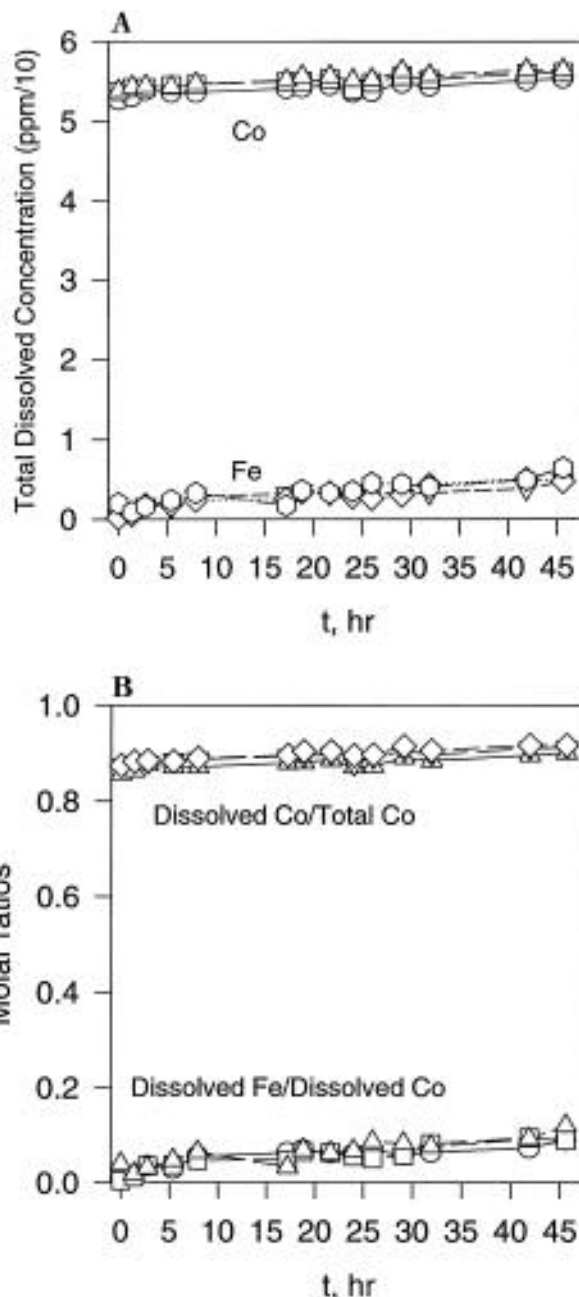


FIGURE 3. Changes of concentrations of dissolved Co and Fe with time in a kinetic reaction in water.  $23 (\pm 2)^\circ\text{C}$ , 0.1 M  $\text{Me}_4\text{NCl}$  as electrolyte, triplicates. (A) Total concentrations. (B) Molar ratios of metals.

where  $C_0$  is the analytical Co concentration,  $A$  is the absorbance measured at each sampling time at 535 nm, and  $\epsilon_{\text{II}}$  and  $\epsilon_{\text{III}}$  are molar extinction coefficients at 535 nm for Co(II)-EDTA and Co(III)-EDTA, respectively. Beer's law was observed in the concentration and wavelength ranges in this study. The absorbance at 535 nm was due to both Co(II)-EDTA<sup>2-</sup> and Co(III)-EDTA<sup>-</sup>. As the conversion proceeded, the contribution from Co(II)-EDTA<sup>2-</sup> to the total absorbance at this wavelength decreased rapidly and became insignificant. A value of  $0.6C_0$  was used in eq 6 and in all other kinetic calculations, representing an average concentration of Co(II)-EDTA<sup>2-</sup> during the reaction process. Solution composition analyses showed that about 80–90% of the total Co remained in the solution phase (Figure 3). However, if 1.0 or 0 were used in eq 6 instead of 0.6, the resulting kinetic rate constants would

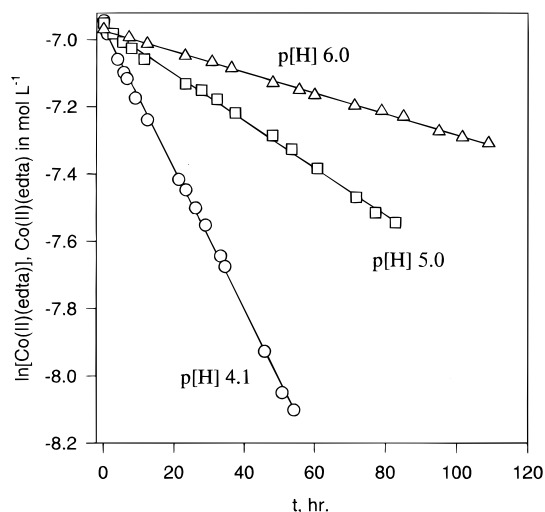


FIGURE 4. Oxidation kinetics of Co(II)–EDTA in water at different p[H]s, 23 (± 2) °C, 0.1 M Me<sub>4</sub>NCl as electrolyte.

still be within one standard deviation of one another. We assumed that Co(III)–EDTA<sup>−</sup> did not adsorb significantly as compared to Co(II)–EDTA<sup>2−</sup> on the solid, so the total Co(III)–EDTA<sup>−</sup> concentration could be obtained by the absorbance measurement. If Co(III)–EDTA<sup>−</sup> adsorption was not negligible, the above calculation would have underestimated the oxidation rate. However, that does not seem to be likely. Zachara et al. showed that Co(III)–EDTA<sup>−</sup> forms weaker surface complexes on goethite than Co(II)–EDTA<sup>2−</sup> (20). Thus, when Co(II)–EDTA<sup>2−</sup> and Co(III)–EDTA<sup>−</sup> co-exist in a goethite suspension, Co(II)–EDTA<sup>2−</sup> is expected to be the dominant surface species. The Co(II)–EDTA<sup>2−</sup> concentration, calculated from eq 6, versus a time relationship was found to follow a pseudo-first-order rate equation (Figure 4), with rate constants of 0.017 (SD = 0.0006), 0.0078 (SD = 0.0002), and 0.0036 (SD = 0.0001) h<sup>−1</sup> for p[H] 4.1, 5.0, and 6.0, respectively, at 23 °C and 0.1 M Me<sub>4</sub>NCl. The calculated pseudo-first-order rate constants referred to the total transformation rate in suspension. The total dissolved Co concentration showed a slight increase with time (Figure 3), indicating reduced adsorption of Co–EDTA. This was likely due to the production of the less adsorbed Co(III)–EDTA<sup>−</sup>. The concentration of total dissolved Fe was always <20% of the concentration of dissolved Co. Dissolved Fe concentrations increased slowly with reaction time (Figure 3), indicating the existence of colloidal iron oxide that passed through the 0.2-μm membrane or dissolution of the goethite by EDTA. Fe was detected by flame AAS in the filtrates from goethite–water suspensions without Co and EDTA. MINTEQA2 (21) calculations indicated that Fe solubilities in the absence of EDTA would be orders of magnitude lower than was observed in the present study. Therefore, the dissolved Fe was likely in the form of colloidal iron oxide and possibly Fe–EDTA. The excess of EDTA in these experiments ensured complete complexation of Co.

At a p[H] value of 5.0 and 0.1 M Me<sub>4</sub>NCl as the supporting electrolyte under air, the rate constant for Co(II)–EDTA<sup>2−</sup> oxidation by goethite was 0.0078 (SD = 0.0002) h<sup>−1</sup>. A value of 0.0078 (SD = 0.00029) h<sup>−1</sup> was obtained under the same conditions in foil-wrapped reaction vessels indicating a lack of photosensitivity.

**Effect of Goethite Concentration.** The pseudo-first-order rate constants increased about linearly with the

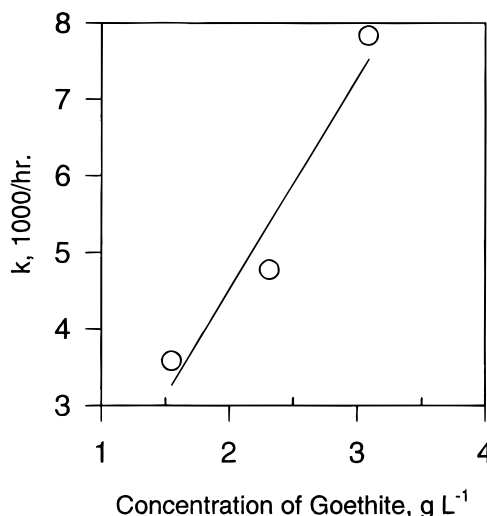


FIGURE 5. Effect of goethite concentration on oxidation kinetic rate *k* for Co(II)–EDTA.

goethite concentration (Figure 5). Oxidation kinetic reactions were also conducted in the absence of the iron oxide under aerobic conditions, with a total Co concentration of 1 mmol L<sup>−1</sup>. Fe(NO<sub>3</sub>)<sub>3</sub> and Fe(III)–EDTA<sup>−</sup> were used in place of goethite, respectively, and the total Fe concentrations were 0.2 mmol L<sup>−1</sup> (11.2 ppm). Total dissolved Fe in the filtrates from the experiments with goethite were around 0.18 mmol L<sup>−1</sup> (10.1 ppm) (Figure 3). Thus, the homogeneous solutions contained roughly the same amount of dissolved Fe as the heterogeneous systems. The reaction rate in the homogeneous solutions was one-sixth of that when goethite was present, at p[H] 5.0. In the case of Fe(NO<sub>3</sub>)<sub>3</sub>, with an EDTA/Co ratio of unity, only about 3% of Co(II)–EDTA<sup>2−</sup> was converted to Co(III)–EDTA<sup>−</sup> after 21 h, at p[H] 5.0. MINTEQA2 (21) simulations were carried out to speciate Fe<sup>2+</sup> in the solution phase. When total Fe concentrations were 2 × 10<sup>−5</sup> and 1.0 × 10<sup>−4</sup> mol L<sup>−1</sup>, at p[H] 5.0, 25 °C, and 0.1 M ionic strength, the calculated concentrations of Fe<sup>2+</sup>(aq) were 1.98 × 10<sup>−5</sup> and 9.92 × 10<sup>−5</sup> mol L<sup>−1</sup>, respectively. Concentrations of Fe(OH)<sup>+</sup> were 2 orders of magnitude smaller than Fe<sup>2+</sup> in both cases. In a homogeneous solution, Fe<sup>2+</sup> is oxidized by dissolved O<sub>2</sub> 6 orders of magnitude slower than Fe(OH)<sup>+</sup> is oxidized (22). When iron oxide is present, the oxidation of adsorbed Fe(II) is about as fast as the homogeneous aqueous oxidation of Fe(OH)<sup>+</sup>, since an –O– group that is coordinated to Fe(II) acts as a bridge for electron transfer (22). It is possible that the Fe(II) species produced during the oxidation of Co(II)–EDTA<sup>2−</sup> was not readily reoxidized by dissolved oxygen at p[H] 5 in the absence of an iron oxide surface, resulting in a decrease in the overall rate of Co(II)–EDTA<sup>2−</sup> oxidation.

Another mechanism may have played a role in the homogeneous system. Fe(III) in solution might have displaced Co(II) from Co(II)–EDTA<sup>2−</sup> faster than it could oxidize Co(II)–EDTA<sup>2−</sup> to Co(III)–EDTA<sup>−</sup>. When Fe(III) was in the iron oxide structure, its ability to replace Co(II) from Co(II)–EDTA<sup>2−</sup> may be reduced so that the redox reaction can occur. Szecsody et al. (3) have reported this type of displacement. Reaction with Co(II)–EDTA<sup>2−</sup> did not change the bulk crystal structure of goethite or create a new crystal phase, as evidenced by XRD analysis (diffraction pattern not shown). However, small changes in the surface structure of the goethite particles could not be ruled out by XRD.

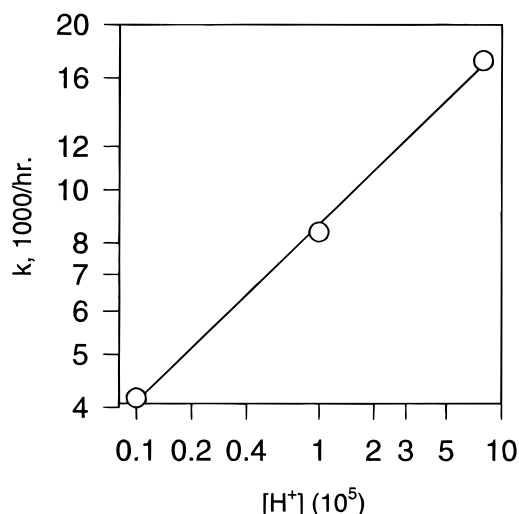


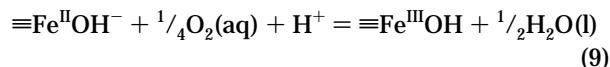
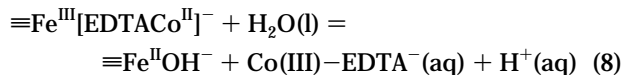
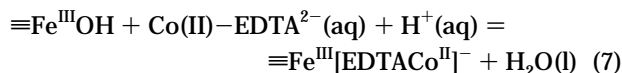
FIGURE 6. Effect of  $p[H]$  of the solution phase on oxidation kinetic rate  $k$  for  $\text{Co(II)-EDTA}$ .

**Effect of Dissolved Oxygen.** When reacted under  $\text{N}_2$  at  $p[H]$  4.1, the oxidation of  $\text{Co(II)-EDTA}^{2-}$  by goethite was significantly slower (decreased by 92.3%) than when purged with air or pure  $\text{O}_2$ . At  $p[H]$  4.1, the pseudo-first-order rate constants for the oxidation reaction were 0.017 (SD = 0.0004)  $\text{h}^{-1}$  in air and 0.017 (SD = 0.004)  $\text{h}^{-1}$  under  $\text{O}_2$ . Using  $10^{-3.066}$   $\text{mol L}^{-1} \text{atm}^{-1}$  as the Henry's law constant for  $\text{O}_2$  at 25 °C (23), the dissolved  $\text{O}_2$  concentration was calculated to be  $2 \times 10^{-4}$   $\text{mol L}^{-1}$  when the  $\text{O}_2$  pressure was 0.21 atm and to be  $8.6 \times 10^{-4}$   $\text{mol L}^{-1}$  when the  $\text{O}_2$  pressure was 1.0 atm. In the anoxic suspension,  $\text{Fe}^{2+}$  ions produced in the redox reactions likely adsorbed onto the goethite surface, and some may have also remained in solution. Because of the accumulation of  $\text{Fe(II)}$  in the suspension, the oxidation of  $\text{Co(II)-EDTA}^{2-}$  was much slower than in aerobic suspensions where  $\text{Fe(II)}$  was rapidly reoxidized so that active surface redox sites were regenerated. Dissolved  $\text{O}_2$  concentration was not rate limiting when the  $\text{O}_2$  concentration was  $10^{-4}$   $\text{mol L}^{-1}$  or higher. This is consistent with the fact that  $\text{Fe(II)}$  cannot exist in aerobic suspensions containing iron oxide, since the half-life of  $\text{Fe(II)}$  is less than 1 min in this situation (22). As a result, the oxidation of  $\text{Co(II)-EDTA}^{2-}$  occurred through an electron transfer to the surface  $\text{Fe(III)}$ . Obviously, oxidation of  $\text{Fe(II)}$  by dissolved  $\text{O}_2$  regenerated  $\text{Fe(III)}$  for further reaction with  $\text{Co(II)-EDTA}^{2-}$  when the goethite surface was present. In any event, in subsurface zones where dissolved  $\text{O}_2$  concentrations can be much smaller than  $10^{-4}$   $\text{mol L}^{-1}$ , the reoxidation of  $\text{Fe(II)}$  could become rate limiting.

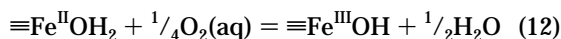
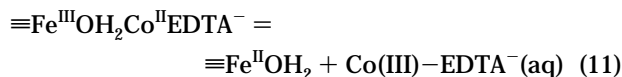
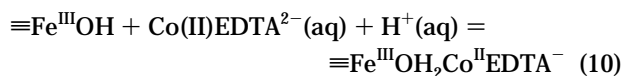
**Effect of  $p[H]$ .** Between  $p[H]$  4.1 and 6.0, lowering  $p[H]$  promoted the oxidation of  $\text{Co(II)-EDTA}^{2-}$  (Figure 6) with the pseudo-first-order rate constant  $k$  approximately proportional to  $[H^+]^{1/3}$ . At neutral or alkaline  $p[H]$ , no transformation was observed over a period of 100 h. Goethite carries a positive charge in the  $p[H]$  range under study because its point of zero charge (pzc) is about 8.0 (16). Thus, lower  $p[H]$  values promote greater positive surface charge. A more positively charged surface can attract the  $\text{Co(II)-EDTA}^{2-}$  complex and surface  $\text{Fe(III)}$  will be more readily exposed to the complex ions.

**Reaction Pathways.**  $\text{Co(II)-EDTA}^{2-}$  can undergo oxidation reactions via an inner-sphere redox mechanism (e.g., with  $[\text{Fe(CN)}_6]^{3-}$  as the oxidant (24)). In contrast,  $[\text{Co(en)(ox)}_2]^-$  (en = ethylenediamine, ox = oxalate) and

$[\text{Co(en)}_3]^{2-}$  can react through an outer-sphere redox mechanism (25). A possible inner-sphere mechanism for the redox reaction studied here could be formulated as follows ( $\equiv$  represents a surface site), analogous to the redox reaction between  $\text{Co(II)-EDTA}^{2-}$  and  $[\text{Fe(CN)}_6]^{3-}$  to form  $\text{Co(III)-EDTA}^-$  and  $[\text{Fe(CN)}_6]^{4-}$  (24):



A possible outer-sphere redox mechanism analogous to the outer-sphere oxidation reaction of  $\text{V}^{\text{II}}\text{L}_3 \rightarrow \text{V}^{\text{III}}\text{L}_3$  (L = unspecified ligand) by the  $\text{Fe(III)/Fe(II)}$  pair of hematite can be written as follows (22):



The most direct way to determine the redox mechanism in a complex system such as this is surface chemical analyses. It is difficult, based on bulk experiments without experimental surface speciation, to distinguish the two alternate pathways because the forms of the kinetic rate laws for the above two mechanisms would be the same. If we assume that the last reactions in eqs 9 and 12 were kinetically fast toward the right side (not rate limiting) and the adsorption/desorption reactions in eqs 7 and 10 were fast enough (i.e., at equilibrium), the rate law derived would be as follows:

$$-d[\text{Co(II)-EDTA}(\text{aq})]/dt = k[\equiv\text{Fe}^{\text{III}}\text{OH}][\text{H}^+(\text{aq})][\text{Co(II)-EDTA}(\text{aq})] \quad (13)$$

However, the experimentally obtained rate was  $\propto [\equiv\text{Fe(III)OH}][\text{H}^+]^{1/3}[\text{Co(II)-EDTA}^{2-}]$ . The dependence of the rate law on  $[\text{H}^+]$  rests on how surface OH species are written, which depends on solution  $p[H]$ . Since the PZC of goethite is approximately 8.0, some surface sites may be protonated beyond  $\equiv\text{FeOH}$ . Plus, one  $\text{H}^+$  could be associated with  $\text{Co(II)-EDTA}^{2-}$  to form  $[\text{Co}^{\text{II}}\text{HEDTA}]^-$ . Thus, an exponential term smaller than one could arise for  $[\text{H}^+]$  in the rate law expression. All these effects would result in a different exponential value for proton concentration in the experimentally obtained rate law expression than that derived from molecular mechanisms as shown in the above two schemes. Knowledge of the redox mechanism becomes important when further theoretical analysis is sought. For example, transition state theory in its usual form cannot be applied to a reaction scheme composed of eqs 10–12 because there are no bonds formed or broken during the electron transfer. Instead, a theory based on the Franck–Condon principles is needed (26).

**Effect of Cosolvents.** When acetone–water mixtures were used instead of just water, the rate of  $\text{Co(II)-EDTA}^{2-}$

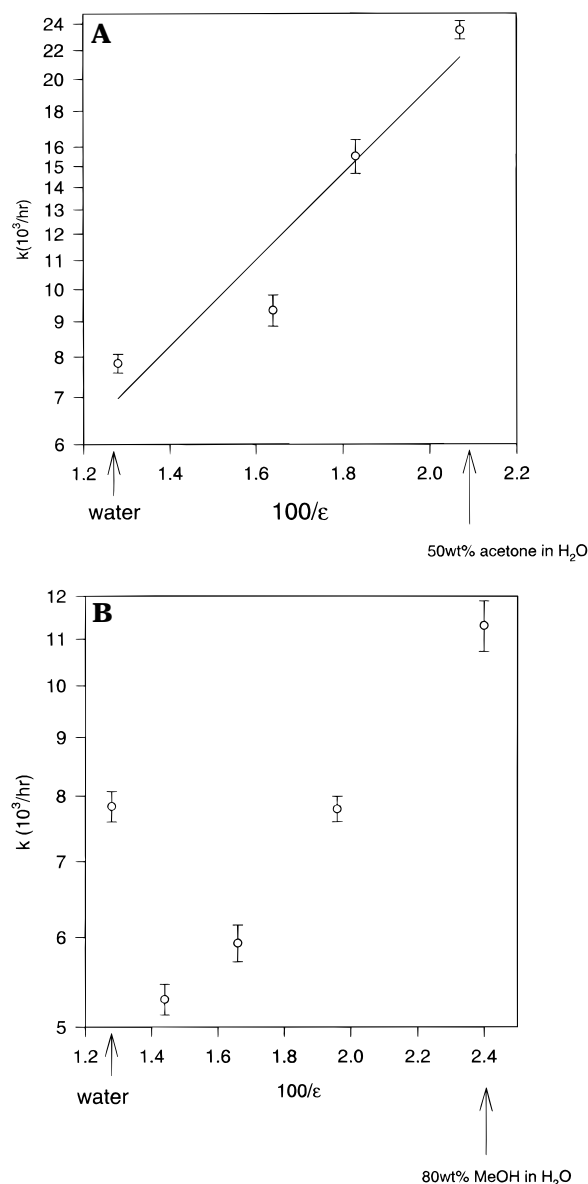


FIGURE 7. Effect of organic cosolvents on Co(II)–EDTA oxidation kinetic rate  $k$ . Error bars are one standard deviation.  $\epsilon$  is dielectric constant of the solution phase. (A) Effect of acetone. (B) Effect of methanol.

oxidation by goethite increased as the acetone content increased (Figure 7A). When the acetone content was 50% by weight, the pseudo-first-order rate constant was  $0.024$  ( $\text{SD} = 0.0007$ )  $\text{h}^{-1}$  at  $\text{p[H]}$  5.0, or three times that in water. The cosolvent may have promoted the association between the negatively charged Co(II)–EDTA $^{2-}$  and the positively charged goethite surface, due to the lowered permittivity of the solution phase, and thus increased the rate constant. However, the cosolvent effect was more complex than could be accounted for by just electrostatic effects. This is shown by the kinetics in MeOH–water suspensions (Figure 7B). The pseudo-first-order rate constant  $k$  decreased first and then increased. The  $k$  at  $\text{p[H]}$  5.0 was  $0.011$  ( $\text{SD} = 0.0006$ )  $\text{h}^{-1}$  or 1.4 times the corresponding rate constant in water. Besides the electrostatic effect caused by the lowered permittivity due to the presence of cosolvents, organic cosolvent molecules may solvate the cations, anions, and the charged surface sites to different degrees than water. This could result in enhanced or reduced surface affinity for Co–EDTA complexes in cosolvents as opposed to

aqueous systems. If the solution phases were merely inert media, a linear relationship would be expected in Figure 7 based on the dielectric continuum medium model (24). In fact, the model is more applicable to nonpolar solvents. The nonlinearity in Figure 7B was evidence of specific solvent effects, which are difficult to theorize. However, once the methanol content exceeded about 20 wt % ( $100/\epsilon \approx 1.45$ ), changes in the dielectric constant of the solvent overwhelmed specific solvent effects, and the rate constant increased monotonically as predicted by theory.

## Conclusions

The oxidation of Co(II)–EDTA $^{2-}$  in an aerobic goethite suspension observed a pseudo-first-order rate law on Co(II)–EDTA $^{2-}$ , with the empirical rate law constant  $k = k'[\text{goethite}][\text{H}]^{1/3}$ , where  $k'$  was a constant, at  $23^\circ\text{C}$  for  $\text{p[H]}$  4–6. The dependence of the reaction rate on the presence and amount of goethite in the experimental systems clearly indicates that Co(II)–EDTA $^{2-}$  was oxidized by  $\text{O}_2$  through the catalysis of the iron oxide. Clearly the presence of goethite and likely other iron(III) oxides and hydroxides will influence the fate and transport of Co–EDTA in subsurface environments. The rate constants determined in this study were composite ones. For example, adsorbed species may react with different activation energies due to the heterogeneity of the adsorption sites on the sorbent (22). The form of the oxidation rate law may be dependent on  $\text{p[H]}$ . For example, the homogeneous oxidation rate of Fe(II) by dissolved  $\text{O}_2$  in water is  $\propto [\text{H}^+]^{2-}$  to  $[\text{H}^+]^{1-}$  at a  $\text{p[H]}$  value below  $\text{p[H]}$  5. The rate constants become  $\text{p[H]}$  independent below  $\text{p[H]}$  3 (22). In moderately acidic and oxic soil environments, Co(II)–EDTA $^{2-}$  complexes would be converted into Co(III)–EDTA $^-$  in a matter of days in the presence of iron oxides. In the groundwater systems where dissolved  $\text{O}_2$  is far below the saturated concentration, the rate law is expected to depend on dissolved  $\text{O}_2$  concentration. The rate will be slower.

It must be noted that the concentrations of dissolved Co in this study likely exceed those found at most waste sites, especially in the downstream plume far from sources. Because the oxidation of Co(II)–EDTA $^{2-}$  by goethite in aerobic conditions observed a pseudo-first-order rate law, the reaction half-life does not depend on Co(II)–EDTA $^{2-}$  concentration. In the mixed solvent systems occurring in nature, the rate could be very much different from that in water. As the rate changes nonlinearly with the change in composition of the mixed solvent solution, environmental modeling of the transport and fate of Co–EDTA complexes becomes more complicated. Near-site or far-from-site conditions will vary as the composition of the mixed solvent solution changes with distance from the disposal site. Additionally, Co(III)–EDTA $^-$  could be reduced to Co(II)–EDTA $^{2-}$  in a reducing environment with abundant free  $\text{Fe}^{2+}$ , as suggested by our preliminary experiments.

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