ABSTRACT

Title of Dissertation: CHROMIUM OXIDATION AND REDUCTION BY HYDROGEN PEROXIDE IN DIVERSE SOILS AND SIMPLE AQUEOUS SYSTEMS

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Hydrogen peroxide is being tested for *in situ* remediation of buried contaminants – either as a direct chemical oxidant in Fenton-type reactions or as a source of oxidizing equivalents in bioremediation. How it affects a common co-contaminant, Cr, is explored here in four chemically diverse high-Cr soils.

Soils contaminated with high levels of soluble Cr(VI) from ore processing and soils containing high levels of recently reduced Cr(III) from electroplating waste showed marked increases in chromate after single applications of 1-25 mM peroxide. Cr(VI) in the leachates exceeded the drinking water standard (2μM) by 1-3 orders of magnitude. Soluble Cr(III), in the form of dissolved organic complexes, contributed to the likelihood of Cr(III) oxidation. Anaerobic soil conditions at a tannery site

prevented oxidation of Cr(III). Naturally occurring Cr in serpentine soil also resisted oxidation. Ambient soluble Cr(VI) in a contaminated aquifer disappeared from peroxide leachates below pH 5, then reappeared as peroxide levels declined.

In solutions prepared under environmentally relevant conditions, aged 280 μM Cr(III) treated with 100 μM H_2O_2 showed increases in Cr(VI) over weeks with maximum oxidation rates achieved in solutions prepared with 2:1 and 4:1 OH^-:Cr. Although Cr(III) speciation differs in fresh and aged aqueous systems, a similar mechanism involving the pre-equilibrium step: $Cr(OH)_2^+ + OH^- \rightleftharpoons Cr(OH)_3^0$ may account for Cr(III) oxidation in both systems. Under alkaline conditions, H_2O_2 enhanced the oxidative dissolution of $Cr_n(OH)_{3n}^0$. The formation of peroxochromium compounds in the presence of H_2O_2 and Cr(VI) may account for the disappearance and reappearance of Cr(VI) in H_2O_2 treated soils; as does the possible formation and subsequent reoxidation of $Cr^{III}_n(OH)_{3n-2}^{2+}$ oligomers.

Mobilization of hazardous Cr(VI) must be considered in plans to use H_2O_2 for remediation of chemically complex wastes. Once Cr(III) is oxidized to Cr(VI) by H_2O_2 it may persist long after applied H_2O_2 treatments have disappeared. Further, hexavalent Cr will behave as a catalyst toward H_2O_2 in soils, enhancing its oxidative capacity while helping to dissipate high levels of applied H_2O_2.

CHROMIUM OXIDATION AND REDUCTION BY HYDROGEN PEROXIDE IN DIVERSE SOILS AND SIMPLE AQUEOUS SYSTEMS

by

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DEDICATION

To my family

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INTRODUCTION

The oxidative treatment of biorefractory organic contaminants in soil and groundwater using hydrogen peroxide has recently attracted strong interest within EPA, but such treatment may oxidize the co-contaminant, Cr(III), if present. Hydrogen peroxide can be applied to remediation sites either as a direct oxidant of organic contaminants or as part of the well-known Fenton's reagent, in which it reacts with catalytic amounts of Fe(II) to produce the powerfully oxidizing hydroxyl radical ($OH^{\bullet}$). It has also been used to enhance aerobic bioremediation through production and delivery of O_2 (Carberry, 1994). The aim of this research is to investigate the possible chemical interaction between peroxide and different forms of chromium that may co-contaminate a site where this treatment is applied. Chromium in soil and groundwater poses an environmental hazard only when the metal is found in its most highly oxidized state, as anionic Cr(VI), in which form it is toxic, mobile and classified as a class A human carcinogen (Calder, 1988; Katz and Salem, 1994). In contrast, chromium(III) is nontoxic, an essential human nutrient involved with glucose metabolism, mostly insoluble in soils and not readily absorbed by plants. If H_2O_2 were to oxidize Cr(III) to Cr(VI), a relatively innocuous waste material would be transformed into a hazardous one.

This introduction will briefly review the chemistry of some of the possible biotic and abiotic reactions of H_2O_2 in groundwater, and describe its use to remediate contaminated soil, both as an enhancement to bioremediation, and as a direct oxidant. It will also treat the chemistry of Cr speciation as it affects its behavior in soil and

groundwater, and the scope and nature of Cr contamination, typified by its presence at Superfund sites. Background will also be given on the known chemistry of Cr/H_2O_2 interactions that could be relevant under conditions of soil remediation. Chapter 2 will discuss four soils high in Cr, but different in almost every other respect, and examine their varied response to H_2O_2. Chapter 3 will examine the chemistry of those results in light of experiments using defined aqueous systems. In conclusion, Chapter 4 will look at current H_2O_2 remediation trends and examine implications for Cr contamination from the use of H_2O_2 to remediate high levels of organic contaminants in soil.

PEROXIDE IN SOILS

Peroxide Soil Chemistry

Hydrogen peroxide levels have been measured in groundwater at 10^{-7} to 10^{-8} M (Holm et al., 1987) and at 10^{-6} M in groundwater exposed to sunlight (Cooper and Zika, 1983). It is thought to be a respiration byproduct of aerobic soil microorganisms, certain *Aerococcus* species of which have been isolated and characterized (Kontchou and Blondeau, 1990). Enzymes such as aerobic dehydrogenases, amine oxidases, lysine monooxygenase, and xanthine oxidase produce H_2O_2 during normal cellular metabolic processes (Pardieck et al., 1992). H_2O_2 is also produced by microbes as the product of the superoxide dismutase catalyzed disproportionation of the superoxide anion radical ($O_2^{\bullet-}$) (Price et al, 1992):

$$2O_2^{\bullet-} + 2H^+ \rightleftharpoons H_2O_2 + O_2 \qquad (1.1$$

The superoxide radical is present in soils as a natural byproduct of microbial

respiration: it results from the reduction of molecular O_2 to H_2O via single electron transfers, along with H_2O_2 and $OH^{\bullet}$:

$$O_2 + e^- \rightarrow O_2^{\bullet-} \quad (1.2$$

$$O_2^{\bullet-} + 2H^+ + e^- \rightarrow H_2O_2 \quad (1.3$$

$$H_2O_2 + H^+ + e^- \rightarrow H_2O + OH^{\bullet} \quad (1.4$$

$$OH^{\bullet} + H^+ + e^- \rightarrow H_2O \quad (1.5$$

Soil microorganism defenses which protect against excess cellular quantities of these reactive intermediate species could be expected to play a role in the response of soil biota to remedial H_2O_2 treatments.

Hydrogen peroxide is a powerful oxidant, used commonly as a disinfectant. In soil, with or without the aid of mineral or biological catalysts, it would be capable of oxidizing reduced species such as Fe^{2+}, Mn^{2+}, or H_2S, as well as some forms of soil organic matter. It may, in turn, be expected to react as a reductant in soils toward oxidized species like MnOOH, or MnO_2. The oxidation state of oxygen in H_2O_2 (-1) is between that of O_2 and H_2O, and it can be oxidized to O_2 or reduced to H_2O_2 by 2 electron transfer reactions. The following half reactions summarize the redox chemistry of H_2O_2 under acidic and basic conditions (Greenwood and Earnshaw, 1994):

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	$E°$/V	1.776	(1.6
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$		0.695	(1.7
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$		0.878	(1.8
$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$		-0.076	(1.9

Its strength as an oxidant decreases with increasing pH, but its reductive strength

increases, allowing disproportionation to be energetically feasible across the entire pH range.

The thermodynamic prediction for the disproportionation of H_2O_2 at 298 K and atmospheric P_{O_2} is that reaction 1.10 will go to the right at any H_2O_2 concentration over 10^{-19}M:

$$H_2O_2\,(aq) + H_2O_2\,(aq) \rightleftharpoons O_2(g) + 2H_2O(l) \qquad (1.10$$

The reaction, however, is kinetically slow in a pure system (Brown et al., 1970). For some time it was thought (Duke and Haas, 1961) that the thermal decomposition of H_2O_2 occurs without a catalyst as a second order process via attack by HO_2^- on H_2O_2 with a rate maximum at pH 11.8, the pK_a of H_2O_2 (Cotton and Wilkinson, 1988). Subsequently, work reviewed by Brown et al. (1970) showed that the H_2O_2 decomposition was probably catalyzed by trace metals present in the experimental reagents, and that when reagents are carefully purified and trace metal contamination controlled, H_2O_2 solutions are essentially stable, even under alkaline conditions.

The thermodynamics of equations 1.6 and 1.7 imply that any redox couple at a potential (E^o) greater than 0.695 V (O_2/H_2O) and less than 1.77 V (H_2O_2/H_2O) would be a catalyst for the H_2O_2 disproportionation reaction, and in soils, Mn(III,IV) (hydr)oxides and Fe (II,III) (hydr)oxides are the most likely non-biological mediators. For example, Mn (II) is oxidized by H_2O_2, while Mn (III,IV) oxides may be reduced (Pardieck et al., 1992):

$$H_2O_2\,(aq) + 2Mn^{2+}(aq) + 2H_2O \rightleftharpoons 2MnOOH + 4H^+ \quad \Delta G = -50.9\ kJ/mol \qquad (1.11$$

$$H_2O_2\,(aq) + 2MnOOH(s) + 4H^+ \rightleftharpoons 2Mn^{2+}(aq) + O_2(aq) + 4H_2O \qquad (1.12$$

ΔG = -24.8 kJ/mol (values for both reactions at pH 7)

Birnessite, (δ-MnO_2) a non stoichiometric Mn mineral common in terrestrial and aquatic environments, was found to decompose H_2O_2 following a first order kinetic rate law (Elprince and Mohamed, 1992) and was found to be the most probable inorganic catalyst of H_2O_2 decomposition in a dry alluvial soil from an Egyptian floodplain (El-Wakil, 1986).

Hydrogen peroxide will also decompose in the presence of the Fe^{3+}/Fe^{2+} redox couple (E^o= 0.771V) via the well known Fenton mechanism (Fenton, 1894; Haber and Weiss, 1932), notable for its production of the highly reactive $OH^{\bullet}$ and $O_2^{\bullet-}$ intermediate species. In the Fenton mechanism, a reduced metal, e.g. Fe(II) or Cr(V), reacts with H_2O_2 in a rate limiting step to produce $OH^{\bullet}$ (equation 1.13 below). Trace amounts of a reduced metal will cycle between oxidized and reduced states in a series of one electron transfer reactions to catalyze the destruction of H_2O_2 (equation 1.10) in a manner consistent with the reactions steps below (Evans and Upton, 1985; Wardman and Candeias, 1996):

$$2Fe^{2+} + 2H_2O_2 \rightarrow 2Fe^{3+} + 2OH^- + 2OH^{\bullet} \quad (1.13$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (1.14$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \quad (1.15$$

$$2Fe^{3+} + 2O_2^{\bullet-} \rightarrow 2Fe^{2+} + 2O_2 \quad (1.16$$

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (1.17$$

$$2\,HO_2^{\bullet} \rightarrow 2\,O_2^{\bullet-} + 2H^+ \quad (1.18$$

Superoxide, ($HO_2^{\bullet}/O_2^{\bullet-}$ $pK_a = 4.8$ Bielski et al., 1985) produced by the oxidation of H_2O_2 by either Fe^{3+} or $OH^{\bullet}$ (equations 1.14 and 1.17 above), serves as a reductant for the oxidized metal, completing the catalytic cycle.

Hydroxyl radicals produced in the initial step may be subsequently scavenged by Fe^{2+} (equation 1.15), or by H_2O_2 (equation 1.17), and in a simple system, the reactions proceed to produce H_2O and O_2 as H_2O_2 is decomposed. In a natural system, the reactive intermediates would be expected to interact with organic compounds. Hydroxyl radicals are second only to F_2 in oxidation potential, reacting non-specifically with organic compounds with bimolecular rate constants of 10^7 to 10^{10} L/mole sec (Dorfam and Adams, 1973). Organic radicals may be produced by hydrogen extraction (Baxendale, 1955):

$$OH^{\bullet} + RH_2 \rightleftharpoons {}^{\bullet}RH + H_2O \qquad (1.19$$

which may subsequently undergo dimerization or hydroxylation. Although the Fenton pathway for the decomposition of H_2O_2 in soil may not predominate under natural conditions, it is purposefully introduced in remediation strategies which apply Fe^{2+} along with H_2O_2 to augment the oxidative treatment capacity with $OH^{\bullet}$ radicals.

Even more significant for the disproportionation of H_2O_2 under field conditions than the mineral composition of the soil, however, is the ubiquitous presence of catalase-positive microrganisms. Catalase is a heme-protein that protects the cell from the reactivity of H_2O_2 by catalyzing its disproportionation through a cycling of Fe(III) and Fe(V), producing O_2 and water. The specific activity of catalase is extremely high, with a turnover number, or number of molecules of substrate decomposed per molecule

of enzyme per minute, of 19 x 10^6 (Herbert and Pinsent, 1948). Spain et al. (1989) showed a rapid loss of H_2O_2 (100 mg/L) applied to the surface of a sand suspension ($t_{1/2}$ = 4 hr), while no decomposition of H_2O_2 was observed in sterile batch reactors. Pardieck et al. (1992) also observed less loss of H_2O_2 in autoclaved soil suspensions than occurred in field condition samples, and a greater loss in a silt loam with an organic matter content of 3.25% than in a sandy loam with 0.95% organic matter. These results both point to the disappearance of H_2O_2 as a result of microbial activity.

In addition to catalase, H_2O_2 may be biotically activated as an oxidant via peroxidase enzymes, which are also heme-proteins present in soil microbes, and reduce H_2O_2 without producing O_2. A metal center in the enzyme is oxidized by H_2O_2, producing H_2O, while an organic substrate donates electrons to reduce the metal center. Thus, a catalytically-active species might behave like catalase in the absence of an organic electron donor (producing H_2O and O_2), and like peroxidase when an organic substrate is present, producing H_2O and an oxidized organic species. In sum, the biotic interactions of H_2O_2 appear to be of three types: formation via superoxide dismutase, dismutation via catalase, and reduction coupled to oxidation of organic matter via peroxidase.

Using H_2O_2 to Enhance Subsurface Bioremediation

In the last decade, augmenting soils with hydrogen peroxide has been considered a means of facilitating the oxidation of organic contaminants by providing a source of O_2 which would enhance bioremediation, a subject reviewed by Pardieck et

al. (1992). A vast array of subsurface organic contaminants are completely degraded by soil microbes under aerobic conditions; some examples include benzene, toluene, xylenes and alkyl benzenes from gasoline or solvent spills, components of diesel or heating oil such as naphthalene and other polynuclear aromatic compounds, and synthetic organic compounds, such as chlorobenzene and methylene chloride. The degradation of those compounds with aromatic structures especially requires the presence of O_2 since ring cleavage occurs via oxygenases that add oxygen atoms to the aromatic ring. Oxidation of compounds which can be degraded under anaerobic conditions tends to be more complete under aerobic conditions because aerobic respiration is more energetically favorable to the microorganisms than the use of oxidants such as nitrate, Mn(IV) or Fe(III) as electron acceptors. Therefore, the rate of *in situ* microbial degradation is frequently limited by oxygen availability in the subsurface. Factors which limit the availability of O_2 include its relatively low solubility in water (9.2 mg/L at 20° C), its slow rate of diffusion through soil solution, and the high biological oxygen demand of the microorganisms. Peroxide is an effective supplier of dissolved oxygen as it is 10^7 times more soluble in water than O_2 (Henry's Law constants are 7.1×10^4 and 1.3×10^{-3} M atm^{-1} for H_2O_2 and O_2, respectively, Seinfeld, 1986) and it tends to disproportionate readily in soil.

The rapid decomposition of H_2O_2 in soil could represent an advantage for its use to enhance bioremediation in that it would not persist in the environment at its high application level. It is also inexpensive and available, can be added at high concentrations because of its high solubility in water. Too rapid a rate of dismutation,

however, could waste oxidant capacity and produce undissolved oxygen in an aquifer, thereby decreasing its permeability. Also, the cell membrane of a microorganism has little resistance to the transport of H_2O_2 across it, and levels within a cell are toxic above 0.1 mM (Schumb et al., 1955), and would have a bactericidal effect.

Bioremediation may have limited utility in treating organics that are biorefractory or toxic to microorganisms; resistance to biodegradation (along with high K_{OW} and low volatility) will determine persistence among surface contaminants. Those with a high degree of halogenation, like pentachlorophenol (PCP), are slowly biodegraded even under aerobic conditions because of their existing high oxidation state. Biodegradation may also be inhibited at the high concentrations characteristic of spills (Pignatello and Baehr, 1994). If the initial oxidation steps for these compounds could be carried out chemically, the resulting partially oxidized products could become more easily degraded than the parent toxic compounds (Carberry, 1994).

Initial, mainly empirical field studies reviewed by Pardieck et al. (1992) on the use of H_2O_2 to enhance bioremediation appeared promising. In one, an aquifer contaminated with over 270 organic compounds at the site of an old lumbermill showed increases in pollutant degradation after it was injected with 3 mM H_2O_2. Another showed marked increases in microbial concentrations at the site of an unleaded gasoline spill (although ambient dissolved oxygen levels did not rise), where recirculated groundwater was treated with inorganic nutrients and 15 mM H_2O_2.

More current thinking, however, according to Pardieck (personal communication, 1997), is that the viability of using hydrogen peroxide to enhance

bioremediation is problematic due to bioinhibitory effects, and will probably depend ultimately on controlling the toxicity of H_2O_2 to microorganisms. As a direct oxidant of recalcitrant organics via Fenton interactions, however, the use of H_2O_2 in contaminated soil, combined with applications of reduced iron, has generated a good deal of scientific interest.

Using H_2O_2 in Fenton Remediation

A number of recent studies have addressed factors influencing the effectiveness of applying H_2O_2 as Fenton's reagent to oxidize biorefractory organic contaminants in soils. These include biotic interactions such as the degree of H_2O_2 decomposition by catalase, formation rates of $OH^{\bullet}$, effects of concentrations and speciation of iron, soil organic matter content and pH range. Zepp et al. (1992) studied the kinetics of $OH^{\bullet}$ production by photolytically-generated Fe(II) and H_2O_2 over a pH range expected to be found in natural waters, and Watts et al. (1990, 1993, 1999), Tyre et al. (1991), Ravikumar and Gurol (1994), and Pignatello and Baehr (1994) investigated in situ H_2O_2 treatment using a variety of contaminants and soils. Results of several of these studies are summarized below.

Zepp's study addresses the need for an understanding of the formation rates of hydroxyl radicals in natural waters via Fenton interactions. As a source of Fe(II), he used photochemically reduced complexes of Fe(III), a form of Fe(II) which may be involved in a "photo-Fenton reaction" oxidizing agrochemicals in surface waters. The photochemical approach to generating Fe(II) from Fe(III) was selected mainly to avoid

the effects of concentration gradients that would occur in the initial stages of the mixing process if Fe^{2+} were to be directly added to a reaction mixture containing hydrogen peroxide. Hexaaquo Fe^{2+} would not be expected to be found uncomplexed in soil, therefore the photoreduced complexes also represent a more realistic system. To determine that $OH^{\bullet}$ is indeed the reaction intermediary and to determine its rate of formation, Zepp used a kinetic approach with anisole and nitrobenzene as $OH^{\bullet}$ probes. Oxalate and citrate were chosen as ligands for the Fe(III) complexes because they would photoreact efficiently without directly producing other transients that would oxidize the probe compounds, their reactions with $OH^{\bullet}$ were slow compared to those of the probe compounds, and they minimized the formation of Fe precipitates at the pH ranges (3-8) used in the study. Hydrogen peroxide was added to the Fe(III)-ligand solutions, which were then continuously irradiated at 436 nm.

A steady state kinetic method was then applied to obtain the rate of generation of the $OH^{\bullet}$ radical. The kinetic approach involves using a dilute probe compound under conditions of continuous irradiation in which the reactive transient ($OH^{\bullet}$) will rapidly reach a steady state. Rates of $OH^{\bullet}$ formation in both the Fe(III) citrate and Fe(III) oxalate systems, and across the pH range of 3 to 8 gave a one to one correspondence with the measured rate of Fe(II) formation, indicating that the Fe(II) complexes reacted quantitatively with H_2O_2 across the pH range to produce hydroxyl radicals.

One of the first studies to look at the use of Fenton's reagent in contaminated soils was done by Watts et al. (1990). Their purpose was to follow the degradation of

pentachlorophenol (PCP), and determine the optimum pH for soil treatment. Two fine-loamy soils and silica sand were spiked with PCP and mixed in batch systems with 6.5% H_2O_2 and 480 mg/L $FeSO_4$. H_2O_2 consumption corresponded to PCP degradation. The reaction was carried out in silica sand at pH 3; such a low pH was required to prevent precipitation of the iron via hydrolysis. Even at that pH, the soluble iron concentrations decreased over the first three hours, and the decomposition rates of PCP and H_2O_2 also decreased after the first three hours, indicating the importance of soluble iron to the Fenton reaction. Although the rate of PCP degradation in sand was minimal without the addition of iron, PCP decomposition in the natural soil samples proceeded without amendment by iron, probably because of the natural presence of iron oxides which may have dissolved or served as catalysts at the mineral surfaces. Degradation rates did increase upon addition of iron as well. The soil with lower organic content (0.05% vs. 0.58%) showed an overall efficiency of PCP degradation (k_{PCP}/k_{H2O2}) about four times greater than that of the soil with higher organic content, probably due to competition by organic matter as an $OH^{\bullet}$ scavenger, or perhaps due to the greater activity of catalase and subsequently greater decomposition rate of hydrogen peroxide in the soil containing higher levels of organic matter.

A subsequent study by Watts et al. (1993) showed that amending silica sand with goethite (FeOOH), was more effective than adding a soluble Fe (II) salt. The loss of PCP with the goethite system was well described by a zero order expression: $-dC/dt = k$, where results gave $[PCP] = -1.53t + 245$ ($R^2 = 0.97$) where the PCP concentration is in mg/L and time is in hours. It is expected that a Fenton system is zero order,

because the production of $OH^{\bullet}$ approaches steady state, which appears to be the case when goethite is used. This is not observed on addition of an Fe(II) salt because of the changing concentration of soluble Fe in the system due to hydrolysis. The data suggest that iron minerals in the presence of H_2O_2 are able to catalyze Fenton-like reactions on mineral surfaces.

Tyre(1991) investigated the conditions affecting the relative efficiency of the Fenton treatment of four contaminants: PCP, trifluralin, hexadecane and dieldrin. Soil samples with a range of organic matter content were used, and all four contaminants were added to each soil sample. PCP and trifluralin were degraded faster than hexadecane and dieldrin, probably because the rate constants for $OH^{\bullet}$ attack on dieldrin and hexadecane are slower than for PCP and trifluralin. Also, a higher percentage of trifluralin and PCP were present in the aqueous phase than dieldrin and hexadecane, indicating that preferential partitioning to organic matter by dieldrin and hexadecane may also have affected their oxidation rates. Efficiencies were determined by comparing rate constant ($k_{contaminant}/k_{H2O2}$) ratios. Since H_2O_2 will probably be the primary cost of remediation, the most efficient conditions favor contaminant degradation with minimal H_2O_2 consumption. As a result, the high iron concentrations that were found to favor contaminant degradation, but also favored H_2O_2 decomposition, were not necessarily the most efficient. The efficiency ratios were highest in soils with low levels of organic matter, which also did not receive iron amendment. Existing levels of iron minerals in soil appear to contribute to the efficiency, as well as effectiveness of the Fenton treatment.

A 1994 study by Pignatello and Baehr addresses the issue of remediation in a more neutral pH range. All the prior studies in soil were carried out at pH 3 or lower. In application, the need to acidify the soil would make the remediation technology impractical because of the high buffering capacity of soil, and the polluting effects of acidification. Pignatello proposes to circumvent the low pH requirement by using Fe(III) complexes to catalyze the hydrogen peroxide, producing reactive high valent ferryl species $(L)Fe_{IV}$, instead of, or in addition to $OH^{\bullet}$. Metolachlor and 2,4-D were selected as contaminants to give contrasting sorption behavior since metolachlor will sorb much more readily to organic matter than 2,4-D. Of the ligands tested, the best results for contaminant oxidation were obtained using Fe-nitrilotriacetate (NTA) or Fe-hydroxyethyleniminodiacetate (HEIDA) at 0.01 mol/kg and H_2O_2 at greater than 0.5 mol/kg. Interestingly, these Fe(III) complexes were much more effective than Fe(II) in combination with hydrogen peroxide. Simple addition of hexaaquo Fe^{2+} removed 61% of 2,4-D and only 7% of metolachlor, while Fe-NTA removed 99.3% of 2,4-D and 87% of metolachlor.

Ho (1995) published a design for an injection system and a pilot scale test which suggested successful injection of H_2O_2 into inaccessible contaminated sandy soil, and found that H_2O_2 decomposition increased with injection pressure and injection depth.

Although the Fenton reagent approach represents a promising combination of biotic and abiotic techniques for contaminant remediation, the reaction mechanisms in heterogeneous soil systems are far from being well understood. Complexation of

contaminants and scavenging of hydroxyl radicals by soil organic matter, the effects of contaminant adsorption and of the adsorption of Fe complexes, the impact of the Fenton treatment on soil microorganisms and their ability to further degrade byproducts of the Fenton degradation process, and the effects of different types of soil are all parts of the complex picture of this remediation strategy that remain to be pieced together.

Since the evidence is convincing that Fenton type reactions in soil solution are oxidizing organic pollutants, the effect that the strong oxidants might have on co-contaminants, in particular on reduced chromium, becomes a compelling question. Given that both oxidized and reduced iron are common soil constituents, the presence of H_2O_2 in groundwater, whether natural or anthropogenic, might result in chromium's oxidation and mobilization. We will now turn to a discussion of chromium in the subsurface, its chemistry, and issues relating to its deposition, remediation, and possible oxidation in soils.

CHROMIUM IN SOILS

Extent of Chromium Contamination in Soils

Millions of tons of industrial chromium are processed each year for use in ferrous and non ferrous alloys, pigments, electroplating, corrosion inhibitors, printing inks and refractories (Greenwood and Earnshaw, 1994). Widespread chromium disposal was practiced without discrimination near industrial sites up to the 1970s, resulting in significant pollution of soils and groundwater, and chromium is second only

to lead in its incidence of contamination at Superfund sites (U.S. EPA., www.epa.gov/superfund/sites).

On December 11, 1980, Congress passed the Superfund Law (Comprehensive Environmental Response Compensation and Liability Act). Along with establishing federal authority to respond to releases of hazardous waste, it taxed the chemical and petroleum industries to set up a fund for the long term remedial treatment of the country's most polluted and hazardous sites. The National Priorities List (NPL) was created to designate those sites considered to be most dangerous to the environment and to public health. It is possible to access the EPA data on the current NPL sites through their website (www.epa.gov/superfund/sites) and search the database by geographical location and form of contamination found at a site. The following charts were compiled in this way to obtain a sense of the relative importance of chromium as a contaminant compared to other metals and organic contaminants, the prevalence of chromium contamination in our region, and the form of chromium contamination found in most sites.

As of October 7, 1998, 1192 sites were on the final National Priorities List, 152 federally owned, 1040 privately owned. Of these, 510 were contaminated with chromium. As Table 1-1 shows, many of the sites have multiple contaminants, for example, 799 of the 1192 sites are also contaminated with VOC's, implying that at the very least, 117 of these sites are contaminated with both Cr and organic waste. Different kinds of contamination (soil, air, sediment, etc.) are present at most sites. Soil and groundwater contamination account for more than half the contamination media,

Table 1-1.

Data from the 1192 sites on EPA's National Priorities List

Selected Contaminants	Number of sites on the final NPL	Instances of contamination for all media	Instances of contamination for soil and groundwater
All	1192	60,405	38,855
metals	746	18,949	11,613
VOC's	799	18,696	13,089
PAH's	538	8,207	5,573
PCB's	302	1,628	865
pesticides	295	3,648	2,372
radioactive waste	46	781	539
nitroaromatics	43	232	179
dioxins/dibenzofurans	152	541	327
chromium	510	1,895	1,210
lead	561	2,477	1,463
arsenic	516	1,869	1,165
mercury	297	857	490
zinc	391	1,308	743
nickel	367	1,010	679
selenium	178	386	227
cobalt	141	350	219

and are especially important for metals. Of 1,895 instances of all types of Cr contamination, 1,210 were in soil and groundwater. The different media considered by EPA are shown in the following counts for chromium:

Table 1-2. Instances of Cr contamination in different media at the NPL sites

Groundwater	576	Debris	79
Soil	634	Surface Water	150
Air	32	Leachate	25
Sediment	145	Sludge	53
Solid Waste	81	Liquid Waste	63
Other	55	Residuals	2
All Media	1895		

Geographic distribution of superfund chromium contamination reflects the industrial activity of the northeastern states and, again, the prevalence of soil and groundwater contamination, as seen in Table 1-3.

Chromium Soil Chemistry

The two prevailing oxidation states of chromium found in soil differ markedly in their chemical behavior: the Cr(VI) oxyanion is a soluble and toxic carcinogen which can cause both skin ulceration and lung cancer (Nriagu and Niebor, 1988), while Cr(III), in contrast, is mainly insoluble in soil, and a required trace element with a daily intake recommended by the NRC of 50-200 μg (National Research Council, 1990). Therefore, to accurately evaluate the environmental threat posed by the exposure of chromium to H_2O_2 in contaminated sites, it is important to first examine chromium

Table 1-3. Geographic distribution of chromium contamination at Superfund sites.

Selected States and Territories	Total number of Superfund Sites	Instances of Cr contamination in all media	Instances of Cr contamination in soil and groundwater
Maryland	16	23	17
Delaware	17	15	11
Virginia	25	33	19
New Jersey	107	232	140
Pennsylvania	98	117	62
West Virginia	6	2	1
Connecticut	14	4	3
Massachusetts	30	64	41
New Hamp.	18	43	25
California	90	93	83
Florida	52	79	55
Texas	30	24	19
Puerto Rico	9	13	11

speciation and its effects on the metal's geochemical behavior. The chromium deposition process and geochemistry of a particular site will in turn influence chromium speciation. The environmental behavior of chromium can be generally described by the processes of oxidation-reduction reactions, precipitation-dissolution reactions, and adsorption-desorption exchanges (Palmer and Wittbrodt, 1991). The speciation of chromium, however, is a prime factor in determining its precipitation or adsorption, because the two oxidation states behave differently in aqueous solution.

Cr(VI) does not strongly adsorb to surfaces, and tends to form oxy-compounds, the tetrahedral $HCrO_4^-$ / CrO_4^{2-} ($pK_a = 6.4$) being the most common in groundwater (Bartlett, 1991). At concentrations greater than 0.01M, and at low pH (<6) it will dimerize to form dichromate ($Cr_2O_7^{2-}$), although this form is extremely rare in contaminated sites. Its tendency to adsorb to surfaces will increase with decreasing pH, especially in the presence of variably charged oxide minerals. At sites with high Cr(VI) concentrations, its solubility may be controlled by sparingly soluble salts such as $CaCrO_4$ (James, 1994). As an oxyanion, chromate is strongly oxidizing at low pH, but will persist in soils at neutral or high pH (James, 1996a). Transformation of Cr(VI) to Cr(III) within soils is caused by reduction with ferrous iron in solution, ferrous iron minerals (e.g. biotite and green rusts), reduced sulfur compounds, or soil organic matter (Eary and Rai, 1988). Chromium mobility is therefore significantly reduced in soils in the presence of Fe(II) or organic matter.

Cr(III) has 3 d-electrons in a high spin state in readily formed octahedral complexes, although it demonstrates kinetic inertness toward ligand exchange. As a

result, the rate of substitution of waters of hydration is extremely slow (half times in the range of several hours) (Cotton and Wilkinson, 1988). In soil it will form complexes with organic ligands, which increases its solubility. James and Bartlett (1983a) observed that Cr(III) remained in solution in the presence of citric acid and diethylenetriaminepentaacetic acid (DTPA) at pH values greater than 5, where it becomes insoluble in water. Trivalent Cr may be expected to have some mobility and availability for redox interactions at very low pH, at very high pH, or in the presence of high levels of organic matter with which it may form complexes, especially in the process of its reduction from Cr(VI) (Wittbrodt and Palmer, 1996).

The pϵ-pH stability diagram shown in Figure 1-1 depicts the various Cr species that may be present in groundwater and soils. At low pH in its reduced state, as hexaaquochromium (III), chromium shows a strong tendency to adsorb to negatively charged clay surfaces (Cranston and Murray, 1978). As pH approaches 6, $Cr(H_2O)_6^{3+}$ becomes hydrolyzed, with $CrOH^{2+}$ more stable than $Cr(OH)_2^+$ in an aqueous system (Rai et al., 1987) until it precipitates as $Cr(OH)_3$. The positive species may polymerize through oxo- and hydroxo-bridging, forming dimers, trimers, tetramers and higher weight oligomers in solution in a process similar to the aging process at the surface of a chromium precipitate (Stunzi and Marty, 1983). These multimers remain stable in solution due to the relative inertness of the Cr(III) inner coordination sphere.

In the aging process, changes in the chemical structure and composition of chromium(III) hydroxide reduction products take place, which involve hydrolytic polymerization and a concurrent loss of coordinated water or of protons from

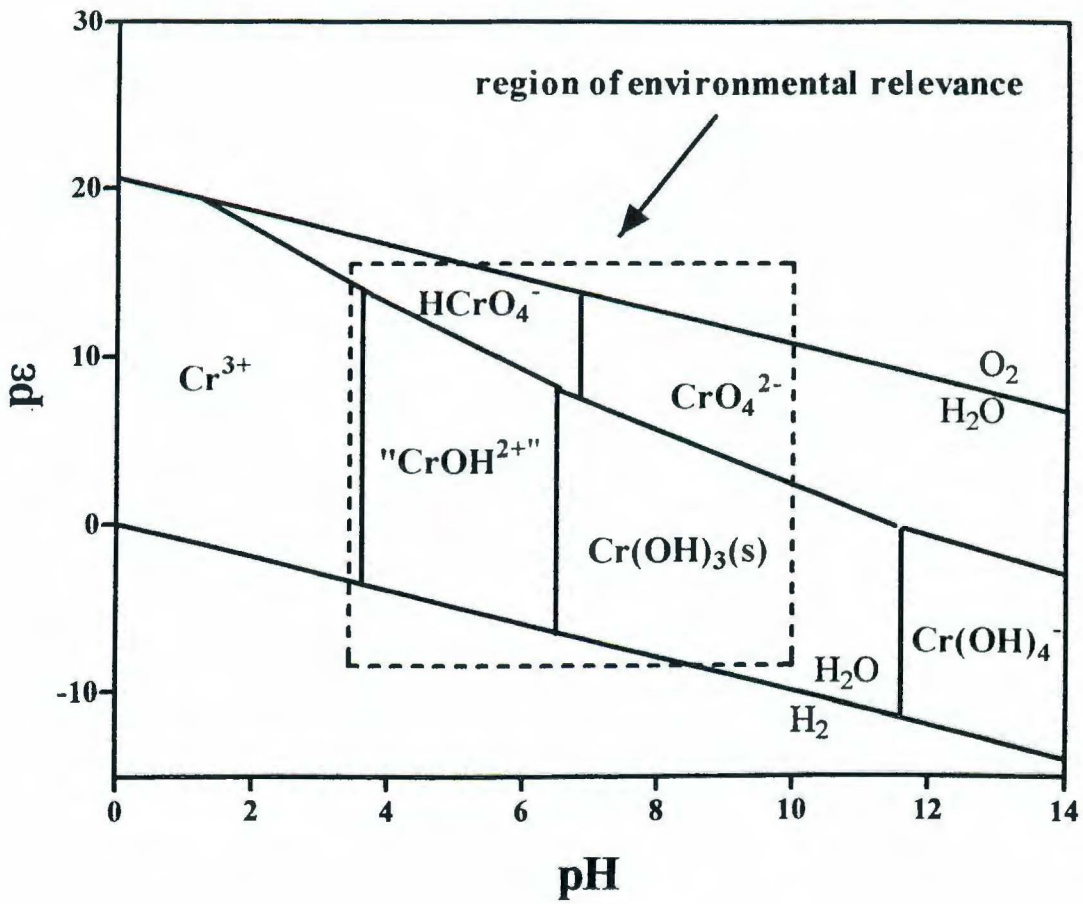


Figure 1-1. Stability diagram for aqueous Cr(III) and Cr(VI) species. From Cr data compiled by Ball and Nordstrom, 1998. Activities of aqueous species = 10^{-4} M, activities of $Cr(OH)_3(s)$ and $H_2O(l)$ = 1. P_{O_2} = 0.21 atm, P_{H_2} = 10^{-4} atm.

coordinated H_2O or OH^-. Spiccia and Marty (1986) have described the formation of an initially crystalline "active" $Cr(OH)_3 \cdot 3H_2O$ solid phase which forms on addition of base to aqueous solutions of $Cr(H_2O)_6^{3+}$. It does not contain any bridging hydroxide ligands; its octahedral units are linked through hydrogen bonds between the OH^- and H_2O ligands of adjacent Cr(III) centers. In a site where Cr(VI) is discharged and initially reduced under acidic conditions (e.g. discarded chromium plating baths), "active" chromium hydroxide might form. It is, however, thermally unstable, and with time "ages" and becomes an amorphous phase of unknown composition, with an accompanying loss of reactivity (Spiccia and Marty, 1986). Bartlett (1991) has also noted that freshly precipitated Cr(III) will be oxidized by Mn(III, IV) (hydr)oxides in soil faster than aged materials or well-ordered minerals. Eventually, amorphous oxyhydroxides of Cr(III) in soil will slowly change to an even less reactive and more crystalline α-Cr_2O_3 phase. The aged $Cr(OH)_3$ solid form has an extremely low solubility product ($K_{sp} = 6.7 \times 10^{-31}$) (DeFilippi, 1994). When it co-precipitates with iron, as $Cr_xFe_{1-x}(OH)_3$, the chromium will be even less soluble and less subject to oxidation (Sass and Rai, 1987). Above pH 9 or 10, Cr(III) regains some solubility in its anionic form, as $Cr(OH)_4^-$.

Deposition of Chromium in Industrial Sites

The mineral crocoite ($PbCrO_4$) from Siberia was identified by L.N. Vauquelin in 1797, and chromium was isolated a year later by reduction with carbon (Katz and Salem, 1994). Its name derives from the myriad colors of its compounds, trace

quantities provide the characteristic color of emeralds and rubies, and today it is mined mainly as chromite ($FeO{\cdot}Cr_2O_3$) in Russia, South Africa and the Phillippines. Chromite is reduced with coke or ferrosilicone in an electric arc furnace for the iron/chromium alloys that are added to stainless steel. For other industrial purposes, chromite is processed via aerial oxidation in molten alkali (Na_2CO_3 and $CaCO_3$) to give Na_2CrO_4. The chromate is then leached with water and may be reduced to Cr_2O_3 by carbon, and further reduced with aluminum or silicon to obtain the pure chromium metal. Residues from ore processing sites contain high levels of insoluble Cr(III) which was resistant to processing, as well as high residual levels (50 mg/kg or more) of soluble Cr(VI) which was not completely removed in the leaching process. The pH of these sites is from 8-12, reflecting the alkaline refining process. From 1900 to 1970 in Hudson County, New Jersey, over two million tons of the chromium ore processing residue (COPR) was disposed of and used as general or low land fill (Burke, et al., 1991).

Chromium electroplating was in great demand during World War II, when dozens of small plating shops set up operations. The process uses chromic acid/sulfuric acid baths, and the washing, dripping and spent plating solutions were often discharged into adjacent wetlands and discharge ponds, creating levels of Cr in the soil that reached as high as 6% (see Table 2-1). The pH of these soils, in contrast to the COPR soils, tend to be low, from 4-5. Beginning in the 1830's, chromium was also used extensively at tannery sites. In the tanning process Cr(VI) was reduced to form stable Cr(III) complexes that protected the leather from deterioration. The soils at these sites tend to become depleted of oxygen and form highly reducing environments, due to the

quantities of animal organic matter added to them. Although chromium appears to be completely reduced in these sites, it has a surprising degree of mobility in the groundwater, probably due to the enhanced solubility of Cr(III) organic complexes (Davis et al., 1994).

The three types of chromium waste sites described above differ, due to the site conditions and deposition process, in soil pH, soil oxidizing or reducing conditions, and chromium speciation as chromate or bichromate, organic or inorganic chromium(III). These conditions are important to consider both when evaluating possible remediation strategies, and when trying to predict the effect of adding remedial reagents like H_2O_2.

Chromium Reduction and Oxidation in Soils

Other than removal and sequestering, remediation strategies for chromium need to effect the reduction and immobilization of Cr(VI), and the resulting Cr(III) precipitates must not be subject to reoxidation, once the natural aquifer conditions are again obtained. Bioremediation may be a viable method for chromium (Palmer and Puls, 1994), and may proceed directly, as when chromium serves as the terminal electron acceptor for carbohydrate metabolism by a species such as *Bacillus subtilis* under reducing conditions (Melhorn et al., 1994). It may also be an indirect process, where Cr(VI) is reduced by sulfides produced by sulfate reducing bacteria (Suthersan, 1997).

Certain organic materials may also be effective reductants of chromium (James, 1996a). One of the major factors affecting the rate and extent of this type of reduction

is the presence of mineral surfaces which catalyse the reaction. Deng and Stone (1996) used goethite and aluminum oxides to investigate the catalytic effect of those surfaces on the reduction of Cr(VI) by low molecular weight organic compounds e.g. glycolic acid, lactic acid, mandelic acid, tartaric acid and their esters. They found that none of the compounds investigated would reduce Cr(VI) (pH 4.7, reductant/Cr(VI) ratio 10/1) in the absence of catalytic surfaces. The formation of Cr-surface complexes on the minerals (Fendorf, et al., 1997) alters the reactivity of Cr(VI) toward organic compounds, facilitating the formation of Cr(VI) esters with organic materials containing R-OH functional groups. Formation of a chromate ester has been shown to be the preliminary step in the transfer of electrons from a phenolic compound in the reduction of Cr(VI) (Elovitz and Fish, 1995).

Both Fe(II) and zero valent iron are capable of reducing and immobilizing Cr(VI) (Eary and Rai, 1988; James, 1994; Buerge and Hug, 1998, Seaman et al., 1999), and both may be applied in situ, for instance by injecting a reactive barrier with ferrous sulfate, or filling one with iron filings. The two forms of iron will react with chromium to form different products, and have different effects on site geochemistry.

Under alkaline conditions, Fe (II) will reduce chromate to Cr (III), which will hydrolyze and precipitate, or co-precipitate with Fe (III):

$$3Fe^{2+} + CrO_4^{2-} + 8H^+ \rightleftharpoons Cr^{3+} + 3Fe^{3+} + 4H_2O \qquad (1.20$$

$$Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3 \downarrow + 3H^+ \qquad (1.21$$

$$\underline{3Fe^{3+} + 9H_2O \rightarrow Fe(OH)_3 \downarrow + 9H^+} \qquad (1.22$$

$$3Fe^{2+} + CrO_4^{2-} + 8H_2O \rightarrow 3Fe(OH)_3 + Cr(OH)_3 + 4H^+ \qquad (1.23$$

The overall reaction will produce acidity, and injection of ferrous sulfate will be likely to be done in acid media, further enhancing acidity. Large molar excesses of Fe(II) may be necessary to overcome competition for the reduced iron from oxygen. At pH above 6.5-7.0 dissolved oxygen could begin to compete with chromate:

$$4Fe^{2+} + O_2 + 10\ H_2O \rightarrow 4Fe(OH)_3 + 8H^+ \qquad (1.24$$

James (1994) found Fe(II) treatment more effective than leaf litter, steel wool and lactic acid in removing soluble and exchangeable Cr(VI) from a contaminated alkaline soil with 460 mg/kg total Cr(VI) at a pH about 10. The presence of organic matter may enhance Fe(II) reduction of chromate. Buerge and Hug (1998) found that chromate reduction was enhanced by the addition of Fe(III) stabilizing ligands such as carboxylates and phenolates, which made the Fe(II) a stronger reductant.

A full scale field application of zero valent iron remediation of chromate has been constructed at a plating waste site in Elizabeth City, New Jersey (Power et al., 1995). Elemental iron reduces chromate, and unlike reduction with Fe(II), the process generates alkalinity:

$$Fe^{\circ} + CrO_4^{2-} + 4H_2O \rightarrow Fe(OH)_3 + Cr(OH)_3 + 2OH^- \qquad (1.25$$

A much narrower range of reactions is responsible for the natural oxidation of Cr(III) in soil; before Barlett and James (1979) demonstrated that fresh soils would oxidize up to 15% of added Cr^{3+} by way of indigenous Mn (III,IV) (hdyr)oxides, the oxidation of Cr(III) was not thought to take place at all. More recent studies characterizing the process (Eary and Rai, 1987; Fendorf and Zasoski, 1991; Fendorf et al., 1993; Johnson and Xyla, 1991; Manceau and Charlet, 1992; Silvester et al., 1995)

have shown Cr(III) oxidation to be controlled by the oxidation state and morphology of the Mn, and by the transport of dissolved Cr to the oxide surface, either as the hexaaquo cation, $Cr(H_2O)_6^{3+}$, or as a soluble Cr(III) organic complex. These experiments tended to be run between pH 3-5, where Cr(III) solubility and oxidation rates were greatest. By contrast, a soluble oxidant such as H_2O_2 may oxidatively dissolve Cr(III) compounds (Cr_2O_3, $Cr(OH)_3$, Cr(III)-humates, $FeCr_2O_4$) under the higher pH conditions more commonly found in soils.

In order to evaluate the potential threat of chromium at a contaminated site and design appropriate remediation strategies, the tendency for chromium to oxidize under prevailing site conditions needs to be understood. One approach has been to devise a numerical rating scheme to evaluate the need for remediation at a given site (James et al., 1997). The model rates the site based on the form of chromium: (oxidized or reduced, soluble or insoluble), the soil pH, the presence of manganese oxides and the presence of soil organic matter or other soil components that could reduce Cr(VI). In this way, remediation strategies can be based on a more realistic appraisal of the chromium hazard than a simple measure of chromium concentrations would provide.

CHEMISTRY OF CHROMIUM AND PEROXIDE INTERACTIONS

H_2O_2 is thermodynamically capable of both oxidizing and reducing chromium across a broad pH range, as illustrated by the position of the H_2O_2/H_2O and O_2/H_2O_2 reduction lines on a stability diagram for aqueous chromium species (Figure 1-2):

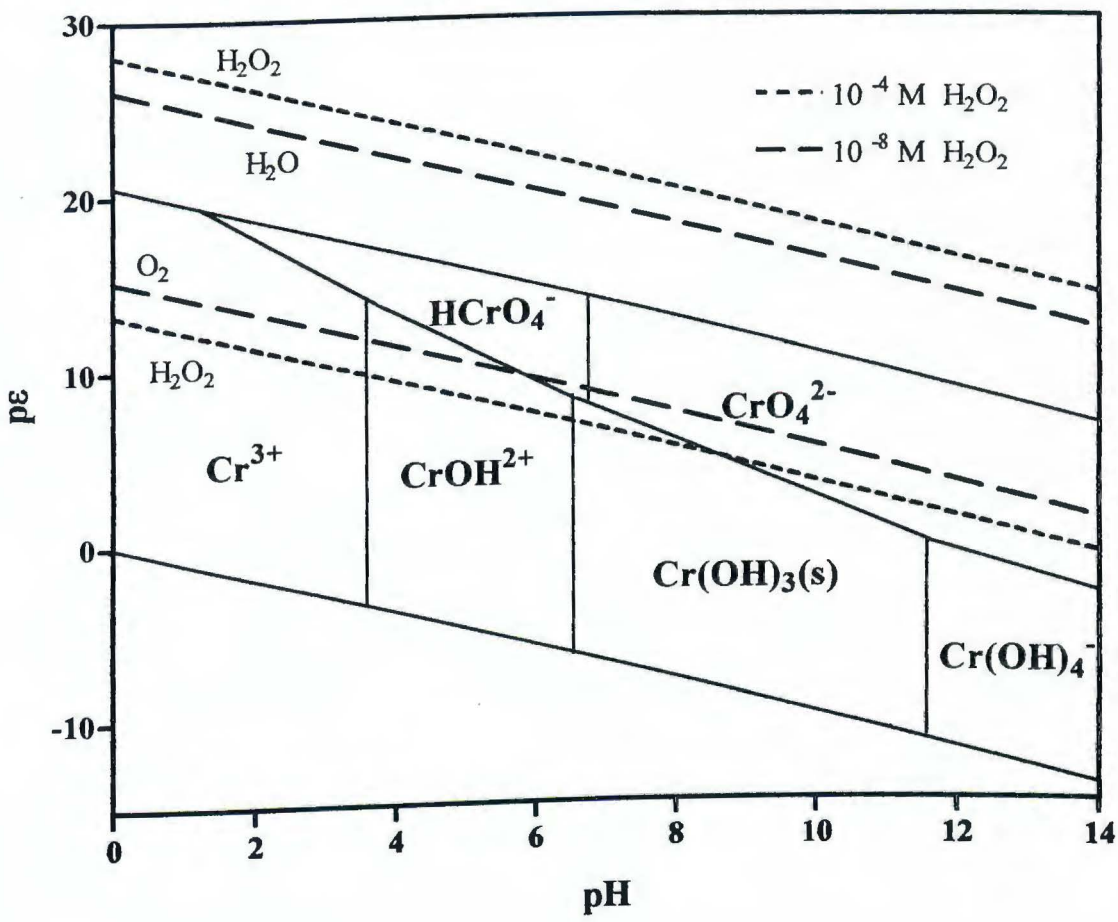


Figure 1-2. Stability diagram for aqueous Cr(III) and Cr(VI) species with oxidation and reduction lines for H_2O_2. From Cr data compiled by Ball and Nordstrom, 1998; H_2O_2 data from Woods and Garrells, 1987. Activities of aqueous species = 10^{-4} M except where noted for H_2O_2, activities of $Cr(OH)_3(s)$ and $H_2O(l)$ = 1. P_{O_2} = 0.21 atm.

$$3H_2O_2(aq) + 2CrOH^{2+} = 2HCrO_4^- + 6H^+ \quad (1.26$$

$$2HCrO_4^- + 6H^+ + 3H_2O_2(aq) = 2CrOH^{2+} + 6H_2O + 3O_2(g) \quad (1.27$$

Two H_2O_2 concentrations are shown, one at 10^{-4} M and one at 10^{-8} M. At low concentrations, the lines for the oxidation and reduction of H_2O_2 will tend to converge; as H_2O_2 activity increases, the lines on the diagram move apart (1 pe unit for each ten-fold increase in $[H_2O_2]$), indicating that at higher concentrations being considered for remediation, H_2O_2 would potentially behave both as a stronger oxidant and as a stronger reductant of chromium. At high H_2O_2 concentrations, since H_2O_2 can be both an oxidant and a reductant, it will be out of equilibrium with dissolved Cr, regardless of the Cr oxidation state. Kinetics, not thermodynamics, will control the oxidation state of Cr. As H_2O_2 diminishes, Cr(VI) becomes stable in the presence of H_2O_2, first at high pH, and with further H_2O_2 diminution, at low pH. Figure 1-2 shows that above pH 8.5 Cr(VI) and 10^{-4} H_2O_2 could be stable, but below this pH Cr(VI) would oxidize H_2O_2 to O_2. Throughout the pH range, Cr(III) would reduce H_2O_2 to water, and this behavior will persist to low H_2O_2 concentrations.

Cr(VI)/H_2O_2 Interactions

The chemistry of Cr(VI) and H_2O_2 has been studied for decades, and is particularly complex in the 4-7 pH range relevant to soils. Oscillating behavior, hysteresis, reduction to Cr(V) and Cr(IV) intermediate species, and mono-, di-, tri- and tetra- peroxochromium species have all been reported. Several reviews discuss progress in characterizing the system in studies conducted over the past century

(Spitalsky, 1907, 1908; Baxendale, 1952; Brown et al., 1970; Dickman and Pope, 1994; House, 1997). Interest in unraveling its intricacies has historically stemmed from two applications: the synthesis of stable cationic organochromium(III) complexes (House, 1997), and the determination of intermediate species that could be responsible for the toxicity and mutagenicity of chromium (VI) in living cells (Aiyar et al., 1991; Shi et al., 1999).

The chemistry of many of these intermediate species has been approached from the addition of hydrogen peroxide to a solution of chromate (CrO_4^{2-}) or bichromate ($HCrO_4^-$), and has been well reviewed by Brown et al., (1970), Dickman and Pope, (1994), and House (1997). A plethora of possibilities for these species have been reported, covering a range of chromium oxidations states (II-VI), degrees of substitution by the peroxo ligand, and protonated or deprotonated forms. An understanding of the Cr(VI)/H_2O_2 reaction and its intermediates is further complicated by the catalytic decomposition of H_2O_2, which varies with pH and Cr/H_2O_2 ratios. The system also varies with temperature and reactant concentrations, and intermediates are unstable and cannot be measured spectroscopically at moderate concentrations. A broad range of reaction conditions, including the use of various buffers and solvents, are reported in the literature and make data comparisons difficult. Regeneration of the Cr(VI) reactants has been reported by dissociation of Cr(VI) peroxo intermediates (Perez-Benito and Arias, 1997), as well as the disproportionation of Cr(V) or Cr(IV) peroxo intermediates (Buxton and Djouter, 1996), further complicating the reaction mechanisms. For example, in weakly acidic solution (pH 2.5-5.5) in an isothermal

stirred tank reactor, Beck et al. (1991) observed hysteresis and oscillation in the Cr(VI)/H_2O_2 interaction. As a result, characterization of the intermediate species has mainly been accomplished under more extreme reaction conditions (pH, reactant concentrations) than would be relevant in soil. Nevertheless, well characterized intermediate species of this fascinating system give us important clues as to its possible behavior under more environmentally relevant conditions.

Under acidic conditions in the presence of alcohol, $HCrO_4^-$ is reduced in a reversible reaction first to a $[Cr^{IV}O(H_2O)_5]^{2+}$ complex, and then to $[Cr^{II}(H_2O)_6]^{2+}$, which in turn, in the presence of O_2 produces a Cr(III) superoxocomplex, $[Cr^{III}O_2(H_2O)_5]^{2+}$ (House, 1997). The superoxochromium(III) complex will decompose to produce $HCrO_4^-$ and the Cr(III) dimer, $[(H_2O)_4Cr(OH)_2Cr(OH_2)_4]^{4+}$, as well as compete with O_2 to react reversibly with the Cr(II) complex from which it was formed. The reaction of the Cr(II) species with H_2O_2 is the reaction important for the synthesis of stable Cr(III) alkyl complexes. Cr(II) acts as a Fenton metal with peroxide to produce OH· radicals; these react rapidly with added organic substrates to form alkyl radicals, and they in turn, react with $(Cr^{II}(H_2O)_6]^{2+}$ to form the stable Cr(III) alkyl compounds.

Without the reducing influence of the alcohol, the addition of H_2O_2 to a strongly acidified solution of Cr(VI) results in the rapid formation of a blue "perchromic acid" (Brown, et al., 1970). It quickly decomposes on standing in aqueous solution, evolving oxygen, partially decomposing excess peroxide, and leaving chromium reduced to the trivalent state. The blue perchromic acid can be stabilized by extraction into a non aqueous solvent such as pyridine. Funahashi et al. (1978)

propose two-phase kinetics for the overall reaction (1.28): rapid formation of the peroxo complex (1.29), followed by its reduction (1.30):

$$2HCrO_4^- + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 3O_2 + 8H_2O \quad (1.28$$

$$HCrO_4^- + 2H_2O_2 + H^+ \rightarrow CrO(O_2)_2 + 3H_2O \quad (1.29$$

$$2CrO(O_2)_2 + 6H^+ \rightarrow 2Cr^{3+} + 3O_2 + H_2O_2 + 2\,H_2O \quad (1.30$$

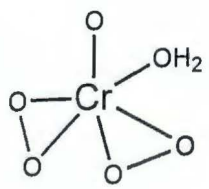
The equilibrium constant for the formation of the oxodiperoxochromium(VI) complex was found to be $K = [CrO(O_2)_2][HCrO_4^-]^{-1}[H^+]^{-1}[H_2O_2]^{-2} = 2.0 \pm 0.2 \times 10^7\ M^{-3}$ (25 °C). In a subsequent XAFS study of the blue complex, Inada and Funahashi (1997) confirm a pseudo pentagonal pyramidal geometry with an oxo group at the apex, and the two peroxo ligands and a coordinating water molecule making up a five pointed base (Figure 1-3). They found a shortening of the Cr-O (peroxo) bond length relative to that found when the complex was prepared with pyridine (which substitutes for the water ligand), helping to explain the instability or ease of reduction of the Cr(VI) center in aqueous solvent.

Above pH 7, the Cr(VI)/H_2O_2 reaction results in the red-brown anion, tetraperoxochromate(V), $[Cr(O_2)_4]^{3-}$. This complex has a distorted dodecahedral arrangement around a central Cr atom (D_{2d} symmetry), and slow catalytic decomposition of hydrogen peroxide proceeds in its presence in alkaline solutions.

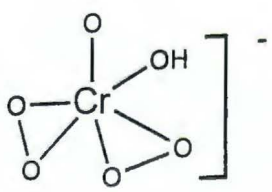
Studies done to understand chromium toxicology under near physiological pH conditions may give a better indication of what may be expected in the soil environment. Cr(VI), unlike Cr(III), is readily transported across cell membranes via

Figure 1-3. Structure of peroxochromium complexes as described in Dickman and Pope (1994).

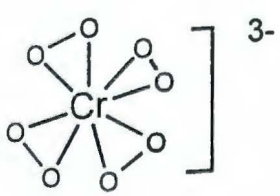
a) blue "perchromic acid," $[CrO(O_2)_2 \cdot H_2O]$



b) violet chromium(VI)oxodiperoxo complex, $[CrO(O_2)_2(OH)]^-$



c) red-brown tetraperoxochromate(V), $[Cr(O_2)_4]^{3-}$



non specific anion pathways, and it is thought that reduction by cellular constituents is necessary for Cr(VI)-induced DNA damage because Cr(VI) does not react directly with isolated DNA (Jennette, 1979; De Flora et al., 1990; Cohen et al., 1993). Compounds found in cells such as ascorbate (Stearns and Wetterhahn, 1994; 1997), and glutathione (Shi and Dalal, 1989; Kortenkamp, 1990) have been shown to reduce Cr(VI) to Cr(V) and Cr(IV), and these complexes of incompletely reduced chromium have come to be considered potentially powerful carcinogens (Zhang and Lay, 1996; Chiu et al., 1998). A Fenton type generation of hydroxyl radicals is thought to proceed from the reaction of the Cr(V, IV) intermediates with H_2O_2 that may also be present in the cell as a by-product of oxygen cellular metabolism (Shi and Dalal, 1990; Aiyar, et al., 1991; Itoh et al., 1996). If these or similar reduced complexes formed in chromate contaminated soils and were subsequently treated with peroxide, a Fenton type generation of the strongly oxidizing OH· radical could significantly affect the oxidizing capacity of the soil.

Zhang and Lay (1998) have recently identified three Cr(V) peroxo complexes using EPR spectroscopy in the pH 4-7 range that form in the presence of Cr(VI) and peroxide alone. By analogy with V(V) chemistry, they identify three degrees of substitution by the peroxo ligand: $[CrO(O_2)(OH_2)_n]^+$ in relatively low H_2O_2 concentrations in low pH, $[CrO(O_2)_2(OH_2)]^-$ in weakly acidic (pH 4-7) and somewhat low H_2O_2 solutions, and $[Cr(O_2)_3(OH)]^{2-}$ at solutions slightly above neutral. The trend for higher levels of substitution with rising pH continues with the previously identified tetraperoxochromate(V), $[Cr(O_2)_4]^{3-}$ which was prevalent in alkaline solutions. These

species provide evidence for the potential of Fenton interactions in the Cr(VI)/H_2O_2 system even without the presence of cellular (or soil) reductants, and all of them decompose H_2O_2 catalytically. However, the unstable, soluble, violet chromium(VI) oxodiperoxo complex $[CrO(O_2)_2(OH)]^-$ also forms in the pH 4-7 range, and also decomposes peroxide catalytically (Perez-Benito and Arias, 1997). Its formation is favored by the use of phosphate buffers. This complex is the deprotonated form of the blue complex noted earlier, and may decompose peroxide under mildly acidic conditions via the auto reaction of its protonated and deprotonated forms, as with the decomposition of peroxide at alkaline pH, near its pK_a (11.8), rather than by a redox cycling with Fenton products.

Cr(III)/H_2O_2 Interactions

The Cr(III)/H_2O_2 system has been much less extensively investigated than the Cr(VI)/H_2O_2 system. Shi et al. (1993) have reported the generation of hydroxyl radicals from the interaction of Cr(III) and H_2O_2 using an ESR spin trapping methodology. They found the production of $OH^{\cdot}$ to increase with increasing pH, and used tartaric acid/phthalate (pH 3.0), phosphate (pH 7.2) and tetraborate/carbonate (pH 10.0) buffers and reactant levels of 1 mM $CrCl_3$ and 10 mM H_2O_2. In a later work, using Cr(III) acetate with xanthine and xanthine oxidase as a source of superoxide ($O_2^{\cdot -}$) and H_2O_2, Shi (1998) suggested that the mechanism of hydroxyl production in the Cr(III)/H_2O_2 system involves a Fenton cycling between Cr(II) and Cr(III), rather than oxidation to Cr(V) or (VI).

Several reports in the literature point to the possible oxidation of chromium by peroxide in natural systems. Although two of these address the Cr-H_2O_2 interaction in seawater, their results may predict aspects of Cr-H_2O_2 behavior in soils. Pettine and Millero (1990) have asserted that H_2O_2 in seawater controls Cr speciation. They studied the rates of oxidation of Cr(III) (1.9 μM) with H_2O_2 (447 μM) at pH 8.5. The rate of oxidation of Cr(III) in artificial seawater was found to be first order with respect to [OH^-] and [H_2O_2]. Their pseudo first order rate constant increased with increasing pH, up to pH 8.75; a decrease above that pH was attributed to the formation of Cr(III) oligomers in solution. This effect may be analogous to the effect of chromium (III) "aging" in the soil after its initial formation via reduction of Cr(VI).

Kieber and Helz (1992) recorded a diurnal cycle in the oxidation state of Cr in a shallow estuary. In this case, a decrease in Cr(VI) to Cr(III) ratios during the day was attributed to the reduction of Cr(VI) by photolytically generated ferrous iron. Hydrogen peroxide levels were shown to increase as the Cr(VI)/Cr(III) ratio decreased. The peroxide could be a byproduct of the photolytic reduction process, and may in turn behave as an oxidant toward Cr(III). No connections between the two trends were established, although it might be postulated that the higher daytime levels of H_2O_2 reoxidized Cr(III), returning Cr(VI)/Cr(III) to ambient levels.

In work comparing soil flushing to pump-and-treat methods of chromium remediation, Davis and Olsen (1995) used groundwater augmented with 30 mg/L H_2O_2 (0.9 mM) in a shallow vadose zone soil column (141 mg/kg Cr(III)) in an attempt to

oxidize and mobilize the chromium. Total Cr(VI) in the effluent was double that of a control column, representing about 2.3% of the total soil Cr.

CURRENT INQUIRY

The possible oxidation of Cr in a soil or waste site by H_2O_2 being used for remedial purposes has never before been evaluated. Hydrogen peroxide could oxidize Cr(III) present as a co-contaminant in soils or form harmful peroxochromium intermediates which have been studied in the context of their possible toxicity and carcinogenicity in biological systems. To better predict the response of chromium to H_2O_2 under different conditions, this project used soils from each of the three types of industrial depostion sites described above, plus one soil naturally high in chromium. The soils include samples from a chromite ore processing residue waste site in Hudson County, New Jersey; a site contaminated with electroplating waste in Putnam, Connecticut; a site in the Aberjona watershed contaminated with tannery waste in Woburn, Massachusetts; and a serpentine barrens naturally enriched in Cr northwest of Baltimore, Maryland. The soils represent four different chromium deposition processes, and vary in their geochemical attributes and in their ambient chromium species.

The diverse conditions under which Cr is found in these soils may affect its response to treament with peroxide, and the aim of this research was to assess more completely the potential for oxidation of chromium by peroxide in soils under these diverse conditions. Batch studies were conducted with soils from each site, and Cr(VI) and H_2O_2 were monitored using spectroscopic methods. The following chapters

present the results of experiments done with soils, as well as with simpler aqueous systems.

Chapter 2

Hydrogen Peroxide Effect on Chromium Chemistry in Four Diverse Chromium-Enriched Soils

INTRODUCTION

To date, H_2O_2 has not been extensively considered as a potential oxidant for chromium in soils. The lack of research on H_2O_2-Cr interactions in soil may be attributed to the low levels of H_2O_2 (10-100 nM) (Holm et al., 1987; Cooper and Zika, 1983) that have been measured in the subsurface, especially in groundwater which is not exposed to sunlight. In the past year, however, EPA has been supporting field demonstrations of *in situ* chemical oxidation of recalcitrant organic contaminants using treatment with high levels of H_2O_2, often combined with Fe(II) to effect Fenton oxidation via strongly oxidizing hydroxyl radicals. One such process, in Anniston, Alabama, used 109,000 gallons of 50% hydrogen peroxide over a 120 day period to remediate an estimated 33,000 kg of trichloroethylene (U.S. EPA, 1998). At lower levels (3-300 mM), H_2O_2 has been applied to contaminated soils as a means of delivering O_2 to groundwater and enhance bioremediation (Pardieck, et al., 1992). The use of H_2O_2 to remediate organic contaminants in soils gives rise to concern over its possible interaction with any chromium that may co-contaminate these waste sites, especially if the chromium were to be oxidized by H_2O_2.

In its highest oxidation state, Cr(VI) is a Class A human carcinogen that exists in soils and natural waters predominantly as a soluble anion, almost always as a result of the disposal of industrial waste. In contrast, Cr(III) is nontoxic and relatively immobile in the same environments. Cr contamination in soils has arisen from a number of different processes (e.g. electroplating, leather tanning, ore processing). As a result, the speciation and chemical behavior of Cr is different in different waste sites,

and for an accurate understanding of the response of Cr in the soil to H_2O_2, the effect of H_2O_2 on Cr at each type of site should be evaluated.

Identifying those soil chemical conditions under which chromium may be oxidized or reoxidized by peroxide from its relatively immobile and benign form as Cr(III) to its toxic, carcinogenic and mobile hexavalent form, will be important when designing any remediation strategy which involves using peroxide to clean up biorefractory organic waste. The aim of this research was to assess more completely the potential for oxidation of chromium by peroxide in soils under the diverse conditions that might be found in contaminated sites. Chromium reactivity toward H_2O_2 may vary widely in different Cr-enriched soils. To this end, peroxide-chromium interactions have been examined in samples collected from profiles of four dissimilar Northeastern U.S. soils with either naturally or anthropogenically elevated levels of chromium. The sites differ, due to the site conditions and chromium deposition processes, in total Cr levels, soil pH, oxidizing or reducing conditions, Cr(VI) speciation as chromate or bichromate, and Cr(III) speciation as complexed with soil organic matter, or as inorganic Cr(III) oxides or hydroxides. Chromium speciation and site conditions were found to be crucial in determining the behavior of chromium when exposed to peroxide, behavior which was found to be highly variable, in some instances even within the same soil profile.

The four soils chosen were: a) a chromite ore processing residue waste site on the Coastal Plain of New Jersey, b) a site contaminated with electroplating waste in soils derived from glacial materials in Connecticut, c) a site in the Aberjona watershed

contaminated with tannery waste in Massachusetts, and d) a serpentine barrens naturally enriched in Cr on the Piedmont in Maryland. Experimental H_2O_2 levels (3.0 - 50 mM) were chosen based on the range being considered for enhanced bioremediation treatments. The mM range of H_2O_2 levels in soil may also be sustained for some time after the addition of much higher H_2O_2 levels (1 M-17 M) being used in direct or Fenton oxidation treatment methods.

MATERIALS AND METHODS

Chromite Ore Processing Residue (COPR)

COPR soil from New Jersey has a number of salient features which distinguish it from other Cr-elevated soils, including high pH (9-10), a relatively large Cr(VI):Cr(III) ratio (0.10), and high ambient levels of soluble Cr(VI)(~1 mM in 10:1 solution:soil) (Table 2-1). A powder X-ray diffraction (XRD) spectra of a sample of COPR soil is shown in Figure 2-1a (data shown in Appendix A). Quartz and calcite were matched as likely phases in the sample using JADE (1999) software identification techniques.

In the original ore processing, chromite ore was crushed to less than 100 mesh size, mixed with soda ash and lime (Na_2CO_3 and $CaCO_3$), and roasted to produce soluble Na_2CrO_4, as described by:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8\ Na_2CrO_4 + 2Fe_2O_3 + 2CO_2 \qquad (2.1$$

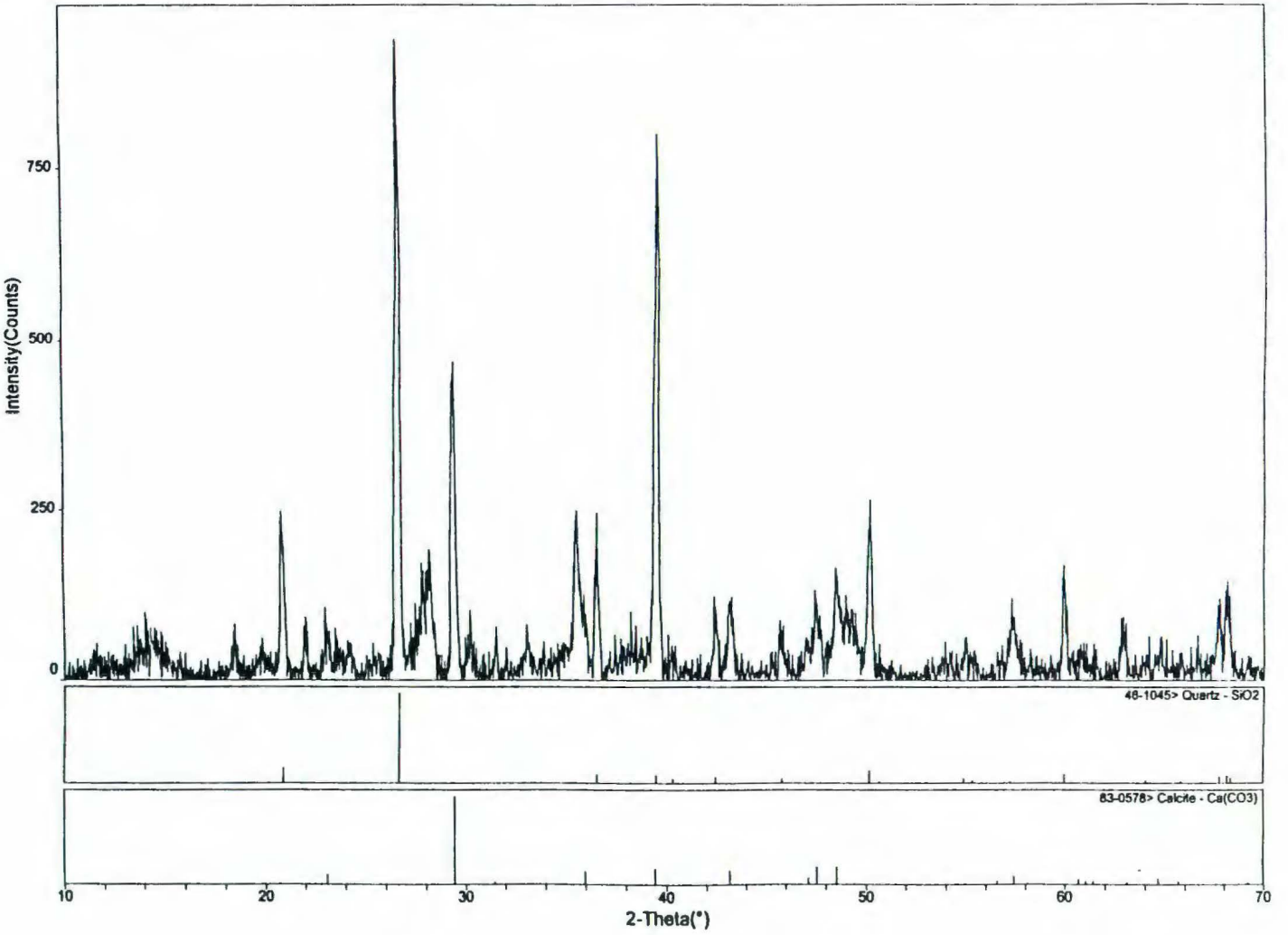
The sodium chromate was then leached with water, the process repeated, and the remaining, highly alkaline residue discarded. $CaCO_3$ was added before roasting to react with aluminum present in the ore material (~13%) and prevent it from dissolving and

Table 2-1. Soil properties. Soluble Cr(VI), Fe,(II), Eh, pH and color were determined in field moist samples. Data is reported as ± 1 SD.

Soil	Horizon (cm)	Total Cr mg/kg soil	Total Cr(VI) mg/kg soil	Soluble Cr(VI) µM 10/1 soln/soil	Soluble Fe(II) µM 5/1 soln/soil	Eh (Pt electrode)	pH ± 0.1	Org C g/kg soil	Soil Moisture	Munsell Color
COPR	surface	8,600 ± 500	914 ± 22	940 ± 40 (53)††	< 0.3	NA	8.8	66 ± 0.3†	404 ± 29†	7.5YR3/4
Connecticut	0-14	61,000 ± 5,000	71 ± 7	95 ± 6 (68)††	1.5 ± 0.5*	605 ± 2*	5.4	280*	1915*	10YR3/2*
Connecticut	14-40	21,000 ± 1,300	79 ± 5	< 0.1	1.2 ± 0.1*	616 ± 3*	5.0	118*	1546*	5Y2.5/1*
Connecticut	> 100	400 ± 30	79 ± 0.3	48 ± 1 (32)††	2.0 ± 0.4*	636 ± 2*	4.9	5.2*	261*	2.5Y5/2*
Aberjona	0-20	1,300 ± 100	< 0.05	< 0.1	2.7 ± 0.8*	568 ± 2*	6.7	154*	4424*	10YR2/2*
Aberjona	20-40	4,700 ± 200	< 0.05	< 0.1	6.7 ± 0.2*	458 ± 1*	5.7	202*	2462*	10YR2/2*
Serpentine	53-75	2,500 ± 150	< 0.05	< 0.1	< 0.3*	631 ± 2*	6.5	4.2*	212*	10YR5/3**

† James, 1994.
* Typrin, 1998 (Eh values are corrected for an Ag/AgCl reference electrode; Fe(II) determined colorimetrically with 2,2'-dipyridyl).
** Rabenhorst, 1982.
†† Expressed as % of Total Cr(VI)
NA - field measurement not available

Figure 2-1a. X-ray diffraction spectra for COPR soil. For peak identification tables see Appendix A.



contaminating the leachate. The residue therefore retained high levels of Ca salts, insoluble Cr(III) which had been resistant to processing, and residual levels of sparingly soluble Cr(VI) salts. As pH increases, chromate requires more strongly reducing conditions in the soil for its reduction to Cr(III), (as reflected in the stability diagram, Figure 1-2), and at the high pH of COPR soil, it has persisted for decades (Burke et al., 1991; Weng et al., 1994). Soluble chromate salts wick to the surface and will "bloom" as a bright yellow precipitate during periods of drying and evaporation. An organic, C-rich "meadow mat" underlying the COPR soil may act as a natural, reducing barrier for Cr(VI), and may explain the lack of chromate contamination of the Hackensack River flowing adjacent to the residue sites (James, 1996b).

Soil samples were previously sampled at a historic COPR waste disposal site in Kearney, New Jersey on the flood plain about 600 m from the Hackensack River. Depth to groundwater was 2-3 m. Since they have been significantly disturbed by the disposal of industrial waste, the soils have not been mapped, although they may be described as "disused and mixed industrial land."

Electroplating Waste Site in Connecticut

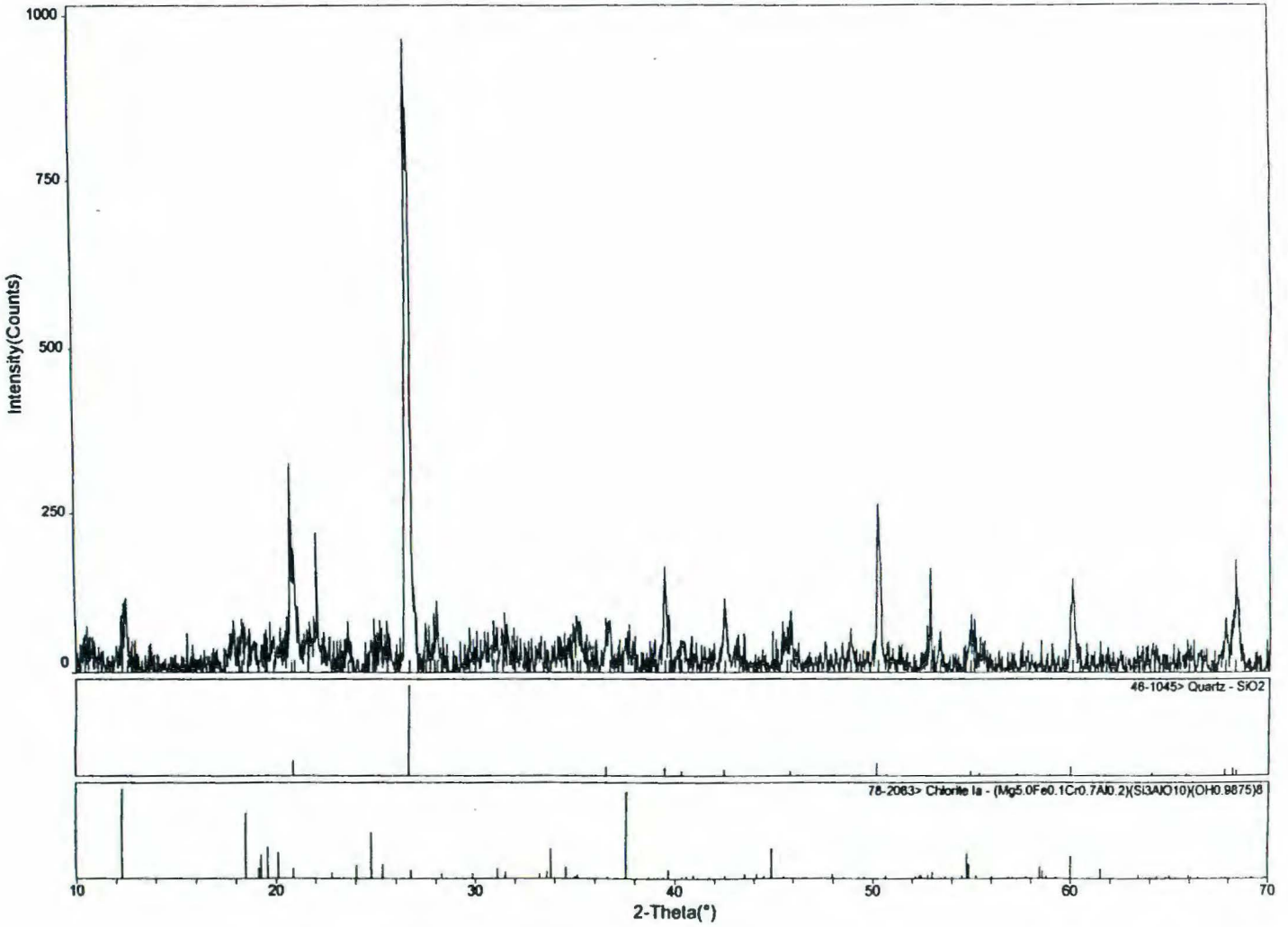
National Chromium, Inc., a small electroplating facility located near Putnam, Connecticut, discharged wastewater from Cr plating directly into an adjacent wetland from the beginning of the operation in 1939 up to 1975 (Nikolaidis et al., 1994), resulting in high levels of chromium contamination. The chromium electroplating process uses chromic acid/sulfuric acid baths, and the washing, dripping and spent plating

solutions were discharged into sewage (where the chromium killed treatment plant bacteria) or into wetlands and discharge ponds.

Soil horizon samples were taken from the peat-like surface to the white, clayey, glacial till in the wetland soil 50 m downslope from the facility. The uppermost horizon contained the highest total Cr levels of any soil in this study: green chromium(III) hydroxide coatings were evident on fallen branches and plant debris surrounding the site, and samples were measured with as much as 6% total chromium (Table 2-1). The soil is very poorly drained, and its pH, in contrast to the COPR soils, is low, from 4-5. Despite high levels of organic matter (200 g C/kg soil) there are ambient levels of Cr(VI) (60-90 μM) in the uppermost horizon. The XRD spectra of soil taken from this horizon (Figure 2-1b) shows quartz, and a Cr(III) rich chlorite that was identified as a possible major phase using JADE. Data identifying the peaks corresponding to these two phases is shown in Appendix A. Another likely form of Cr(III) present at the site is an aged, amorphous $Cr(OH)_3$ (s) formed by reduction of Cr(VI) in the plating waste. An XRD spectra would not identify such a non-crystalline phase.

The soil underlying the organic rich surface horizons is classified as a Saco silt loam (Soil Survey of Windham County, 1981). Chromium behavior in the soil profile is complex, Cr(VI) disappears in the middle horizons (where soluble Cr(III) can be found, perhaps complexed to organic matter), and it reappears in the glacial till. Mattuck (1994) reported Cr(VI) levels of up to 950 μM in groundwater sampled from the underlying aquifer from a well site about 10 m downslope from the electroplating facility. Since no chromate was found in the middle horizons of the soil profile, it is likely that the

Figure 2-1b. X-ray diffraction spectra for Connecticut plating waste soil, 0-14 cm. For peak identification tables see Appendix A.



chromate in the glacial till was transported to the wetland site through fractured flow from the underlying aquifer.

Aberjona Superfund Site

The Aberjona watershed near Woburn, Massachusetts was the site of over 100 chrome tanning operations which operated from 1838 to 1988 and also produced glue and grease from carcass residues. Inorganic arsenical and lead-based insecticides were manufactured in the same locale from the 1860s until the 1920s (Davis et al., 1994). In the tanning process, Cr(VI) was reduced with organic acids over the surface of animal hides, forming stable Cr(III) complexes that preserved the leather. Chromium was mainly discharged into lagoons that were used to dispose of the sludge remnants from leather production (U.S. EPA, 1981). Because of the high levels of animal organic waste, natural biodegradation processes depleted the soils at these sites of oxygen and formed highly reducing environments. Along with organic waste materials, the disposal site contains an array of metal co-contaminants, including As and Pb.

Two horizons of a riverbank soil classified as Freetown muck soil series were sampled at the Superfund site downstream from the tannery disposal lagoons. Conditions in the subjacent groundwater are conducive to sulfate reduction; the sulfide species produced could be expected to reduce any ambient Cr(VI). Although chromium appears exclusively as Cr(III) in these sites, it has a surprising degree of mobility in the groundwater (Davis et al., 1994), probably due to the enhanced solubility of Cr(III)

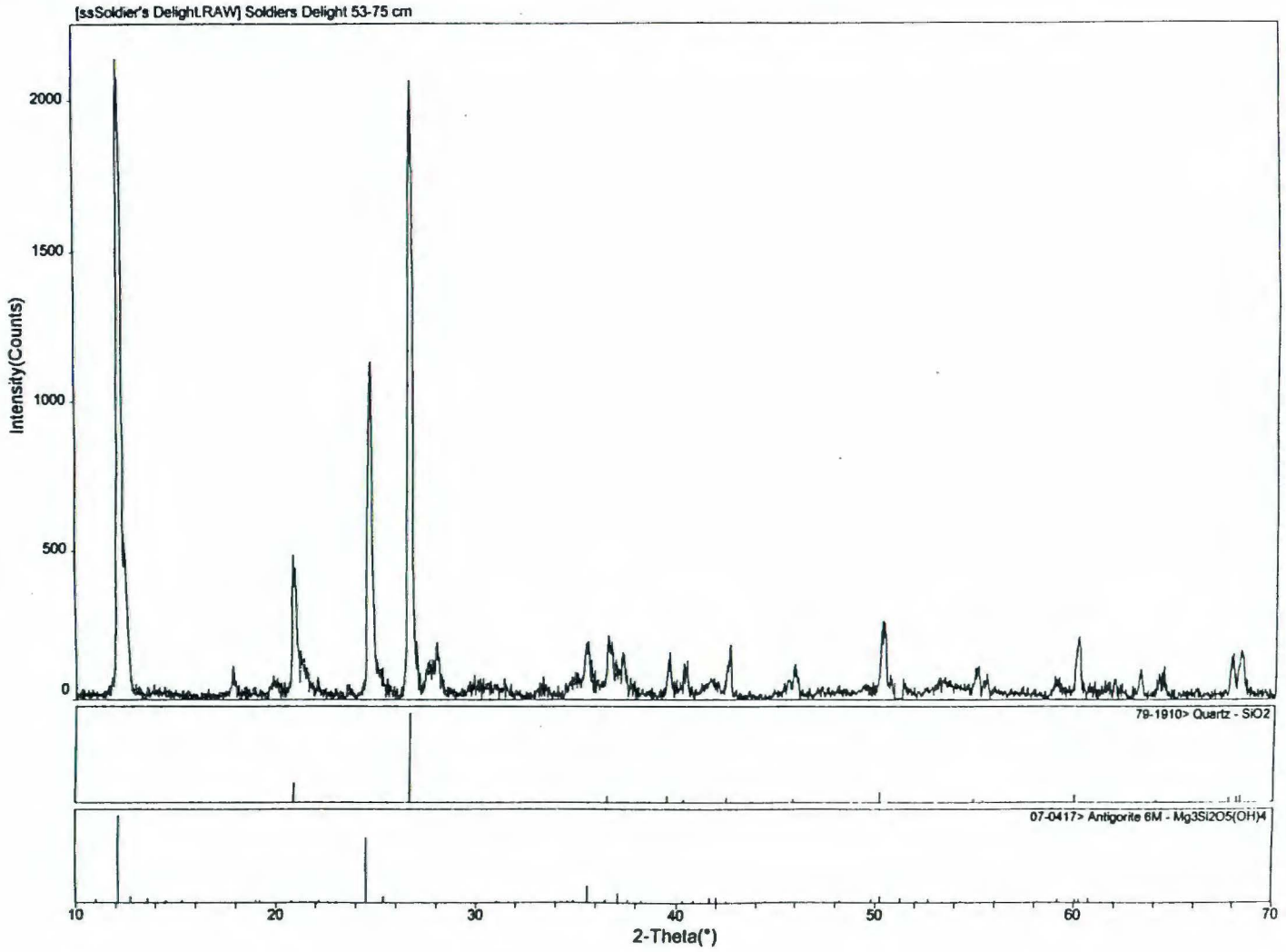
organic complexes (James and Bartlett, 1983a) formed with dissolved organic carbon provided by the decomposing hides.

Maryland Serpentine Barrens

Unlike the three other soils sampled, the samples taken from the Maryland serpentine barrens contain only naturally elevated levels of Cr. In the Piedmont of the eastern United States, a belt of serpentinite bodies extends from New Jersey to Alabama. These bodies are characterized by hydrated magnesian phyllosilicate minerals that are often also rich in chromium. In the early nineteenth century, prospector Isaac Tyson, Jr. associated the low fertility of serpentine soils with the presence of chromite ($FeCr_2O_4$) ore. He purchased land across Maryland, including an area northwest of Baltimore known as Soldier's Delight, which became a major source of industrial chromium in the 1840s. These soils have been previously studied extensively in an effort to determine the cause of their low fertility (Rabenhorst et al., 1982).

Soil was sampled at the Soldier's Delight site, 100 m from an old chromite mine, by horizon to a depth of 107 cm. The soil is classified as a Typic Hapludalf (fine silty, serpentinitic, mesic) and a detailed description of its properties and morphology is given in Rabenhorst et al. (1982). Those workers reported chromium levels as high as 5,850 mg/kg, principally as chromite ($FeCr_2O_4$), at a depth of 50-100 cm. Samples used in this study were taken from the 53-75 cm horizon, and contained 2,500 mg/kg total chromium, with no detectable soluble chromium (Table 2-1). The XRD spectra of soil from this horizon (Figure 2-1c) shows quartz and antigorite, a magnesian serpentine

Figure 2-1c. X-ray diffraction spectra for Serpentine soil, 53-75 cm. For peak identification tables see Appendix A.



mineral. The absence of chromite identified in the spectra does not rule out its presence in the soil under levels of 5%. Total chromite would amount to only 0.5% in a sample of this horizon if calculated on the basis of measured Cr.

Soil Sampling

Laboratory experiments were conducted using seven soil horizons sampled from the above four sites. A similar sampling protocol was followed at each site: an undisturbed area about $1m^2$ was cleared of leaf and plant covering, a pit was dug, soil horizons marked and identified, and samples taken from each horizon. Horizons were kept intact as large blocks, sealed in plastic bags, transported to the laboratory in coolers and stored in a refrigerator at 4° C.

It has been shown that drying a soil may cause the breaking up of soil organic polymers into more easily oxidized fragments (Bartlett and James, 1980). If soluble Cr(VI) is present when such a soil is dried, upon remoistening it may be reduced by the fragmented soil organic matter, altering original levels of Cr(VI) (Bartlett, 1991). It is therefore important to use samples that have been maintained in field moist conditions when investigating the oxidation or reduction of chromium in soils.

Intact blocks of soil from individual horizons were prepared by passing them through a polyethylene sieve using gentle hand pressure to obtain a relatively homogenous fraction. COPR soil samples were prepared using a 0.40 cm sieve; a 0.25 cm sieve was used on all other soils.

Chemicals

Analytical grade K_2CrO_4 aqueous concentrate was obtained from J.T. Baker and diluted to 19.23 mM. This was used to prepare Cr(VI) standards and stock solutions. Cr(VI) solutions were titrated in 0.01M $NaNO_3$ using NaOH or HNO_3 to obtain a desired pH. The laboratory preparation of aged, hydrolyzed solutions of Cr(III) is discussed in detail in Chapter 3. Reagent grade 30% H_2O_2 from Baker was used without stabilizers to make standards, which were freshly prepared for each series of experiments. Concentrations of H_2O_2 stock solutions were verified by titration with $KMnO_4$ using sodium oxalate (NaC_2O_4 determined gravimetrically) as a primary standard (Skoog et al., 1994). Catalase prepared from bovine liver was obtained from Sigma (1540 units/mg where one unit will decompose 1.0 μmol of H_2O_2 per min). Unless otherwise noted, all other chemicals were reagent grade, obtained from Baker, and used without further purification.

Experiments

Batch experiments were conducted in triplicate in 50 mL polycarbonate centrifuge tubes. Suspensions containing solution/soil ratios of 10/1 by mass were prepared by placing 3.00 g of soil in each tube and equilibrating for 24 ± 1 h at 25 °C on an orbital shaker (100 cycles/min, 30 minutes on, 30 minutes off) with 30.0 mL of 0.01M $NaNO_3$. Reactants (H_2O_2, Fe(II)) were added to the soil suspensions in small volumes (50 μL-aliquots) to obtain the desired initial concentration in the soil suspension so as not to

significantly dilute the original concentrations of chromium. Destructive sampling was used to monitor [Cr(VI)], [H_2O_2] and pH of the soil suspensions over time. Samples remained on the orbital shaker until analysis took place, at which time they were centrifuged (12,000 rpm, RCF 14,862, 15 min, 25 °C), and aliquots withdrawn from the supernatant liquid for determination of Cr(VI) and H_2O_2.

Analytical Methods

Soil solution pH (solution/soil ratio 10/1) was measured with an Orion flat surface combination pH electrode (calibrated using pHydrion buffers at pH 4, 7 and 10) inserted directly into supernatant solution in each centrifuge tube to a depth just above the soil plug. All spectral readings were done with a Shimadzu UV-1601 PC scanning spectrophotometer. Powder X-ray diffraction analysis was performed on air dried, crushed soil samples (see XRD data in Appendix for source specifications).

Soluble Cr(VI) in the soil suspensions was measured by the diphenylcarbazide (DPC) colorimetric method (Bartlett and James, 1979) using 0.5 mL of the DPC reagent (add 0.38 g DPC to 100 mL 95% ethanol and add to 120 mL 85% H_3PO_4 in 280 mL distilled H_2O) with a 4.5 mL-aliquot of the reaction supernatant. In cases where Cr(VI) concentrations fell above the linear standard curve (0.1-40.0 μM), 1:10 or 1:20 dilutions were made before withdrawing an aliquot to add to the DPC reagent. Diphenylcarbazide reacts with Cr(VI) in acidic solution to form a Cr(III)-diphenylcarbazone complex which absorbs as 540 nm (detection limit 0.1 μM). At concentrations higher than 10^{-5} M, H_2O_2 causes a negative interference with the DPC

determination of Cr(VI), because it will competitively reduce Cr(VI) under the low pH conditions of the test. Pettine et al. (1988) found that negative interference of H_2O_2 can be avoided at concentrations less than 10^{-4} M by increasing reagent concentrations. In these experiments, however, much higher concentrations of H_2O_2 were used (up to 0.1M), and the removal of peroxide by adding catalytic (10^{-8} M) amounts of catalase to a sample and allowing it to stand 30 minutes prior to analysis was shown to be effective. In those determinations where catalase was used, Cr(VI) standards (0, 1, 5, 10, 20, 30, 40 μM) were also prepared with 10^{-8} M catalase. The catalase raised absorbance readings slightly at 540 nm for all standards, but did not appear to affect Cr(VI). Results for standards using DPC and catalase corresponded well with results obtained using a direct optical method (@350 nm for $HCrO_4^-$ at pH 4).

Total Cr(VI) in the soil samples was determined using a heated carbonate-hydroxide extraction method found to be the most effective of several tested by James et al. (1995). The measurement included soluble, adsorbed or occluded Cr(VI), and Cr(VI) bound in a solid phase within the soil matrix. DPC measurements of extracted Cr(VI) were compared to samples prepared with DPC reagent blanks (without DPC). This accounted for slight discoloration of the sample solutions, probably due to the dissolution of fulvic acid under the initially alkaline, and subsequently acidic conditions of the test.

Total soluble Cr in the soil was determined by atomic absorption, and total Cr in the soil was determined by atomic absorption following a digestion procedure using

H_2SO_4 -H_2O_2 -HF dissolution of oven dried (105 °C) crushed (35-mesh) soil samples (Bowman, 1988).

A slight modification of the 4-amino antipyrene horseradish peroxidase method, reviewed by Frew et al. (1983), was used to determine H_2O_2 concentrations. H_2O_2 will oxidatively couple with 4-amino antipyrene (AAP) and phenol, in the presence of horseradish peroxidase to produce a quinoneimine dye with a maximum absorption at 505 nm. The linear range was 1-300 μM H_2O_2 (Frew et al., 1983). The modified aqueous reagent was mixed in a 500 mL volumetric flask as follows: 0.0010 g horseradish peroxidase (type VI) from Sigma (about $2x10^{-8}$ M), 0.50 g 4-aminoantipyrene, 1.17 g phenol, 5.0 mL 0.1M triphosphate buffer (pH 6.9), 100 μL of 0.01M H_2O_2 (or 2 μM) to give more stable readings. Reagent (2.0 mL) and aqueous sample (3.0 mL) were vortexed; absorbance readings at 505 nm reached a maximum in 30-120 seconds, after which they were no longer stable. Sample color faded at a rate that varied with H_2O_2 concentrations.

Analytic uncertainties are graphically indicated by the presence of error bars associated with each data point. These are based on reproducibility and are calculated as ± 1 SD. In many cases they are too small to be visible. Correlation coefficients (r^2) for standard curves were greater than 0.998 for Cr(VI) methods and greater than 0.995 for H_2O_2 methods. A summary of analytical methods with their associated experimental uncertainties follows in Table 2-2.

Table 2-2. Summary of Analytical Methods

Determination	Method	Analytical Error	Linear Range
Total Cr [1.]	HNO_3, H_2O_2, HF digestion, flame AA determination	3%	1 μM - 120 μM
Total Cr(VI) [2.]	base, carbonate extraction, DPC detemination	2%	0.1 μM - 40 μM
Soluble Cr(VI) in soil supernatant solutions [3.]	Diphenyl carbazide	2%	0.1 μM - 40 μM
Soluble Cr(VI) in aqueous systems, pH 4-5	Direct absorbance @ 350 nm	1%	1 μM - 150 μM
H_2O_2 in soils and aqueous systems [4.]	4-antiaminopyrene	2%	1 μM - 300 μM

1. Bowman, 1988.
2. James et al., 1995.
3. Bartlett and James, 1979.
4. Frew et al., 1983.

RESULTS AND DISCUSSION

Chromite Ore Processing Residue (COPR)

A significant increase in soluble Cr(VI) was shown to take place in samples of the COPR soil treated with single applications of 24 mM H_2O_2 (Figure 2-2), raising 900 μM ambient chromate levels about 30%. The higher levels of chromate were sustained in the alkaline soil for over a week, while 25% of the peroxide disappeared in the first hour after treatment, and was undetectable (under 0.1 μM) in the soil within 24 hours after treatment. Lower concentrations of peroxide treatment produced smaller increases in Cr(VI) concentrations (about 10%, from 900 μM to 1000 μM) over control samples with no added peroxide, but not systematically, i.e., higher H_2O_2 levels didn't necessarily produce higher Cr(VI) concentrations.

Variability in the data exceeds analytical error (2%, due mainly to the 10 or 20-fold dilution necessary to measure mM levels of Cr(VI)). Each data point was obtained from three separate subsamples taken from a larger, surface horizon field sample that was sieved (4.0 mm) and thoroughly mixed. Even after sieving, however, COPR soil contains unevenly distributed, small pellets extremely high in chromate. As a result, a wide range of soluble Cr(VI) (856-1020 μM) was measured in untreated control samples (see Table 2-3). It is probably due to this heterogeneity of the soil mixture that any effects of H_2O_2 treatments below 24.0 mM were not discernible.

Although the chromite ore processing residue was subject to efficient leaching methods to remove soluble Na_2CrO_4, it has continued to release Cr(VI) for decades after its disposal (Burke et al., 1991). Sparingly soluble chromate compounds have been

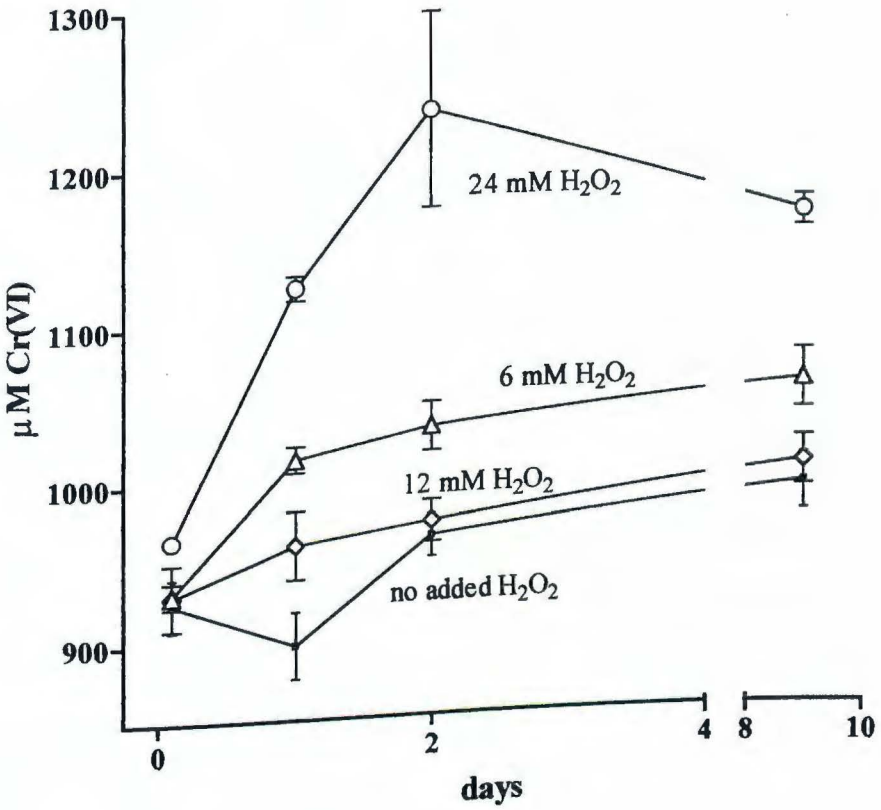


Figure 2-2. Changes in Cr(VI) concentrations in COPR soil (10/1 solution/soil by mass) upon single applications of H_2O_2. For data see Table 2-3. Error bars are shown for each data point as ± 1 SD. Variability in data exceeded expected analytical error of 2% due to the heterogeneity of the COPR soil, which contained unevenly distributed, high-chromate pellets. H_2O_2 disappears within 1 day (see Table 2-3).

Table 2-3. Data for Figure 2-2. Cr(VI) concentrations in COPR soil upon single applications of H_2O_2 (at day zero). H_2O_2 disappearance in soil shown for highest application level. Samples measured at 10/1 solution/soil by mass, pH for all samples 8.8 ± 0.1.

Cr (VI) (μM)

Day	0.1	1	2	9
H_2O_2 added (mM)				
None	896 926 953	911 925 856	937 978 975	960 989 1020
0.75	989 959 980		1040 1010 1070	1040 1000 1060
1.50	932 920 938		978 1010 983	1020 1030 1040
3.00	941 959 929		1010 1030 1020	1050 1050
6.00	921 947 926	1020 1020 998	1020 1060 1010	1050 1090 1030
12.00	914 971 905	960 998 923	954 990 966	975 1030 1010
24.00	971 962 962	1130 1130 1110	1350 1220 1130	1180 1160 1150

H_2O_2 (mM)

H_2O_2 added (mM)	1.5 hour	24 hour
24.00	9.89 10.70 9.61	Not detectable

shown to be present in the residue at concentrations of between 0.7 to 5%. Among these, $CaCrO_4$ may predominate, and other Cr(VI) compounds found in the ore residue include calcium aluminochromate ($3CaO{\cdot}Al_2O_3{\cdot}\ CaCrO_4$), tribasic calcium chromate [$Ca_3(CrO_4)_2$], and basic ferric chromate ($FeOHCrO_4$)(Gancy and Wamser, 1976). Soluble chromate in COPR soil may be controlled by these solid phase Cr(VI) salts. The relatively high K_{sp} of calcium chromate (7.1×10^{-4}) and high levels of calcium (up to 20% as calcium carbonate or calcium oxides) in the soil from the original lime treatment of the chromite ore suggest $CaCrO_4$ as the most likely candidate for controlling Cr(VI) solubility in COPR soils (James, 1994).

The 30% increase in soluble Cr(VI) observed by the addition of 24.0 mM H_2O_2 could be explained in two ways. Hydrogen peroxide either oxidized Cr(III), or dissolved Cr(VI) salts. Cr(VI) dissolution by H_2O_2 would suggest a complexation reaction between Cr(VI) and H_2O_2. The formation of the red-brown anion, tetraperoxochromate(V) ($[Cr(O_2)_4]^{3-}$) has been observed in the reaction between H_2O_2 and CrO_4^- under alkaline conditions (Dickman and Pope, 1994), although its formation from a sparingly soluble Cr(VI) salt has not been shown. Its 4:1 H_2O_2:Cr ratio would make its formation highly dependent on H_2O_2 levels. (Due to the use of catalase in the DPC determination of Cr(VI) under conditions of ambient H_2O_2 ($> 10^{-5}$ M), we would not expect to see any decrease in $[CrO_4^{2-}]$ due to its complexation with H_2O_2, because catalase destroys ambient H_2O_2. The catalase would either shift equilibrium conditions back toward CrO_4^{2-}, or attack the peroxo ligands on the Cr-H_2O_2 complex directly.) If

Cr(VI) salts dissolved through complexation with H_2O_2, the complex would then release CrO_4^{2-} into the soil solutions as H_2O_2 levels dropped.

The swift disappearance of the H_2O_2 in the COPR soil within one day, while enhanced Cr(VI) levels persisted for over a week, also supports the explanation that H_2O_2 oxidized Cr(III) components of the COPR soil. Cr(III) in COPR soil has been shown to be resistant to other oxidants: James found that neither the Cr(III) present in COPR soils, nor soluble Cr(III) added to COPR will oxidize when exposed to Mn (III,IV) (hydr)oxides, despite the high pH and low organic matter conditions favorable to sustaining Cr(VI). This implies that peroxide may be uniquely capable of oxidizing chromium in COPR soil.

Electroplating Waste Site in Connecticut

Within a single soil profile at the Connecticut plating waste site, H_2O_2 treatments produced markedly different results. Results from three horizons are reported: the peat-like uppermost (0-14 cm) horizon, with ambient levels of soluble Cr(VI) ranging between 60-90 μM; the more reducing underlying (14-40 cm) horizon which contained 5-6 μM soluble Cr(III) (Typrin, 1998) probably in the form of soluble organic complexes; and the white and clayey glacial till layer (>100 cm), with ambient soluble Cr(VI) in the 40-60 μM range (see Table 2-1).

Increases in soluble Cr(VI) were observed in the uppermost horizon after single applications of peroxide at various concentrations (Figure 2-3). Unlike results in the

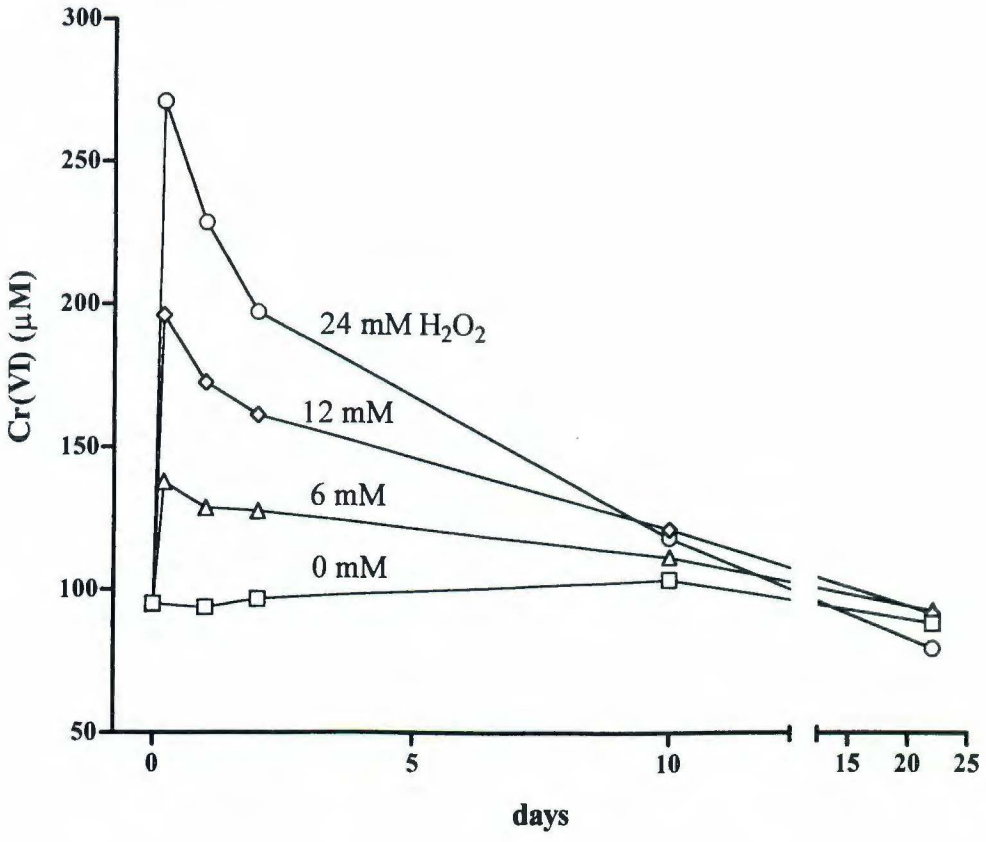


Figure 2-3. Changes in Cr (VI) concentrations (10/1 soln/soil by mass) in Connecticut wetland plating waste soil (0-14 cm horizon) upon single applications of H_2O_2 (at day zero). For data see Table 2-4. Error bars are shown for each data point as ± 1 SD.

Table 2-4. Data for Figure 2-3. Changes in Cr(VI) concentrations in Connecticut wetland plating waste soil (0-14 cm horizon) upon single applications of H_2O_2 (at day zero). Analytical error associated with Cr(VI) determination is ± 2 μM. Initial [Cr(VI)] for all samples taken as 95 ± 6 μM (10/1 soln/soil by mass). Solution pH 5.4 ± 0.1 for all samples after day 1. H_2O_2 not detected day 1-22.

Cr (VI) (μM)

Day	0.2	1	2	10	22
Peroxide added (mM)					
None	90.0 90.0 91.2	92.6 94.1 94.6	94.4 99.1 96.8	104 105 102	88.7 88.9 87.5
0.75	100 101 104	100 108 102	101 102 105	101 101 105	91.0 88.4 92.5
1.50	104 101 105	105 105 107	105 106 103	98.6 99.5 103	82.9 85.5 90.7
3.00	108 110 111	111 111 114	116 113 113	104 104 107	90.1 88.4 92.2
6.00	137 142 134	130 130 126	127 129 127	111 111 113	91.6 92.8 93.9
12.00	198 195 195	174 174 169	159 165 159	122 123 119	91.6 92.5 91.3
24.00	270 271 272	227 229 230	198 195 198	120 116 119	83.4 77.6 77.3

COPR soil, soluble Cr(VI) increases over ambient chromate levels varied with the concentration of H_2O_2 applied, from an increase in Cr(VI) of 30% from a 750 μM application of H_2O_2, to an increase of 250% in soluble Cr(VI) after a single application of 24 mM H_2O_2. Increases in chromate levels reached a maximum 4 hours after peroxide applications. As with the COPR soil, two explanations for the increases in Cr(VI) in this horizon are possible: either H_2O_2 oxidized Cr(III) present in the soil, or it released existing Cr(VI) from the soil matrix.

Cr(III) oxidation is suggested by pH changes observed after applying H_2O_2. Increases in Cr(VI) were accompanied by decreases in soil pH (solution/soil ration 10/1) from original values of 5.5 to as low as 4.6 for the highest peroxide application levels (Figure 2-4). The lowering of pH in these samples may correspond to chromium oxidation (equation 1.26). Although the one unit pH change does not account for total increases in Cr(VI), this is an expected result of the buffer capacity of the soil, further evidenced by the observation that soil pH returned to original levels after a day, while chromate levels still remained high. Within two hours after application, about half of the peroxide in samples spiked with 24 mM levels had disappeared, and peroxide was not detectable in any sample after one day. Enhanced chromate levels, on the other hand, persisted long after the peroxide disappeared, declining over a two week period at rates that varied with chromate concentrations, until they reached initial ambient levels of soluble Cr(VI). At the highest treatment levels, enhanced soluble Cr(VI) levels (270 μM) surpassed Cr(VI) levels that would have been present if all forms of Cr(VI) in the horizon sample had been released into solution (Table 2-1). This provides further

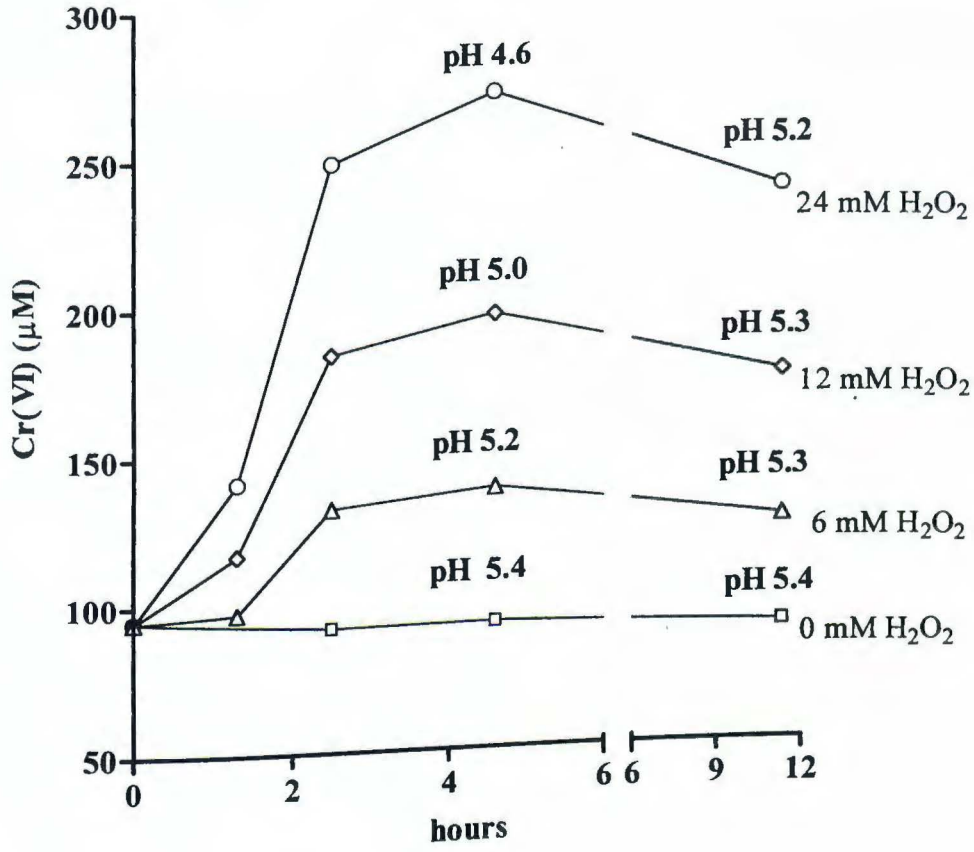


Figure 2-4. Short term changes in pH and Cr(VI) concentrations (10/1 soln/soil by mass) in Connecticut wetland plating waste soil (0-14 cm horizon) upon single applications of H_2O_2. Solution pH given above Cr(VI) data points. Error bars are shown for each data point as ± 1 SD. Analytical uncertainty ± 2 μM for Cr(VI).

Table 2-5. Data for Figure 2-4. Short term changes in Cr(VI) concentrations in Connecticut plating waste site (0-14 cm) after single applications of H_2O_2. Analytical uncertainty for Cr(VI) is ± 2 μM.

Hours	1.3	2.5	4.6	11.3
H_2O_2 added (mM)	Cr(VI) (μM)	Cr(VI) (μM)	Cr(VI) (μM)	Cr(VI) (μM)
6.00	100 95.6 98.0	135 129 132	142 134 137	128 123 127
12.00	119 116 116	187 182 182	198 195 195	176 175 174
24.00	144 139 141	249 247 249	270 271 272	240 237 238

evidence that oxidation of Cr(III) by peroxide contributed to the increase in soluble Cr(VI).

Cr(III) present in this soil (60 g/kg, Table 2-1) was the result of the reduction, over many years, of large quantities of Cr(VI) in an overland flow of the plating plant discharge to the wetland site. Cr(III) in the soil is therefore relatively newly-reduced as amorphous Cr(III) (hydr)oxides or Cr(III)-humates, as opposed to "older" Cr(III) forms found in soil e.g. Cr_2O_3 or $FeCr_2O_4$.

A reducing fraction of the high levels of organic matter in this horizon could account for the return of soluble chromate to levels observed prior to H_2O_2 treatment. Wittbrodt and Palmer (1996) observed the reduction of Cr(VI) by soil humic and fulvic acids across a pH range of 2-7. Nakayasu, et al. (1999) found that gallic and tannic acids (polyphenols that originate in decaying leaves, likely precursors to humic substances) reduced Cr(VI) at pH 5 at even faster rates than humic and fulvic acids. In the first step of the reduction process, Cr(VI) forms an organic chromate ester, bonding to an alcohol or an aldehyde functional group on a particulate organic substrate (Kläning, 1977):

$$HCrO_4^- + ROH \rightarrow ROCrO_3^- + H_2O \qquad (2.2$$

Although small equilibrium constants for this reaction (Kläning, 1958) caused Kieber and Helz (1992) to discount its importance in natural waters, equilibrium between soil solution Cr(VI) and Cr(VI) organic esters forming in this peat-like horizon may be a factor in the return of chromate levels in all samples to the 60-90 μM range.

If ambient soluble chromate levels in this horizon were being controlled by a solid phase source of Cr(VI), one would expect to see an equilibrium concentration of chromate approached as solution to soil ratios were raised above the somewhat arbitrary 10:1 ratio chosen for lab experiments done in centrifuge tubes. Figure 2-5 shows chromate concentrations leveling at about 20 μM as solution-to-soil ratios were raised from 10:1 to 80:1. A solid phase possibility for the control of soluble chromate in this horizon is the iron-chromate precipitate ($KFe_3(CrO_4)_2(OH)_6$) identified by Baron et al. (1996) in an Oregon soil contaminated by chrome plating solutions. Formation of this chromate analog of the sulfate mineral jarosite is consistent with the common occurrence of jarosite in acid sulfate soils (Wagner et al., 1982). In the case of the chromate mineral, Cr(VI), K, Fe(III) and low pH conditions could all be derived from the discarded plating solutions, although K^+ could also be available as a soil exchangeable cation, and Fe(III) from native oxyhydroxides. Baron and Palmer (1996) determined a solubility constant for the chromate mineral, where log Ksp = -18.4 ± 0.6 at 25 °C for the dissolution reaction:

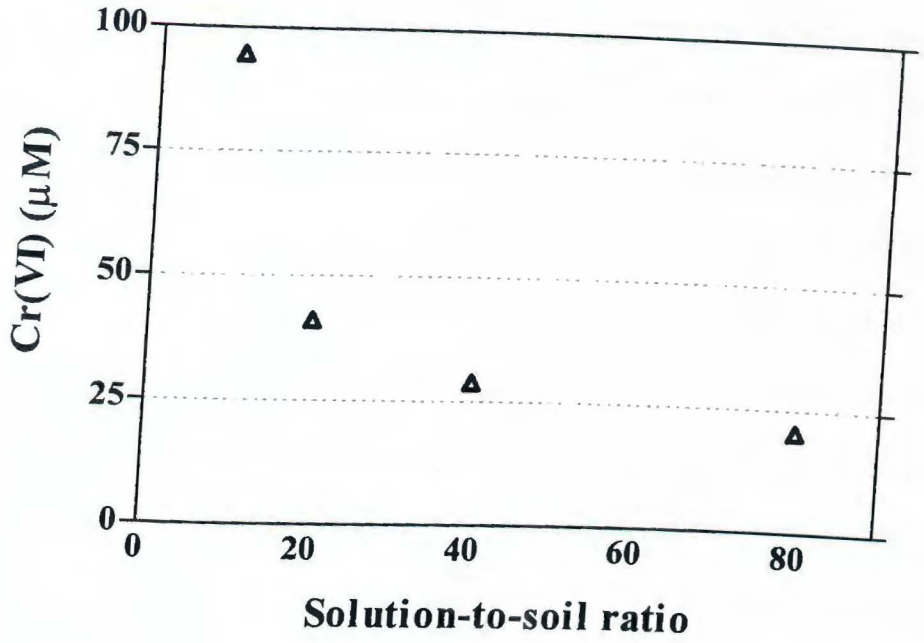
$$KFe_3(CrO_4)_2(OH)_6(s) + 6H^+ \rightleftharpoons K^+ + 3Fe^{3+} + 2CrO_4^{2-} + 6H_2O(l) \qquad (2.3$$

If it is assumed that [Fe(III)] is controlled by ferrihydrite (log K_{sp} = 4.89, Woods and Garrels, 1987):

$$Fe(OH)_3(s) + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O(l) \qquad (2.4$$

and if the protonation of CrO_4^{2-} to form $HCrO_4^-$ (log K_b = 6.4) is also taken into account, the overall reaction becomes:

$$KFe_3(CrO_4)_2(OH)_6(s) + 3H_2O(l) \rightleftharpoons K^+ + 3Fe(OH)_3(s) + 2HCrO_4^- + H^+ \qquad (2.5$$



Soln/soil ratio	10	20	40	80
Cr(VI) (μM)	93.4 95.7	40.0 42.0	29.4 28.2	20.1 20.4

Figure 2-5. Effect of varied solution to soil ratios on Cr(VI) measurements in the 0-14 cm horizon of the Connecticut plating waste soil. Analytical uncertainty for Cr(VI) is ± 2 μM.

with a calculated K = 5.0 x 10^{-21}. If [Cr(VI)] = 20 μM (solution/soil ratio 80/1), and K^+ is assumed to be controlled by the chromate jarosite and is therefore 0.5[Cr(VI)], and pH is 5, then an empirical K = 4.0 x 10^{-20} is obtained, within an order of magnitude of the calculated K. A similar calculation using the less soluble goethite (FeOOH, log K_{sp} = -1.0) would predict 1 M Cr(VI) in solution, clearly far from measured levels.

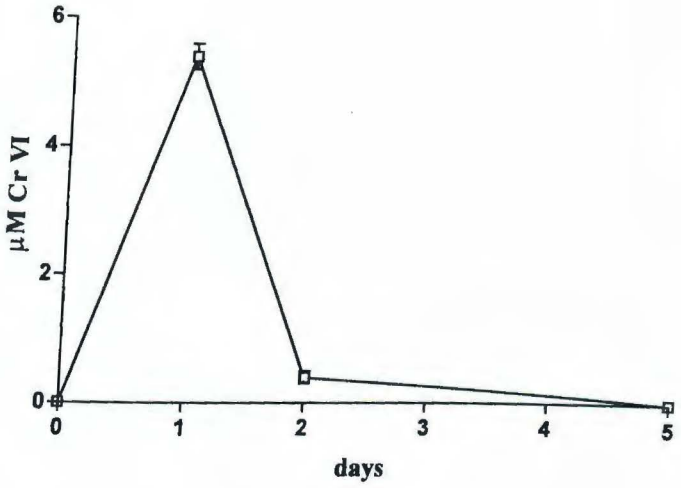
We may therefore consider the chromate jarosite to be a viable possibility as a solid phase controlling ambient Cr(VI) in this horizon, if a relatively unstable Fe phase is also present. High sulfate conditions in plating waste (from H_2SO_4 used in plating solutions) also suggest that solid solutions could form between the ferric chromate salt and a sulfate lattice, and could cause some variation in expected Cr(VI) solubilities.

The hypothesis of a solid phase controlling the solubility of Cr(VI) in this horizon also provides an alternate interpretation of the return of soluble Cr(VI) to ambient levels. Instead of being reduced by an active fraction of soil organic matter, the extra $HCrO_4^-$ generated by oxidation of Cr(III) may be gradually precipitated by reaction with an excess Fe phase.

Since the abundant quantities of Cr(III) oxyhydroxides in this soil have been formed as the result of the reduction of Cr(VI) in plating waste, it is possible that Cr(VI) became sequestered within the Cr(III) precipitation matrix during the reduction process. Such "matrix chromate" could be released in any process affecting dissolution of the solid, such as oxidation of surrounding Cr(III). Attempts to reproduce such a phenomenon in the laboratory yielded some evidence for its occurrence: adsorbed chromate that was exchangeable from the surface of a chromium hydroxide precipitate

by equilibration in phosphate solution (method of James et al., 1995) was three to four times higher in a system that was prepared with chromate added after the hydroxide precipitation of a Cr(III) salt than in a similar system where precipitation took place in the presence of the chromate. Attempts to measure any Cr(VI) that may have been sequestered in the solid phase of the latter system were unsuccessful due to the oxidation of Cr(III) during the base extraction process (James et al., 1995) designed to release solid phase Cr(VI).

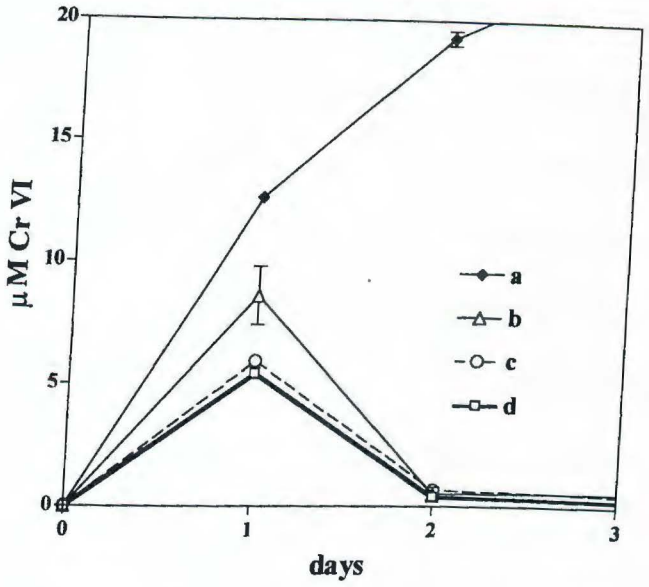
Whatever may be controlling ambient levels of soluble Cr(VI) in the uppermost Connecticut horizon, it is clear that chromium in this soil does oxidize in response to treatment with peroxide. Chromium (III) in the adjacent underlying horizon, which has no ambient soluble chromate, was also oxidized by peroxide, but to a lesser extent. Chromate levels reached 5-6 μM (Figure 2-6), which corresponded to initial levels of soluble Cr(III) in this horizon. If Cr(VI) were being released from a solid phase by H_2O_2, higher Cr(VI) levels should have been seen in this horizon after H_2O_2 treatment, since it contained total Cr(VI) levels comparable to the surface horizon (Table 2-1). Figure 2-7 shows no significant enhancement of Cr(III) oxidation in this system by the addition of catalytic amounts of Fe(II), and also shows the effect of spiking this soil with 100 μM aged, hydrolyzed, Cr(III). An increase in resulting chromate is observed, but it only accounts for about 4-5% of the added Cr(III), indicating that chromium reduction is favored by soil processes in this horizon, which is also observed in the rapid disappearance of chromate after it forms.



Cr(VI) (µM)

days	a		
	Y1	Y2	Y3
0.0	0.0	0.0	0.0
1.0	5.2	5.8	5.2
2.0	0.5	0.5	0.2
5.0	0.0	0.0	0.0

Figure 2-6. Cr(III) oxidation by a single application of 12.0 mM H_2O_2 in the 14-40 cm horizon of Connecticut wetland plating waste soil. Error bars are shown for each data point as ± 1 SD. Analytical uncertainty for Cr(VI) is ± 0.2 µM.



day	a			b		
	Y1	Y2	Y3	Y1	Y2	Y3
0	0.0	0.0		0.0	0.0	0.0
1	12.6	12.6		9.7	9.9	6.2
2	19.6	19.0		0.5	1.0	0.5
4	26.0	26.6				
5				1.0	0.7	0.5

day	c			d		
	Y1	Y2	Y3	Y1	Y2	Y3
0	0.0	0.0	0.0	0.0	0.0	0.0
1	5.9	6.0	5.8	5.2	5.8	5.2
2	0.9	0.6	0.5	0.5	0.5	0.2
5	0.0	0.1	0.1	0.0	0.0	0.0

Figure 2-7. Cr(III) oxidation by H_2O_2 in 14-40 cm horizon of Connecticut wetland plating waste soil (10/1 solution/soil by mass for all soil samples). a) aqueous control using 100 µM aged, hydrolyzed Cr(III)(2 OH^-/1 Cr(III)) and 1.00 mM H_2O_2 b) soil spiked with 100 µM aged, hydrolyzed Cr(III) (2 OH^-/1 Cr(III)) and 12.0 mM H_2O_2 c) soil spiked with 1.00 µM Fe(II) and 12.0 mM H_2O_2 d) soil only with 12.0 mM H_2O_2. Error bars are shown for each data point as ± 1 SD. Analytical uncertainty for Cr(VI) is ± 0.2 µM.

Not surprisingly, peroxide took twice as long to disappear in the 14-40 horizon than in the 0-14 horizon, which contained much higher levels of organic matter (Table 2-6). Reduced chromium may be "tanning" the organic matter in this horizon, stabilizing it, and rendering it less bioavailable. In their study of the products of Cr(VI) reduction by gallic and tannic acids, Nakayasu et al. (1999) observe the polymerization of the polyphenols during Cr(VI) reduction, and complexation of Cr(III) with the polymerized compounds. This effect may prevent the high organic matter soil from becoming completely anaerobic, perhaps explaining why chromium oxidation occurs to any extent in this poorly drained horizon.

Application of 3 mM peroxide to the glacial till horizon produced an entirely different effect (Figure 2-8): an initial rise in pH and a loss of ambient chromate levels, followed by a return of chromate to its initial concentration. A sample spiked with 50 μM $HCrO_4^-$ showed a similar pattern. Figure 2-9 is taken from data presented in Chapter 3 (Figures 3-5a, 3-5b) from experiments in an aqueous Cr(VI)/H_2O_2 system with an original pH of 4.5, and shows similar behavior, albeit over a longer time period. The Cr(VI) disappearance and reappearance in this horizon could be explained by Cr(VI) reduction and Cr(III) reoxidation, or by the formation of a soluble peroxochromium (VI) complex, which reverts to $HCrO_4^-$ as H_2O_2 levels in the aqueous system drop.

The low levels of soil organic matter in this horizon allowed for a direct determination of Cr(VI) by absorbance at 350 nm, rather than via the determination of the DPC derivative. The behavior of a Cr(VI) peroxo complex which could not be observed in the other soils due to the addition of catalase to avoid H_2O_2 interference in

Table 2-6. Disappearance of 24.0 mM H_2O_2 after a single application in three soils.

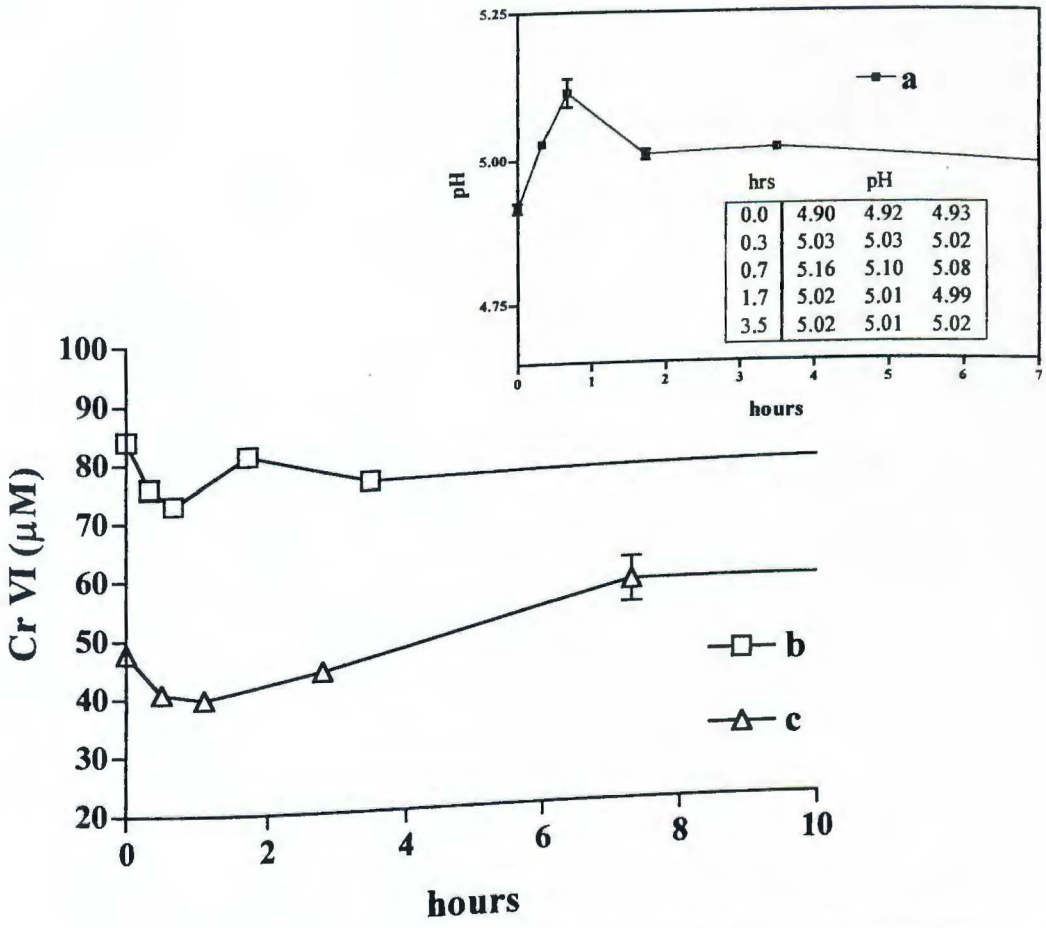
H_2O_2 (mM)

Soil	1.5 hr	24 hr	48 hr
COPR	9.9 ± 0.3 10.7 9.6	<0.005 for all samples	<0.005 for all samples
Connecticut 0-14 cm	11.5 ± 0.3 11.8 11.7	2.5 ± 0.3 2.8 2.5	<0.005 for all samples
Connecticut 14-40 cm	18.2 ± 0.3 18.6 18.6	<0.005 for all samples	<0.005 for all samples

Table 2.7. Cr(VI) (μM) was not detected over the course of one week in two soils treated with single applications of 0.1, 0.05 and 0.025 M H_2O_2. Data was the same for all three treatment levels.

Cr(VI) μM

	1day	2day	4day	7day
Aberjona	< 0.1	< 0.1	< 0.1	< 0.1
Serpentine	< 0.1	< 0.1	< 0.1	< 0.1



hours	b		
	Y1	Y2	Y3
0.0	83	86	84
0.3	74	79	75
0.7	72	74	74
1.7	81	83	79
3.5	76	74	79
22.5	81	82	82

hours	c		
	Y1	Y2	Y3
0.0	47	47	49
0.5	40	41	42
1.1	39	40	41
2.8	42	44	47
7.3	53	54	65
24.5	58	59	61
50.0	51	52	53

Figure 2-8. Short term changes in Cr(VI) concentrations in glacial till underlying a Connecticut wetland plating waste soil after a single application of 3.00 mM H_2O_2 a) pH in soil amended with 50 μM $HCrO_4^-$ b) Cr(VI) changes in amended soil c) Cr(VI) changes in unamended soil. Analytical uncertainty for Cr(VI) is ± 2 μM.

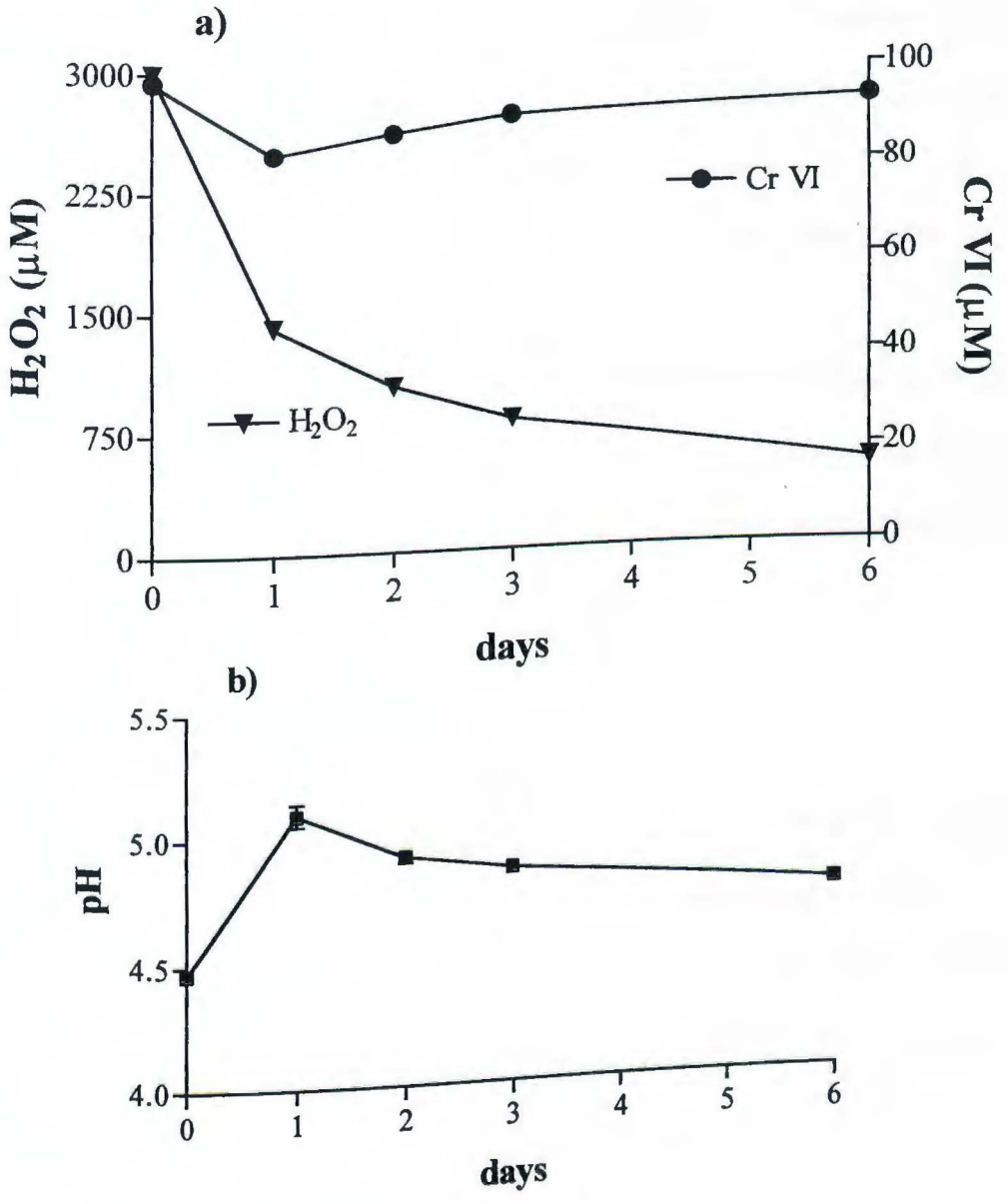


Figure 2-9. Reaction of 3000 μM H_2O_2 and 100 μM $HCrO_4^-$ in aqueous solution of 0.01 M $NaNO_3$ at initial pH 4.5. a) Changes in H_2O_2 and $HCrO_4^-$ concentrations b) changes in pH. Data in Figures 3-4a, 3-4b, 3-4c.

the DPC test, may possibly be evident here. A violet, diperoxochromium(VI) complex has been shown to form at pH 4-7 (Funashi, 1978; Perez-Benito and Arias, 1997):

$$HCrO_4^- + 2H_2O_2 = Cr(O)(O_2)_2OH^- + 2H_2O \quad (2.6$$

Determination of its K_f continues to be problematic due to the complicated behavior of H_2O_2 in its presence (Zhang and Lay, 1998).

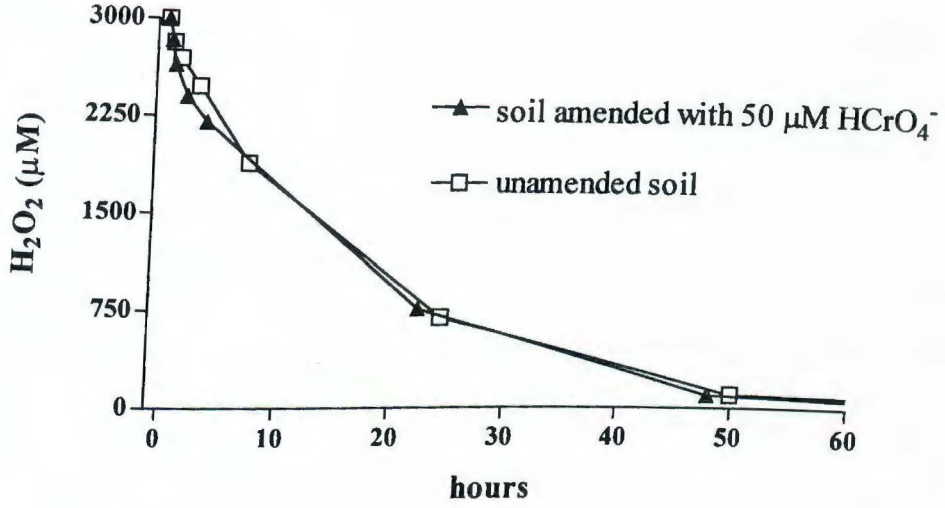
Initial concentrations of peroxide (3 mM) in the glacial till took about two days to disappear in the soil (Figure 2-10). Any peroxochromium complex formed in the soil would presumably undergo degradation via surface reactions more quickly than in an aqueous system.

Aberjona Superfund Site

Oxidation of chromium was not observed in the highly reducing environment of the Massachusetts tannery waste site soil, at peroxide application levels of up to 0.1M (Table 2-7). Bartlett and James (1979) did observe the oxidation of soluble Cr(III) added to a high Mn sewage sludge and tannery waste, and observed its subsequent reduction over a period of two months.

Maryland Serpentine Barrens

Samples high in chromium (2,500 ± 150 mg/kg soil) did not produce soluble chromate on treatment with up to 0.1 M H_2O_2 (Table 2-7). Cr(III) has been shown to appear in serpentine soils as chromite ($FeCr_2O_4$) (Rabenhorst et al., 1982), and it has been observed that co-precipitation with iron will reduce chromium reactivity and



hours	a		
	Y1	Y2	Y3
0.0	3000	3000	3000
0.3	2822	2846	
0.7	2745	2546	2642
1.7	2400	2424	2374
3.5	2214	2177	2217
22.5	796	727	756
48.0	85	107	95
72.0	25	27	23

hours	b		
	Y1	Y2	Y3
0.0	3000	3000	3000
0.5	2742	2779	2925
1.1	2647	2660	2774
2.8	2485	2469	2475
7.3	1947	1942	1770
24.5	727	727	626
50.0	122	108	75
121.0	0	0	0

Figure 2-10. Changes in H_2O_2 concentrations (μM) in glacial till underlying a Connecticut wetland plating waste soil after a single application of 3.00 mM H_2O_2. Analytical uncertainty in H_2O_2 determination is 2%. Error bars are shown for each data point as ± 1 SD.

solubility (Sass and Rai, 1987). Samples spiked with 100 μM soluble Cr(III) showed only a 1% oxidation of chromium when treated with 3 mM peroxide, but the Cr(VI) persisted at 1 μM for days showing no decreasing trend (Appendix Figure A-3, A-4).

CONCLUSIONS

Soils with elevated chromium from four different sites, and even soils from horizons within the same profile responded differently to treatment with H_2O_2. Soils with high ambient levels of soluble Cr(VI), such as ore processing residues, and high levels of recently reduced Cr (III), such as electroplating waste sites, showed marked increases in chromate after single applications of mM peroxide over a 4-10 pH range. Soluble Cr(III), in the form of dissolved organic complexes, as found in the 14-40 cm horizon of the plating waste site also contributes to the likelihood of Cr(III) oxidation by peroxide. Anaerobic soil conditions found in the Aberjona tannery site, however, may prevent the oxidation of soluble Cr(III). Chromium (III) present in soil as chromite, as in the Serpentine Barrens site, also appeared to be resistant to peroxide oxidation.

The disappearance of soluble Cr(VI) after treatment with peroxide in soils above pH 4 could be due to the formation of soluble Cr(VI) peroxo complexes and should not be assumed to be caused by chromate reduction. Once H_2O_2 levels dissipate in a soil, soluble Cr(VI) which disappeared upon initial H_2O_2 treatment could reappear.

It should be kept in mind that these experiments were conducted with one application of peroxide, and most remedial peroxide treatments call for continuous delivery of peroxide over many days, and at much higher concentrations than those used in these experiments.

The extent and persistence of chromium oxidation under such conditions would be much greater, as would be the possibility of forming reactive peroxochromium intermediate species.

Chapter 3

Chromium Oxidation, Reduction and Complexation by Hydrogen Peroxide in Defined Aqueous Systems

INTRODUCTION

Understanding the interaction of chromium and hydrogen peroxide has become relevant to environmental science due to clean-up strategies currently being tested by EPA which use high levels of H_2O_2 (U.S. EPA, 1998) to oxidatively remediate biorefractory organic contaminants in soils. In the context of soil remediation, not only are we compelled to look at the possibility of the oxidation of chromium in soils by hydrogen peroxide to its soluble and toxic hexavalent form, we should also consider the formation of intermediate species which may be generated in the soil in the presence of peroxide and chromium, and which may be the very species responsible for the toxicity and mutagenicity of Cr(VI) (Kawanishi, et al., 1986; Aiyar et al., 1991; Shi et al., 1999).

The kinetics of Cr(III) oxidation by H_2O_2 under highly alkaline conditions (pH 12) has been reported by Baloga and Earley (1961), and under very low [Cr(III)] (1.9 μM) conditions in artificial seawater (Pettine and Millero, 1990; Pettine et al., 1991). Shi et al. (1993, 1998) used buffered solutions (pH 3.0, 7.2, and 10.0) to study free radical production in the Cr(III)/H_2O_2 system, but did not monitor Cr(VI). In this study, Cr(III)/H_2O_2 interactions were examined using aged, aqueous Cr(III) systems in order to observe whether Cr(III) would be oxidized by relatively low concentrations of H_2O_2 under conditions relevant to soils.

Chromium(VI)/H_2O_2 interactions were examined to determine conditions under which Cr(VI) could be reduced by H_2O_2 and for evidence of the possible formation of peroxochromium complexes under pH conditions and reactant concentrations that

could be present in the context of soil remediation. If high levels of H_2O_2 were added to a contaminated soil containing Cr(III) and Cr(VI) in an alkaline environment (e.g. COPR soil), the tetraperoxochromate(V), $[Cr(O_2)_4]^{3-}$ species could form (Dickman and Pope, 1994). Under more neutral conditions, peroxide has been shown to oxidize Cr(III) to Cr(VI) in a contaminated plating waste site (Chapter 2), and high H_2O_2 levels could produce peroxochromium intermediates. In particular, an intermediate such as the soluble violet chromium(VI) oxodiperoxo complex $[CrO(O_2)_2(OH)]^-$, which forms in the pH 4-7 range (Perez-Benito and Arias, 1997), may be capable of forming under high H_2O_2 and Cr(VI) conditions in this type of contaminated waste site. Formation of chromiumperoxo intermediates in the presence of high levels of H_2O_2 could exacerbate the threat already posed by Cr(VI) in contaminated soils.

In keeping with our inquiry into the possible oxidation of chromium by peroxide in soils, our aim has been to investigate chromium/peroxide behavior under environmentally relevant conditions, and to any extent possible, find clues that could help establish intermediate species forming under those conditions. Experiments were conducted without buffers, using moderate reactant levels, and were followed over days to observe long-term outcomes.

MATERIALS AND METHODS

Chemicals

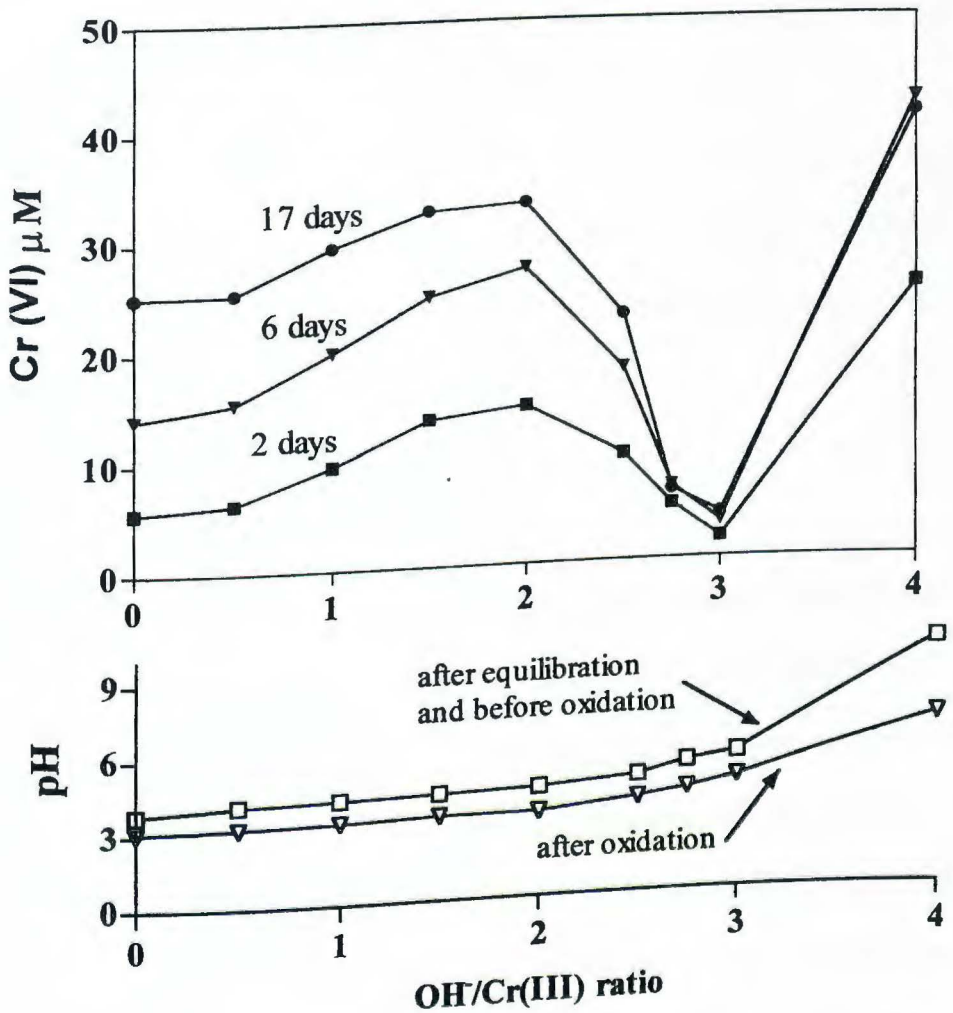
Reagent grade $Cr(NO_3)_3 \cdot 9H_2O$, $NaNO_3$, NaOH, HNO_3, $FeSO_4$, $KMnO_4$, $H_2C_2O_4$ and 30% H_2O_2 were obtained from J.T. Baker and used without further

purification. Analytical grade aqueous K_2CrO_4 concentrate was also obtained from Baker, diluted to 19.23 mM and used to prepare Cr(VI) standards and stock solutions.

Preparation of Reactant Solutions

Hexaaquochromium(III) will dimerize and undergo further polymerization via oxo and hydroxo bridging as solution pH is raised to levels commonly found in soils (pH 4-5). Since our inquiry relates to the response of Cr(III) in the environment to peroxide, these experiments were conducted with operationally defined "aged" and "hydrolyzed" solutions of Cr(III). This allowed us to assume consistency in our reactant solutions at a mid range pH (3.8-5.5). Cr(III) stock solutions (500 mL) were prepared in 0.01 M $NaNO_3$ using OH^-/Cr ratios of 0, 0.5, 1.0, 1.5, 2.0, 2.5, 2.75, 3.0 and 4.0. Hydroxide was added as 0.005 M NaOH dropwise at a rate of 2 mL/min just below the liquid surface, while stirring, in order to avoid high local OH^- concentrations. Formation of a solid phase was observed only in the 3:1 and 4:1 OH^-:Cr solutions. Blue-green, floc-like particles appeared suspended in these solutions, and settling occurred slowly in the absence of stirring. The solutions were then equilibrated with gentle swirling on an orbital shaker (50 cycles/min) for at least one week, after which time, pH values remained stable for several months (see Day 0 pH data, Figure 3-1).

Cr(VI) solutions were titrated in 0.01M $NaNO_3$ using NaOH or HNO_3 to obtain a desired pH. Reagent grade 30% H_2O_2 was used without stabilizers to make standards, which were freshly prepared for each series of experiments. Concentrations of H_2O_2 stock solutions were verified by titration with $KMnO_4$ using sodium oxalate



OH-/Cr	Cr(VI) µM 2 days	4 days	6 days	17 days	115 days	pH Day 0	Day 17
0.0	5.6	9.9	14.1	25.1		3.8	3.1
0.5	6.3	11.0	15.4	25.3	28.7	4.1	3.2
1.0	9.4	15.1	19.9	29.4	33.1	4.2	3.3
1.5	13.4	20.4	24.7	32.5	35.1	4.3	3.4
2.0	14.4	21.9	27.1	33.1	37.2	4.4	3.4
2.5	9.7	15.0	17.6	22.5	24.8	4.7	3.8
2.8	5.0	7.2	6.6	6.3		5.2	4.1
3.0	1.8	3.0	3.3	4.0	7.1	5.5	4.5
4.0	25.0	39.5	42.3	41.0	46.8	10.0	6.9

Figure 3-1. Oxidation of nine 280 µM Cr(III) solutions, using 100 µM H_2O_2. Solutions were prepared and equilibrated with OH^-/Cr(III) ratios from 0/1 to 4/1. Extent of oxidation is shown after 2 days, 6 days, and 17 days. Analytical uncertainty for Cr(VI) is ± 0.1 µM. Solution pH values are shown after equilibration but before oxidation and after 17 days of oxidation.

($Na_2C_2O_4$, determined gravimetrically) in 0.1 M H_2SO_4 as a primary standard (Skoog and West, 1994).

In order to avoid possible effects that have been noted from the interaction of buffers with Cr/H_2O_2 intermediate species (Perez-Benito and Arias, 1997; Beck et al., 1991), and in order to observe pH changes in the systems we investigated, solutions were prepared without the addition of buffers.

Experiments

Batch experiments were conducted in duplicate in 50 mL polycarbonate centrifuge tubes. Reactants (H_2O_2, Fe(II)) were added to the chromium stock solutions in small volumes to obtain the desired initial concentration in solution without diluting the original concentrations of chromium. Samples were immediately vortexed and remained on a bench-top orbital shaker (100 cycles/min, 30 minutes on, 30 minutes off) at 25 °C until analysis took place. Destructive sampling was used to monitor [Cr(VI)], [H_2O_2] and pH of the reaction mixtures over time.

Analytical Methods

Solution pH was measured with an Orion flat surface combination pH electrode inserted just below the solution surface in each centrifuge tube. All spectral readings were done using a Shimadzu UV-1601 PC spectrophotometer.

Where peroxide concentrations were low ($< 10^{-5}$ M) the diphenylcarbazide (DPC) colorimetric method (Bartlett and James, 1979) was used to determine soluble

Cr(VI) using 0.5 mL of the DPC reagent (add 0.38 g DPC to 100 mL 95% ethanol and add to 120 mL 85% H_3PO_4 in 280 mL distilled H_2O) with a 4.5 mL-aliquot of the reaction supernatant. In cases where Cr(VI) concentrations fell above the linear standard curve (0.1-40.0 μM), 1:10 or 1:20 dilutions were made before withdrawing an aliquot to add to the DPC reagent. Diphenylcarbazide reacts with Cr(VI) in acidic solution to form a Cr(III)-diphenylcarbazone complex which absorbs at 540 nm (detection limit 0.1 μM). The test is specific for Cr(VI): addition of the DPC reagent to hexaaquo Cr^{3+} produces no absorbance at 540 nm. Under conditions of $[H_2O_2]$ greater than 10^{-5} M, soluble concentrations of $HCrO_4^-$ or CrO_4^{2-} were determined by direct absorbance measurements of the reaction mixtures at 350 nm (ϵ = 1600 cm^{-1} M^{-1}) and at 372 nm (ϵ = 4800 cm^{-1} M^{-1}) respectively. Although this method is not as sensitive (detection limit 1 μM for $HCrO_4^-$ for a 1 cm pathlength) as the diphenylcarbazide (DPC) colorimetric method, it avoids the negative interference of peroxide with the DPC determination of Cr(VI), which is significant above 10^{-5} M concentrations of H_2O_2 (Pettine et al., 1988). In regions of overlap, where $[H_2O_2]$ was less than 10^{-5} M, the DPC and direct optical methods agreed within 0.5%, and correlation coefficients (r^2) of standard curves for both methods were greater than 0.9998. Error bars are shown graphically for each measured data point, and represent the range between duplicate sample values.

A slight modification of the 4-amino antipyrene horseradish peroxidase method reviewed by Frew et al., (1983) was used to determine hydrogen peroxide. Hydrogen peroxide will oxidatively couple with 4-aminoantipyrene (AAP) and phenol, in the

presence of horseradish peroxidase to produce a quinoneimine dye with a maximum absorbance at 505 nm. The linear range was 5-300 μM peroxide (Frew et al., 1983). The modified reagent was mixed as follows: 0.0010 g horseradish peroxidase (type VI) from Sigma (about $2x10^{-8}$ M), 0.50 g 4-aminoantipyrene, 1.17 g phenol, 5.0 mL 0.1M triphosphate buffer (pH 6.9), and 100 μL of 0.01M hydrogen peroxide (or 2 μM) added to give more stable readings. Reagent (2.0 mL) and aqueous sample (3.0 mL) were vortexed; absorbance readings at 505 nm were taken when they reached a maximum (30-120 seconds after mixing), after which time they began to decrease at a rate that depended on the concentration of H_2O_2 in the sample.

RESULTS

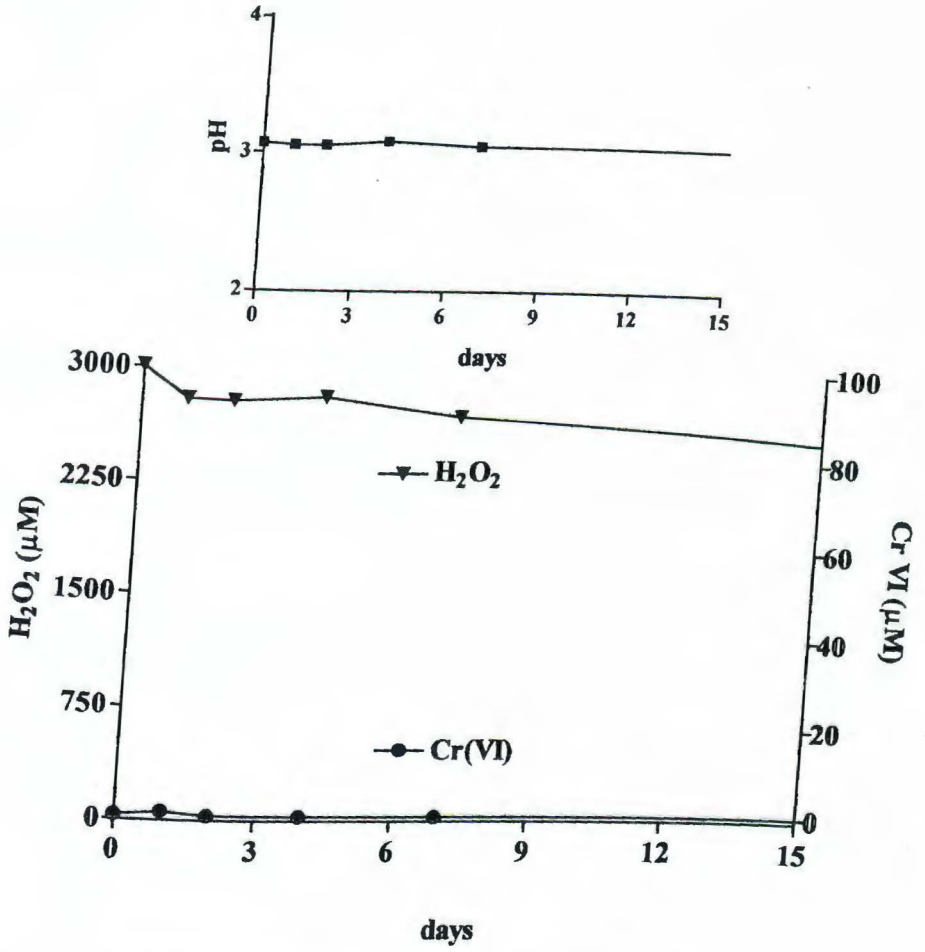
Cr(III)/H_2O_2 Interactions

Figure 3-1 shows the response of aged 280 μM Cr(III) solutions (prepared with OH^-/Cr ratios from zero to four) to treatment with 100 μM H_2O_2. Oxidation of Cr(III) to $HCrO_4^-$ (CrO_4^{2-} at the 4:1 OH^-/Cr ratio) occurred across the range of OH^-/Cr ratios. Cr(VI) continued to appear slowly over days. Overall pH values decreased, as shown in Figure 3-1.

An increase in OH^-/Cr ratios resulted in increased Cr(III) oxidation up to a maximum at the 2:1 ratio, then decreased Cr(III) oxidation up to the 3:1 region where flocculation became visible and oxidation ceased. The greatest oxidation occurred at OH^-/Cr = 4, where, at the end of 115 days, 71% of stoichiometric yield of chromate expected from 100 μM H_2O_2 was obtained.

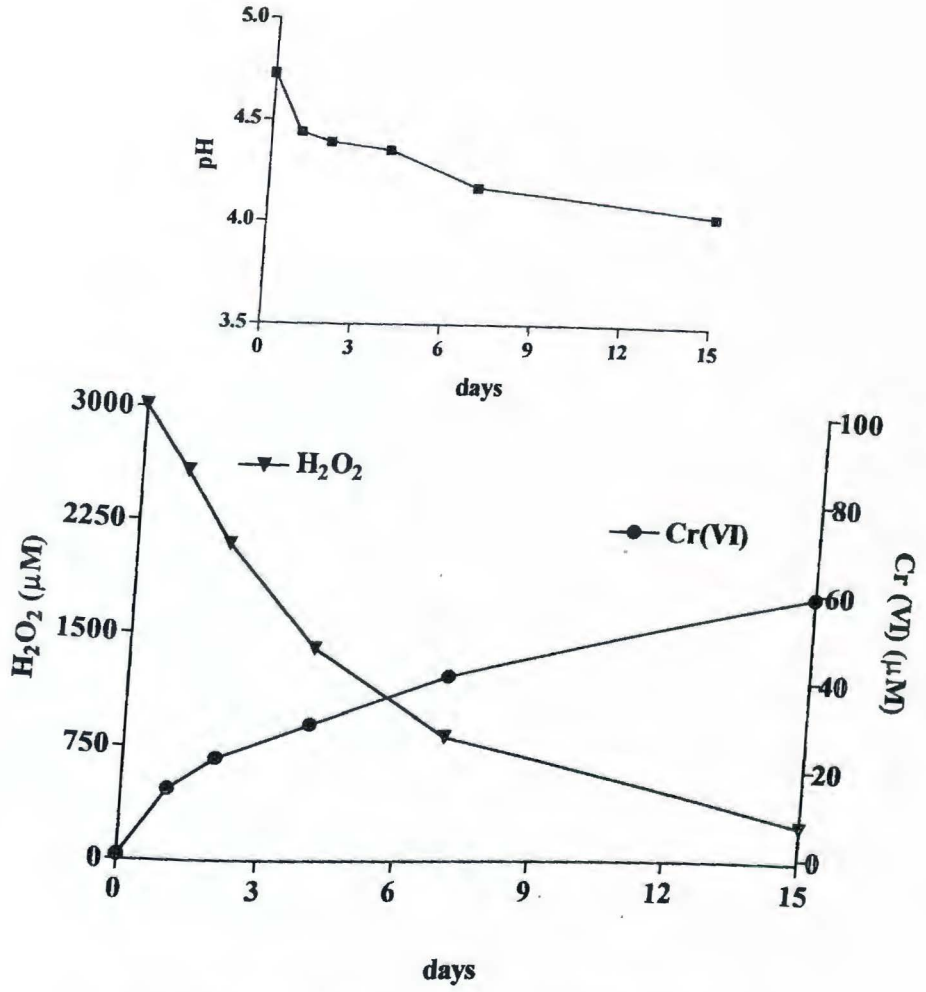
Initial solution pH strongly affected the production of Cr(VI) and the destruction of H_2O_2 in the Cr(III)/H_2O_2 system (Figures 3-2 a-c). Excess peroxide (3000 μM) was applied to three different 100 μM preparations of aged Cr(III): a) Cr(III) titrated with HNO_3 to pH 3; b) Cr(III) prepared with a 2:1 OH^-/Cr ratio at pH 4.75; and c) Cr(III) slowly titrated to pH 10 with NaOH. Oxidation of Cr(III) at pH 3 was not observed, nor was a change in pH measured (Figure 3-2a). H_2O_2 decreased slightly after several days. The 2:1 OH^-:Cr(III) solution showed a steady increase in Cr(VI) over 15 days (Figure 3-2b) along with catalytic decreases in H_2O_2, with 46 times as much peroxide used as chromate produced. At an initial pH of 10 (Figure 3-2c), initial rates of chromium oxidation were higher than at pH 4.7, and rates of H_2O_2 destruction were lower, but still catalytic in nature with about 20 times as much H_2O_2 destroyed as chromate produced in two weeks. At the end of four weeks, about 92 % of the chromium was oxidized.

When 100 μM 2:1 OH^-/Cr(III) solutions were treated with peroxide levels from 500 μM to 4500 μM (Figure 3-3 a-c) a linear relationship ($r^2 = 0.999$) between the amount of Cr(VI) produced in 7 days and the initial H_2O_2 concentration was seen for the lower (500, 750, 1000 and 1500 μM) H_2O_2 levels. Above 1500 μM initial H_2O_2, the pattern became erratic, with less Cr(VI) produced in seven days when using 3000 μM H_2O_2 initially, and about the same amount of Cr(VI) produced when using 4500 μM H_2O_2 as when using 1500 μM H_2O_2. Peroxide disappeared catalytically when initial levels were above 1000 μM (Figure 3-3b), and at seven days, measurable peroxide levels in the 3000 and 4500 μM initial H_2O_2 solutions have reached



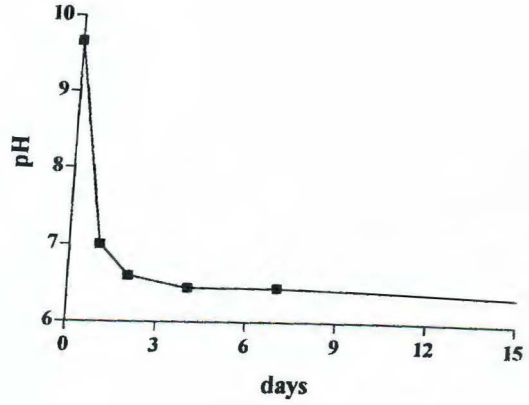
days	Cr(VI)		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	0.0	0.0	3000	3000	3.07	3.07
1.0	1.2	0.6	2770	2820	3.06	3.05
2.0	0.0	0.0	2770	2800	3.05	3.06
4.0	0.0	0.0	2830	2800	3.09	3.08
7.0	0.0	0.0	2700	2680	3.06	3.05
28.0	0.0	0.0	2350	2260	3.05	3.06

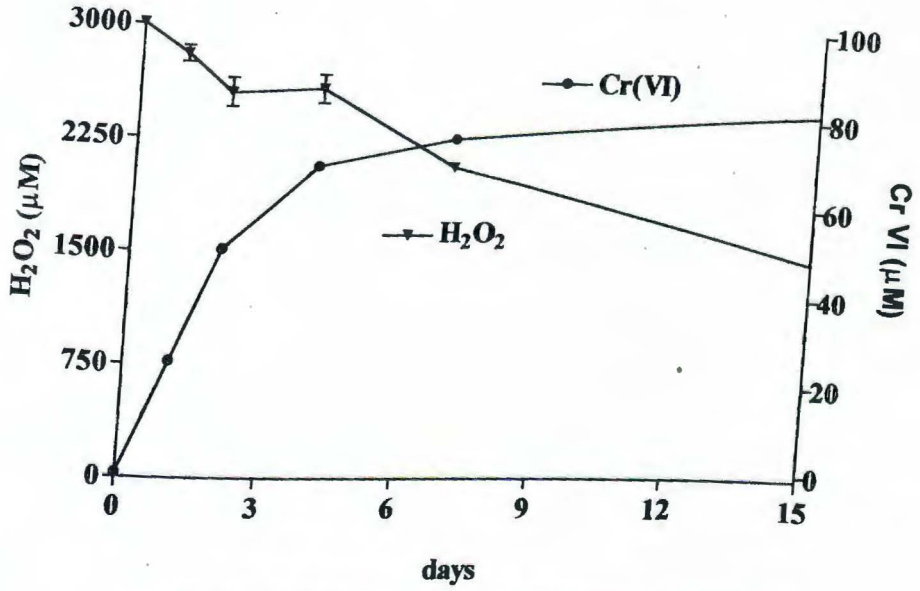
Figure 3-2a. Effect of initial pH on the reaction of 100 μM Cr III) and 3000 μM H_2O_2. Aqueous Cr(III) prepared with initial pH 3 by titrating with HNO_3 in 0.01 M $NaNO_3$. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM.



days	Cr(VI)		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	0.0	0.0	3000	3000	4.73	4.73
1.0	14.9	14.9	2590	2560	4.44	4.44
2.0	21.8	21.8	2110	2090	4.39	4.39
4.0	30.1	28.9	1410	1420	4.35	4.36
7.0	40.0	40.7	826	829	4.18	4.17
15.0	58.8	59.4	243	246	4.05	4.05

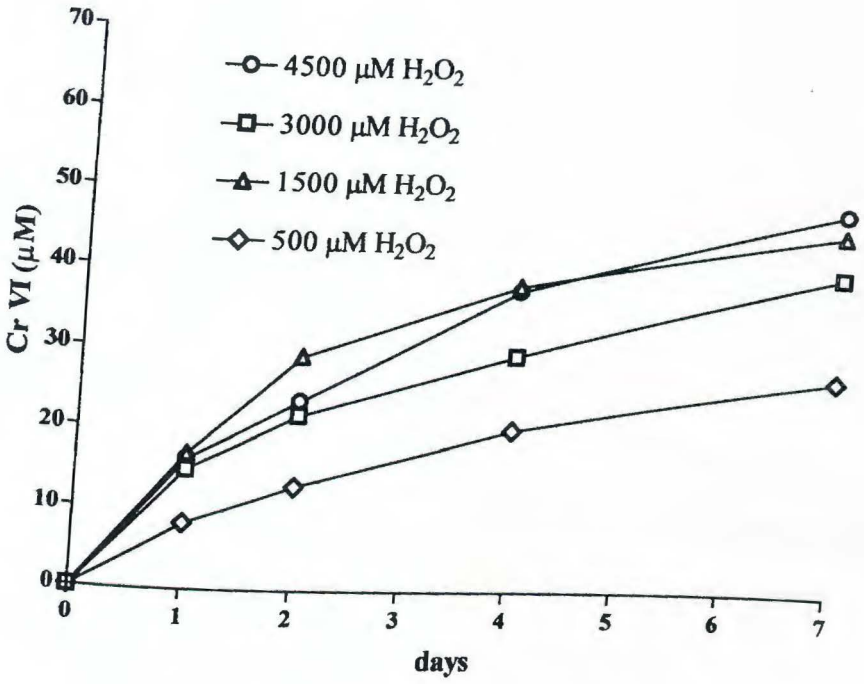
Figure 3-2b. Effect of initial pH on the reaction of 100 μM Cr (III) and 3000 μM H_2O_2. Aqueous, hydrolyzed Cr(III) prepared in 0.01 M $NaNO_3$ using 2 OH^- /1 Cr(III). Initial pH 4.75. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM.





days	Cr(VI)		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	0.0	0.0	3000	3000	9.67	9.67
1.0	24.0	26.0	2860	2750	7.00	7.01
2.0	49.0	51.0	2650	2460	6.59	6.62
4.0	69.0	68.2	2490	2680	6.44	6.46
7.0	75.9	74.0	2060	2080	6.43	6.47
28.0	93.4	91.7	467	461	6.23	6.21

Figure 3-2c. Effect of initial pH on the reaction of 100 μM Cr(III) and 3000 μM H_2O_2. Aqueous Cr(III) prepared with initial pH 10 by titrating with NaOH in 0.01 M $NaNO_3$. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM.

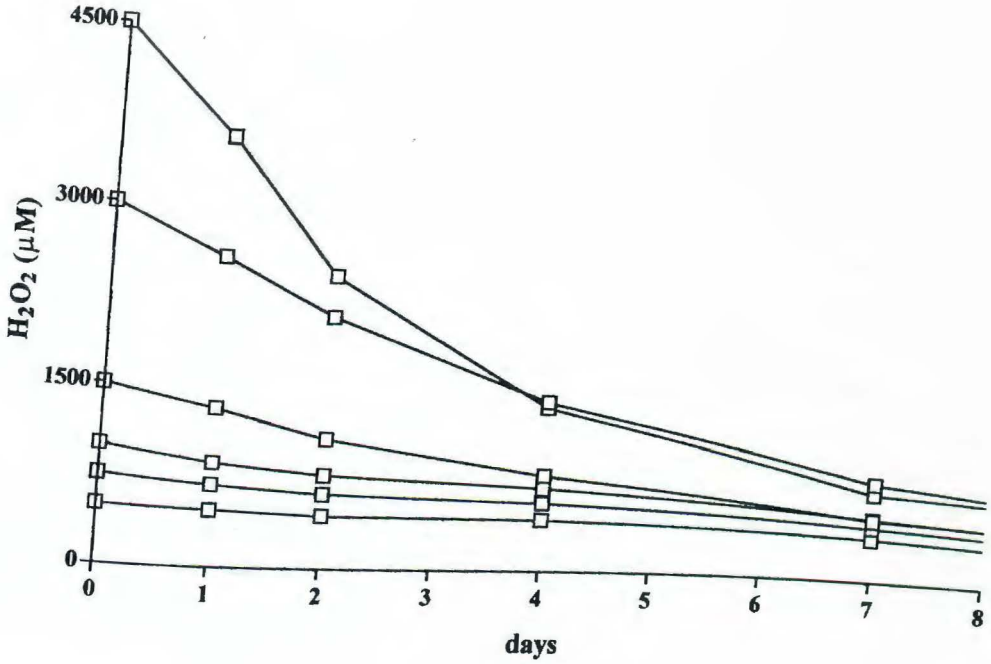


Cr(VI) (μM) with different initial H_2O_2 (μM) levels

days	500		750		1000	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0	8.2	8.2	10.7	10.1	12.6	12.6
2.0	12.6	13.3	16.4	16.4	19.6	19.0
4.0	20.2	20.2	24.1	23.4	26.0	26.6
7.0	26.6	27.9	32.3	31.7	36.1	35.5
14.0	44.2	45.3	47.4	47.4	50.6	52.5

days	1500		3000		4500	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0	17.6	16.3	14.9	14.9	16.3	16.3
2.0	28.9	29.6	21.8	21.8	23.9	23.3
4.0	38.3	38.3	30.1	28.9	38.3	37.0
7.0	45.7	45.7	40.0	40.7	48.8	48.2
15.0			58.8	59.4		
28.0	64.2	64.8			69.9	69.2

Figure 3-3a. Oxidation of 100 μM Cr(III) solutions, using varying concentrations of H_2O_2. Aqueous, hydrolyzed Cr(III) solutions were prepared in 0.01 M $NaNO_3$ with 2 OH^-/1 Cr(III). Experimental error for Cr(VI) is ± 0.5 μM.

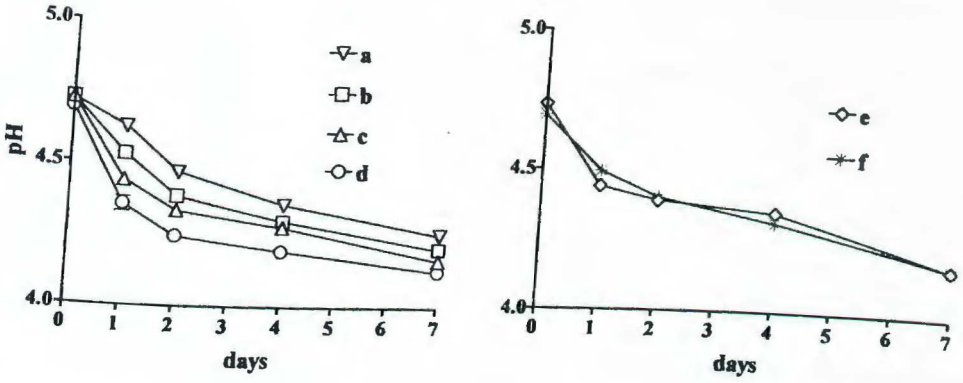


H_2O_2 (μM)

days	500		750		1000	
	Y1	Y2	Y1	Y2	Y1	Y2
0	500	500	750	750	1000	1000
1	473	476	680	688	868	873
2	441	443	626	615	773	781
4	430	433	568	575	690	700
7	369	353	457	459	526	534
14	194	195	236	239	263	247

days	1500		3000		4500	
	Y1	Y2	Y1	Y2	Y1	Y2
0	1500	1500	3000	3000	4500	4500
1	1350	1290	2590	2560	3520	3640
2	1080	1080	2110	2090	2390	2480
4	807	796	1410	1420	1350	1390
7	509	526	826	829	732	746
15			243	246		
28	56	56			52	52

Figure 3-3b. Disappearance of H_2O_2 when different initial concentrations are added to 100 μM aqueous, hydrolyzed Cr(III) solutions (2 OH^-/1 Cr(III)) in 0.01 M $NaNO_3$. Analytical uncertainty for H_2O_2 determination is 2%.



pH data

days	a)		b)		c)	
	Y1	Y2	Y1	Y2	Y1	Y2
0	4.72	4.72	4.72	4.72	4.72	4.72
1	4.61	4.64	4.53	4.53	4.43	4.45
2	4.46	4.48	4.38	4.39	4.33	4.34
4	4.34	4.38	4.30	4.30	4.29	4.27
7	4.25	4.26	4.21	4.20	4.17	4.16
14	4.13	4.14	4.07	4.09	4.04	4.02

days	d)		e)		f)	
	Y1	Y2	Y1	Y2	Y1	Y2
0	4.69	4.69	4.73	4.73	4.69	4.69
1	4.33	4.38	4.44	4.44	4.48	4.51
2	4.25	4.24	4.39	4.39	4.40	4.41
4	4.19	4.20	4.35	4.36	4.31	4.33
7	4.12	4.13	4.18	4.17	4.17	4.18
15			4.05	4.05		
28	3.97	3.98			3.97	3.98

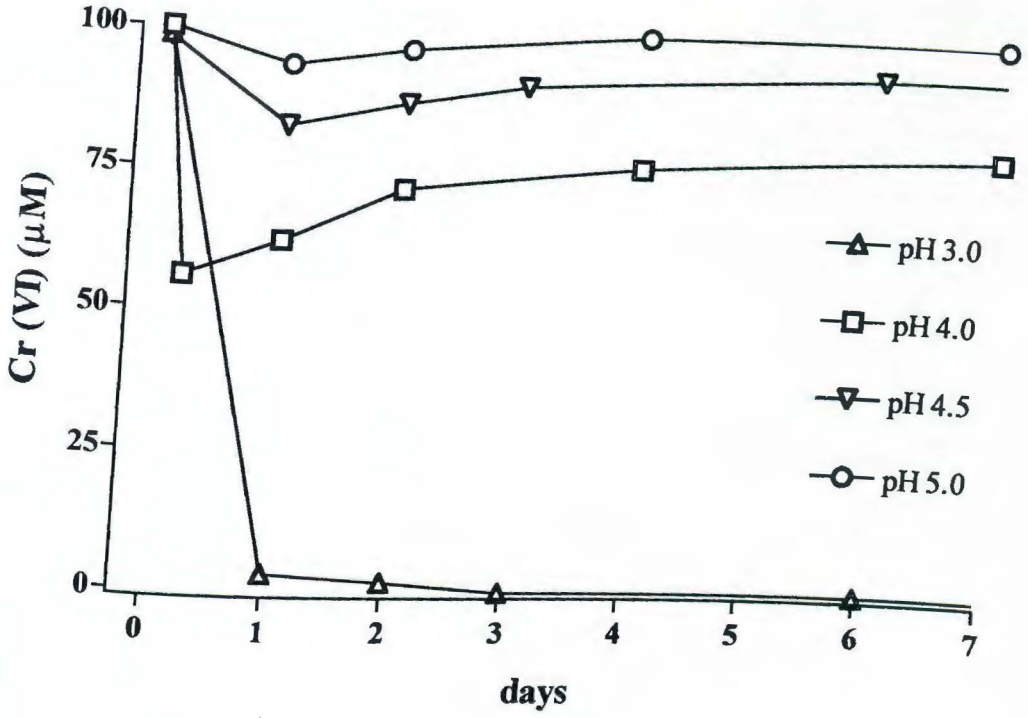
Figure 3-3c. Changes in pH when varying concentrations of H_2O_2 react with 100 μM aqueous, hydrolyzed Cr(III) (2 OH^-/1 Cr(III)) in 0.01 M $NaNO_3$ a) 500 μM H_2O_2 b) 750 M H_2O_2 c) 1000 μM H_2O_2 d) 1500 μM H_2O_2 e) 3000 μM H_2O_2 f) 4500 μM H_2O_2.

comparable levels (700-800 μM). Figure 3-3c shows similar behavior in pH changes in these solutions. The lower initial H_2O_2 levels (up to 1500 μM) show pH decreasing as the amount of Cr(VI) produced increases. However, at the higher H_2O_2 levels, pH did not increase as much, nor was there an appreciable difference in its behavior between 3000 μM and 4500 μM initial H_2O_2.

Cr(VI)/H_2O_2 Interactions

Figures 3-4 a-c show the effect of adding 3000 μM peroxide to 100 μM Cr(VI) at different pH's. When the initial pH was 3, Cr(VI) was completely reduced and H_2O_2 was catalytically destroyed while reduction occurred, after which time it maintained a stable level in solution (Figures 3-4a, 3-4b). The pH of the solution increased (Figure 3-4c), accounting for a change of 400 ± 20 μM H^+, corresponding stoichiometrically to the reduction of $HCrO_4^-$ to $Cr(H_2O)_6^{3+}$ (equation 1.28).

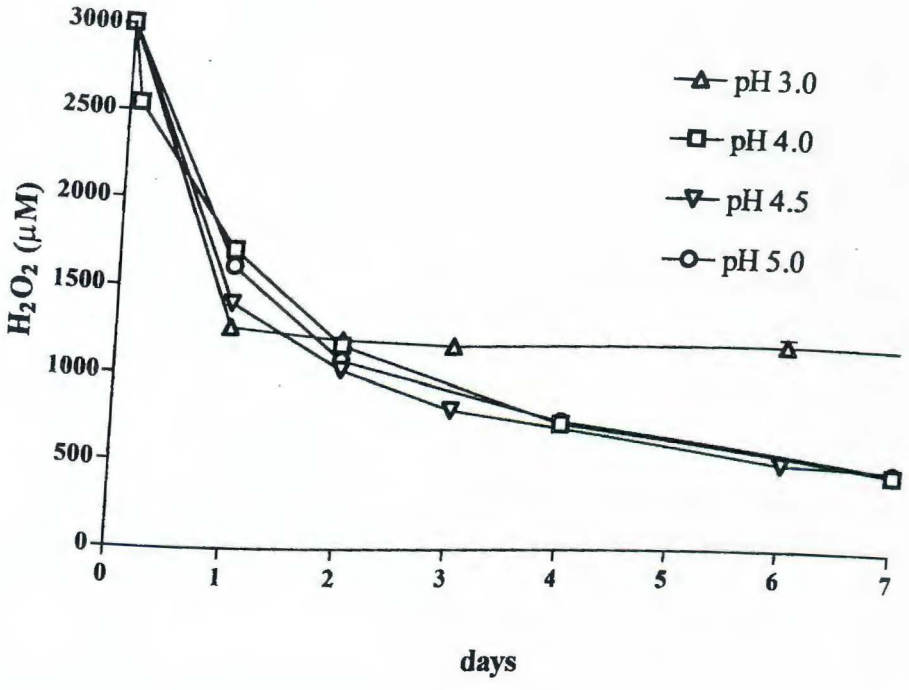
A different pattern emerged between initial pH's 4 and 5. At pH 4, Cr(VI) initially disappeared, reached a minimum value in 2 hours, and began to gradually increase over days, and approached its original concentration. The same pattern was observed at pH 4.5 and 5, only with less of an initial reduction in Cr(VI). Above pH 5, Cr(VI) levels did not change when H_2O_2 was applied. The pH of these solutions increased as Cr(VI) decreased, and decreased as Cr(VI) recovered (Figure 3-4c). Interestingly, the behavior of H_2O_2 was also comparable in all three solutions (Figure 3-4b), disappearing at a similar rate in the pH 5 solution, where very little of the intermediate species was forming, as it did in the pH 4 solution, where over half the



Cr(VI) (μM)

days	pH 3.0		pH 4.0		pH 4.5		pH 5.0	
	Y1	Y2	Y1	Y2	Y1	Y2	Y1	Y2
0.0	97.0	100.0	100.0	100.0	98.5	97.9	100.0	100.0
0.2			55.6	56.2				
1.0	3.1	3.1	61.7	62.9	83.1	82.5	93.2	94.5
2.0	2.1	1.5	71.6	71.6	86.9	86.9	97.0	96.4
3.0	0.0	0.0			90.2	90.2		
4.0			75.8	75.8			99.6	99.6
6.0	0.0	0.0			93.3	93.3		
7.0			79.4	79.4			100.0	100.0
15.0			87.2	87.2			99.3	100.6
27.0	0.0	0.0			99.0	97.1		

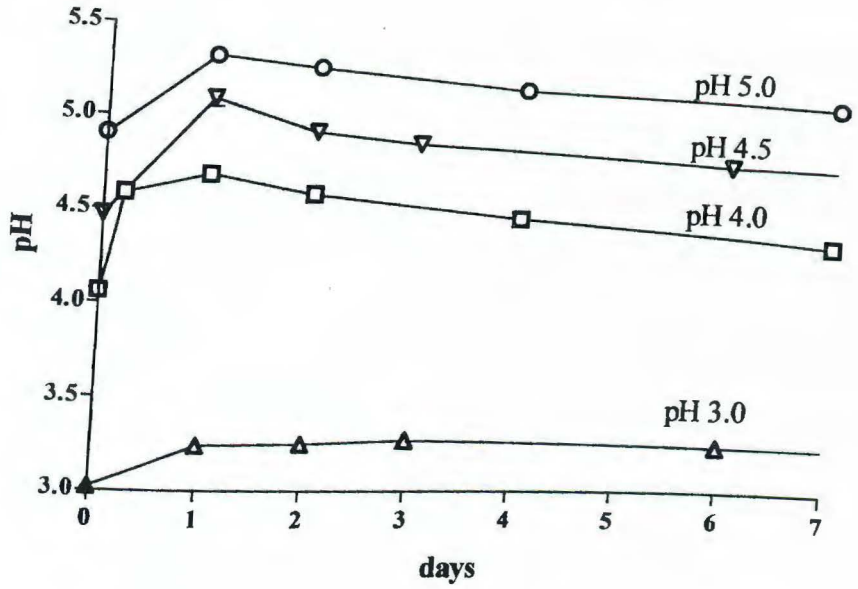
Figure 3-4a. Effect of initial pH on Cr(VI) behavior in the reaction of 100 μM Cr (VI) and 3000 μM H_2O_2. Cr(VI) solutions prepared in 0.01 M $NaNO_3$ and titrated with HNO_3 or NaOH to set initial pH values. Experimental error for Cr(VI) is ± 0.5 μM.



H_2O_2 (μM)

days	pH 3.0		pH 4.0		pH 4.5		pH 5.0	
	Y1	Y2	Y1	Y2	Y1	Y2	Y1	Y2
0.0	3000	3000	3000	3000	3000	3000	3000	3000
0.2			2560	2520				
1.0	1300	1240	1720	1700	1400	1410	1650	1590
2.0	1220	1180	1160	1180	1050	1010	1070	1090
3.0	1150	1190			796	810		
4.0			724	729			752	731
6.0	1145	1235			507	496		
7.0			456	456			465	472
15.0			166	164			192	197
27.0	1023	1069			86	77		

Figure 3-4b. Effect of initial pH on H_2O_2 behavior in the reaction of 100 μM Cr(VI) and 3000 μM H_2O_2. Cr(VI) solutions prepared in 0.01 M $NaNO_3$ and titrated with HNO_3 or NaOH to set initial pH values. Analytical uncertainty for H_2O_2 determination is 2%.



pH

days	pH 3.0		pH 4.0		pH 4.5		pH 5.0	
	Y1	Y2	Y1	Y2	Y1	Y2	Y1	Y2
0.0	3.02	3.02	4.06	4.06	4.47	4.47	4.90	4.90
0.2			4.58	4.57				
1.0	3.24	3.24	4.68	4.69	5.05	5.14	5.31	5.34
2.0	3.24	3.26	4.58	4.58	4.89	4.94	5.25	5.27
3.0	3.27	3.27			4.84	4.87		
4.0			4.43	4.49			5.14	5.16
6.0	3.25	3.24			4.74	4.78		
7.0			4.35	4.34			5.10	5.08
15.0			4.27	4.28			5.04	4.99
27.0	3.24	3.24			4.55	4.59		

Figure 3-4c. pH changes in the reaction of 100 μM Cr(VI) and 3000 μM H_2O_2. Cr(VI) solutions prepared in 0.01 M $NaNO_3$ and titrated with HNO_3 or NaOH to set initial pH values. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM.

Cr(VI) disappeared after one day. The quantity of intermediate species being formed does not appear to affect the catalytic dismutation of peroxide.

Different initial levels of peroxide applied to 100 μM Cr(VI) at pH 4 produced the same pattern of initially disappearing, and then recovering Cr(VI) over days, with higher initial H_2O_2 levels resulting in a greater initial decrease in Cr(VI) (Figure 3-5a). Long term pH changes (Figure 3-5b) inversely reflected Cr(VI) changes, rising as Cr(VI) decreased and falling as Cr(VI) recovered. Peroxide exhibited complicated, oscillatory behavior over the first minutes of these experiments (Figure 3-6a). Initial H_2O_2 oscillations dampened as Cr(VI) concentrations reached their minimum values, and pH reached maximum values, after about 2 hours (Figure 3-6b).

Effects of Adding Methanol or Fe(II)

Adding 9.0 mM methanol to a Cr(III)/H_2O_2 system (100 μM 2:1 OH^-:Cr(III) and 3000 μM H_2O_2) did not affect the initial rate of Cr(III) oxidation, but did inhibit Cr(III) oxidation over time (Figure 3-7a). The extent and rate of H_2O_2 destruction over days was not altered by the addition of methanol. When added to the Cr(VI)/H_2O_2 system (100 μM Cr(VI), pH 4, 3000 μM H_2O_2) (Figure 3-7b), 9.0 mM methanol prevented the recovery of Cr(VI) after its initial disappearance. Control experiments using 9.0 mM methanol with either H_2O_2 or $HCrO_4^-$ showed no effect on H_2O_2 or $HCrO_4^-$ concentrations (data shown on Figure 3-7b). Replacing 9.0 mM methanol with 3.0 mM methanol produced the same results as using the higher concentration of methanol (data shown on Figures 3-7 a-b).

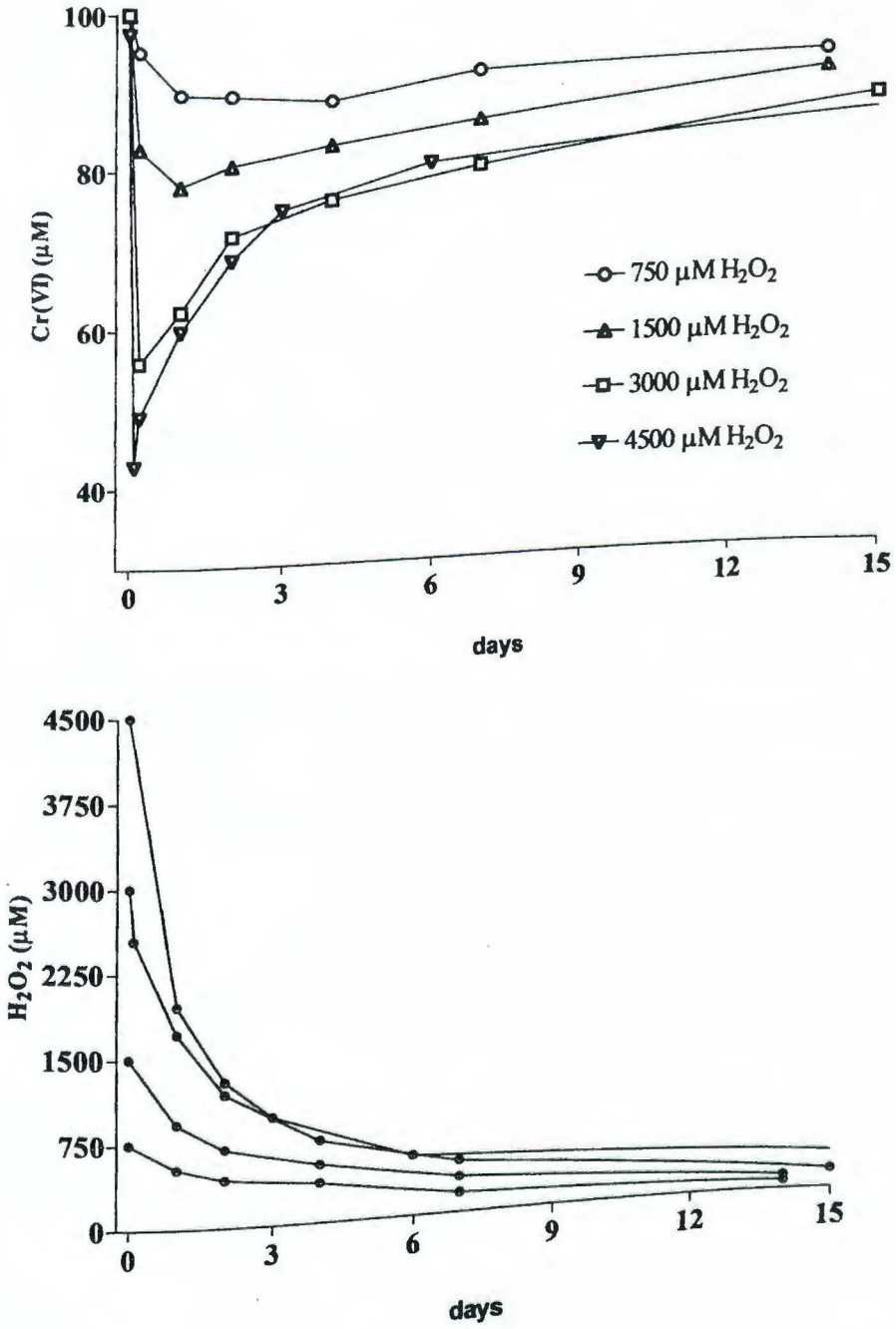


Figure 3-5a. Effect of initial H_2O_2 concentration on its reaction with 100 μM Cr(VI). Cr(VI) solutions prepared at pH 4 in 0.01 M $NaNO_3$.

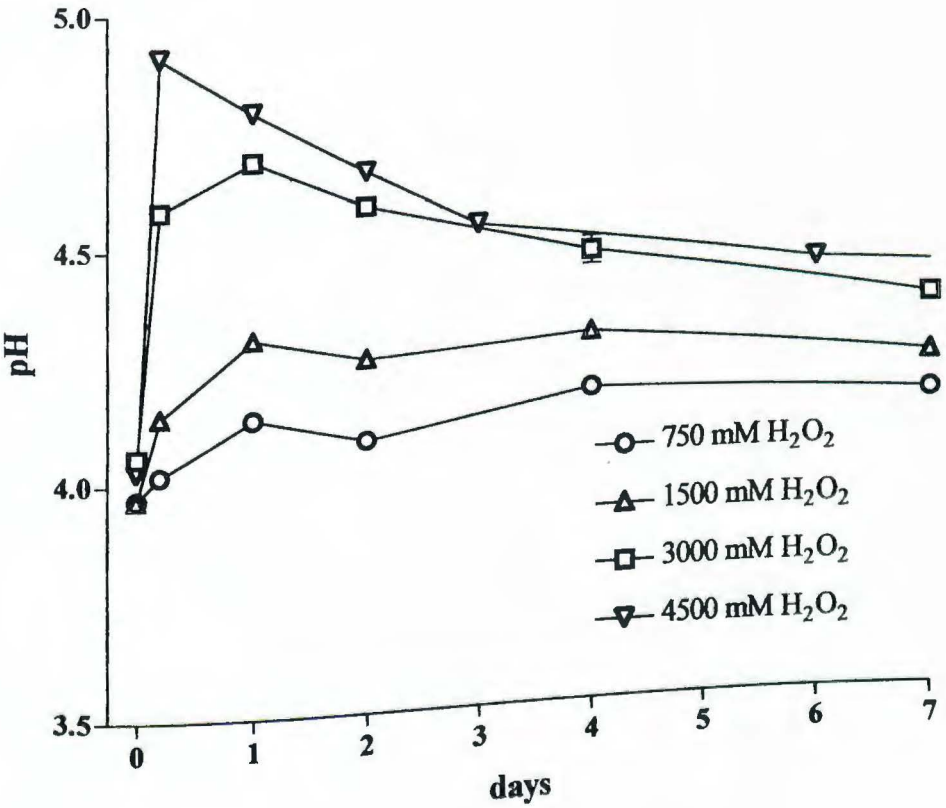


Figure 3-5b. pH changes in the reaction of different initial H_2O_2 concentrations with 100 μM Cr(VI). Cr(VI) solutions prepared at pH 4 in 0.01 M $NaNO_3$.

Table 3-1. Data for Figures 3-5a and 3-5b. The reaction of 100 μM Cr(VI) with varying initial concentrations of H_2O_2. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM. All concentrations are given as μM.

a)

days	Cr(VI)		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	100.0	100.0	750	750	3.97	3.97
0.2	95.1	95.4			4.02	4.02
1.0	89.4	90.0	533	520	4.13	4.14
2.0	90.0	88.8	422	416	4.09	4.07
4.0	88.1	88.8	355	347	4.18	4.15
7.0	91.9	91.3	168	182	4.14	4.14
14.0	92.4	93.6	67	77	4.14	4.15

b)

days	Cr(VI)		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	100.0	100.0	1500	1500	3.97	3.97
0.2	83.0	82.7			4.14	4.15
1.0	78.0	78.0	947	893	4.32	4.29
2.0	80.5	80.5	683	694	4.26	4.25
4.0	83.1	82.4	511	518	4.29	4.28
7.0	85.6	85.0	314	319	4.21	4.23
14.0	91.1	90.5	120	123	4.19	4.16

c)

days	Cr(VI)		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	100.0	100.0	3000	3000	4.06	4.06
0.1			2560	2520		
0.2	55.6	56.2			4.58	4.59
1.0	61.7	62.9	1720	1700	4.68	4.69
2.0	71.6	71.6	1160	1180	4.58	4.58
4.0	75.8	75.8	724	729	4.43	4.49
7.0	79.4	79.4	456	456	4.35	4.34
15.0	87.2	87.2	166	164	4.27	4.28

d)

days	Cr(VI)		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	97.2	97.9	4500	4500	4.03	4.03
0.1	42.9				4.92	4.90
0.2	49.2	49.0			4.78	4.80
1.0	59.8	59.8	1960	1950	4.65	4.66
2.0	68.6	68.6	1300	1260	4.53	4.53
3.0	75.0	74.4	953	959	4.44	4.41
6.0	80.0	80.0	539	528	4.23	4.24
27.0	91.4	93.3	63	55		

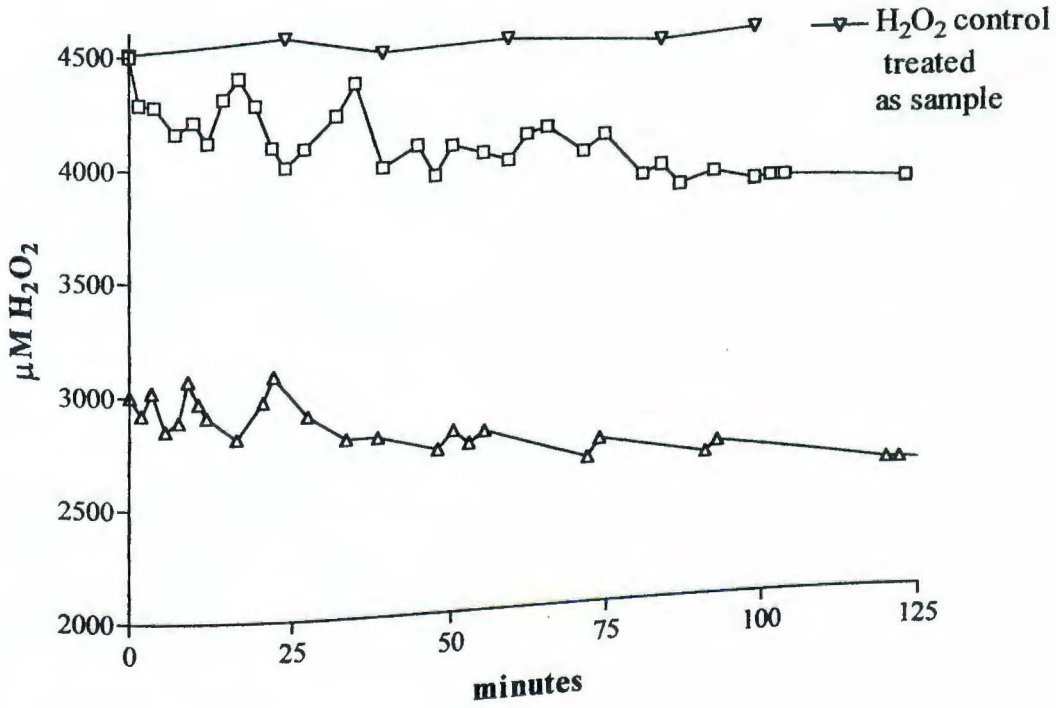


Figure 3-6a. Behavior of 4500 µM and 3000 µM H_2O_2 when added to 100 µM Cr(VI) at initial pH 4.0 in 0.01 M $NaNO_3$. Experimental uncertainty for H_2O_2 is ± 40 µM.

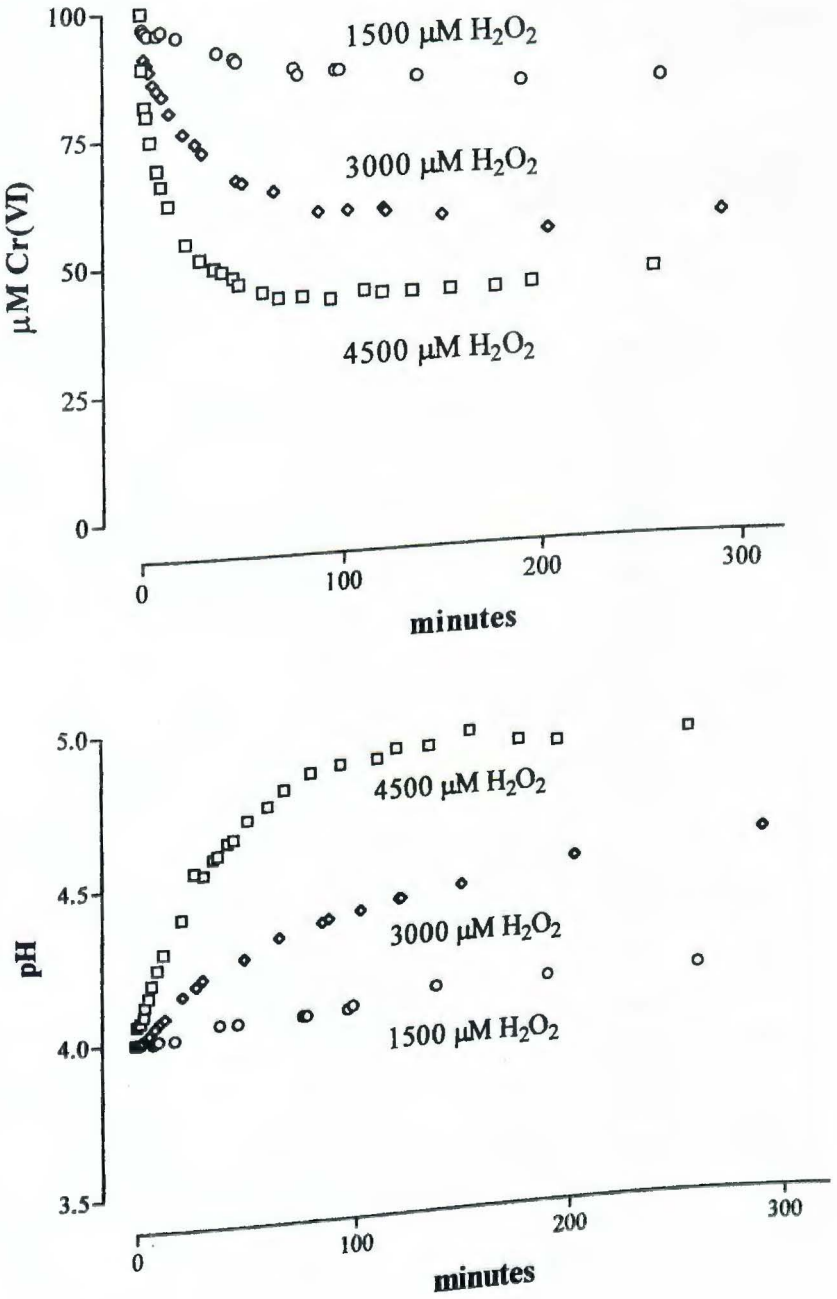


Figure 3-6b. Changes in Cr(VI) and pH after addition of different concentrations of H_2O_2 in 0.01 M $NaNO_3$.

Table 3-2a. Data for Figures 3-6a and 3-6b. The reaction of 100 μM Cr(VI) with 4500 μM H_2O_2 in 0.01M $NaNO_3$. Control data is for peroxide alone. All concentrations (μM). Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM.

minutes	Cr VI	pH
0.0	100.0	4.00
0.5	89.3	4.06
2.0	81.7	4.07
2.8	79.8	
3.5		4.09
4.0		4.12
4.6	74.7	
5.5		4.15
7.0		4.19
8.0	69.0	
9.5		4.24
10.0	65.8	
12.5		4.29
13.5	62.0	
20.5		4.40
22.0	54.3	
26.5		4.55
29.0	51.1	
30.8		4.54
35.0		4.59
36.0	49.2	
37.0		4.60
40.0	48.6	
41.5		4.64
44.5		4.65
45.3	47.3	
48.0	46.0	
51.0		4.71
60.0	44.1	4.75
68.0	42.9	4.80
80.0	42.9	4.85
94.0	42.2	4.87
120.0	42.9	4.91
111.0	43.5	4.88
135.0	42.9	4.91
154.0	42.9	4.95
177.0	42.9	4.91
195.0	43.5	4.90
256.0	45.4	4.92
330.0	49.2	4.93

minutes	Peroxide	Control
0.0	4500	4509
1.5	4290	
3.8	4280	
7.0	4160	
9.8	4210	
12.0	4120	
14.4	4310	
16.8	4400	
19.4	4280	
22.0	4090	
24.0	4000	4570
27.0	4080	
32.0	4220	
35.0	4360	
39.4	3980	4490
45.0	4070	
47.8	3930	
50.5	4060	
55.5	4020	
59.5	3980	4520
62.5	4090	
65.8	4120	
71.5	4000	
75.0	4070	
81.0	3880	
84.0	3920	4480
87.0	3830	
92.5	3880	
99.0	3840	4520
101.5	3850	
103.8	3850	
123.0	3830	

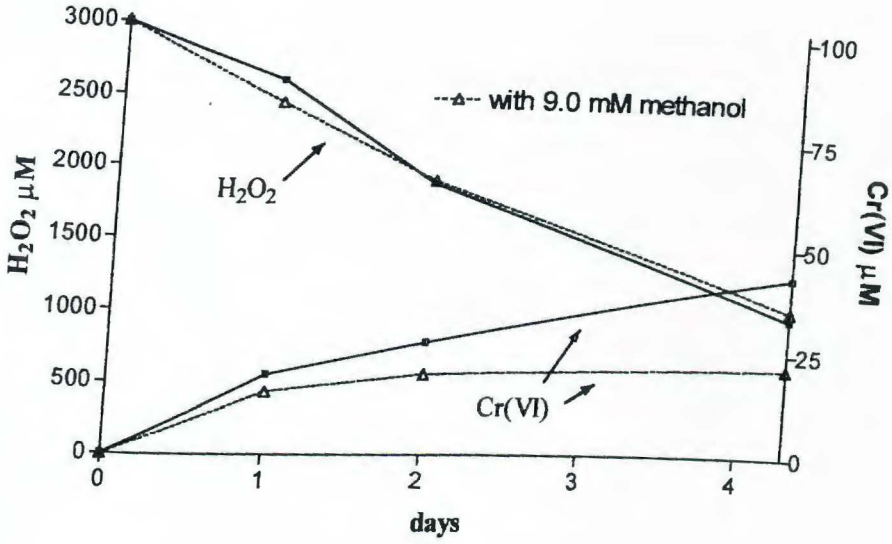
Table 3-2b. Data for Figures 3-6a and 3-6b. The reaction of 100 μM Cr(VI) with 3000 μM H_2O_2 in 0.01M $NaNO_3$. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM. All concentrations (μM).

Minutes	Cr VI	pH
0.0	100.0	4.00
1.5	91.2	4.00
2.8	90.0	4.01
4.1	88.7	
4.5		4.02
6.0	86.1	4.03
8.0	84.9	
8.5		4.05
10.5	83.6	
11.0		4.07
13.0		4.08
14.0	80.4	
20.6	76.0	
21.0		4.15
26.8	74.0	
27.0		4.18
30.0	72.1	4.20
47.0	66.4	
49.0		4.26
50.0	65.8	
65.0		4.32
66.0	63.9	
85.0		4.36
88.0	59.4	4.37
103.0	59.4	4.39
121.0	59.4	4.42
122.0	58.8	4.42
150.0	57.5	4.45
203.0	53.8	4.52
290.0	56.2	4.58

minutes	Peroxide
0.0	3000
1.8	2920
3.4	3020
5.5	2850
7.5	2890
9.0	3070
10.5	2970
11.8	2910
16.4	2810
20.5	2970
22.2	3080
27.5	2900
33.5	2790
38.5	2790
48.0	2720
50.5	2800
53.0	2740
55.5	2790
72.0	2640
74.0	2720
91.0	2630
93.0	2680
120.0	2570
122.0	2570
157.0	2490
160.0	2560
182.0	2520
185.0	2560

Table 3-2c. Data for Figure 3-6b. The reaction of 100 μM Cr(VI) with 1500 μM H_2O_2 in 0.01M $NaNO_3$. Cr(VI) concentrations given in μM (± 0.5).

Minutes	Cr VI	pH
0.0	100.0	4.00
0.8	96.9	4.00
2.0	96.3	4.00
3.5	95.7	
8.0	95.7	4.00
9.0		4.01
10.0	96.3	4.01
17.5	95.1	4.01
37.5	91.9	4.05
46.0	90.6	4.05
47.0	90.0	
76.0	88.1	4.06
78.0	86.8	4.06
97.0	87.4	4.07
99.0	87.4	4.08
138.0	85.5	4.12
190.0	83.6	4.13
260.0	83.6	4.14



µM Cr(VI)

Day	Cr (III)/perox		Cr(III)/pero/meth L		Cr(III)/pero/meth H	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0	19.2	18.6	15.4	14.8	14.8	14.8
2.0	26.7	26.7	18.5	19.1	19.1	19.1
4.3	42.8	43.5	21.4	22.0	21.4	21.4

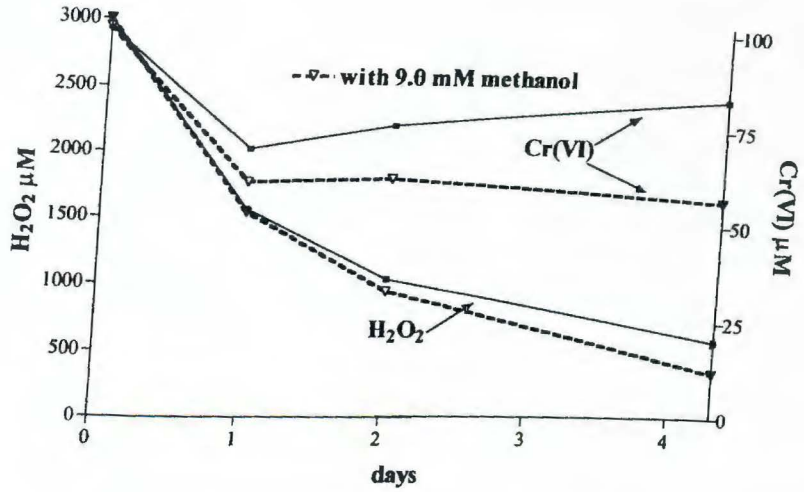
µM H_2O_2

Day	Cr (III)/perox		Cr (III/pero/meth L		Cr (III/pero/meth H	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	3000	3000	3000	3000	3000	3000
1.0	2620	2600	2380	2420	2480	2426
2.0	1870	1910	1920	1940	1910	
4.3	961	1000	1090	1060	1030	1044

pH

Day	Cr (III)/perox		Cr (III/pero/meth L		Cr (IIIpero/meth H	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	4.46	4.46	4.46	4.46	4.46	4.46
1.0	4.33	4.32	4.37	4.37	4.39	4.39
2.0	4.27	4.28	4.27	4.27	4.31	4.30
4.3	4.09	4.09	4.05	4.07	4.09	4.09

Figure 3-7a. Reaction of 100 µM aged, hydrolyzed (2:1 OH^-/Cr) Cr(III) and 3000 µM H_2O_2 in 0.01 M $NaNO_3$. Data shown for reactions with 2 levels of methanol: meth H = 9.0 mM methanol, meth L = 3.0 mM methanol. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 µM.



µM Cr(VI)

Day	Cr(VI)/peroxide		Cr(VI)/perox/meth L		Cr(VI)/perox/meth H		Cr (VI)/meth H	
	Y1	Y2	Y1	Y2	Y1	Y2	Y1	Y2
0.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1.0	69.3	68.7	59.8	60.4	60.4	60.4	100.4	100.4
2.0	75.4	75.4	59.6	60.2	61.5	61.5	99.4	100.0
4.3	83.2	83.2	55.9	55.9	56.5	56.5	100.8	101.4

µM H_2O_2

Day	Cr (VI)/perox		Cr(VI)/perox/meth L		Cr(VI)/perox/meth H	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	3000	3000	3000	3000	3000	3000
1.0	1570	1570	1510	1490	1550	1540
2.0	1040	1040	917	925	945	960
4.3	623	563	333	341	346	357

Day	Perox control		Perox/meth H	
	Y1	Y2	Y1	Y2
0.0	3000	3000	3000	3000
1.0	2970	3000	2930	2960
2.0	2930	3060	2980	3000
4.3	3050	2990	2920	3040

pH

Day	Cr (VI)/H2O2		Cr (VI)/H2O2/meth L		Cr (VI)/H2O2 meth H		Cr (VI)/meth H	
	Y1	Y2	Y1	Y2	Y1	Y2	Y1	Y2
0.0	4.02	4.02	4.02	4.02	4.02	4.02	4.02	4.02
1.0	4.52	4.55	4.42	4.42	4.46	4.47	4.07	4.07
2.0	4.40	4.40	4.26	4.24	4.27	4.28	4.07	4.07
4.3	4.29	4.28	4.09	4.11	4.06	4.06	4.01	4.01

Figure 3-7b. Reaction of 100 µM Cr(VI) and 3000 µM H_2O_2 in 0.01 M $NaNO_3$. Data shown for reactions with 2 levels of methanol: meth H = 9.0 mM methanol, meth L = 3.0 mM methanol. Data also shown for controls with peroxide alone, 9.0 mM methanol with Cr(VI) and 9.0 mM methanol with H_2O_2. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 µM.

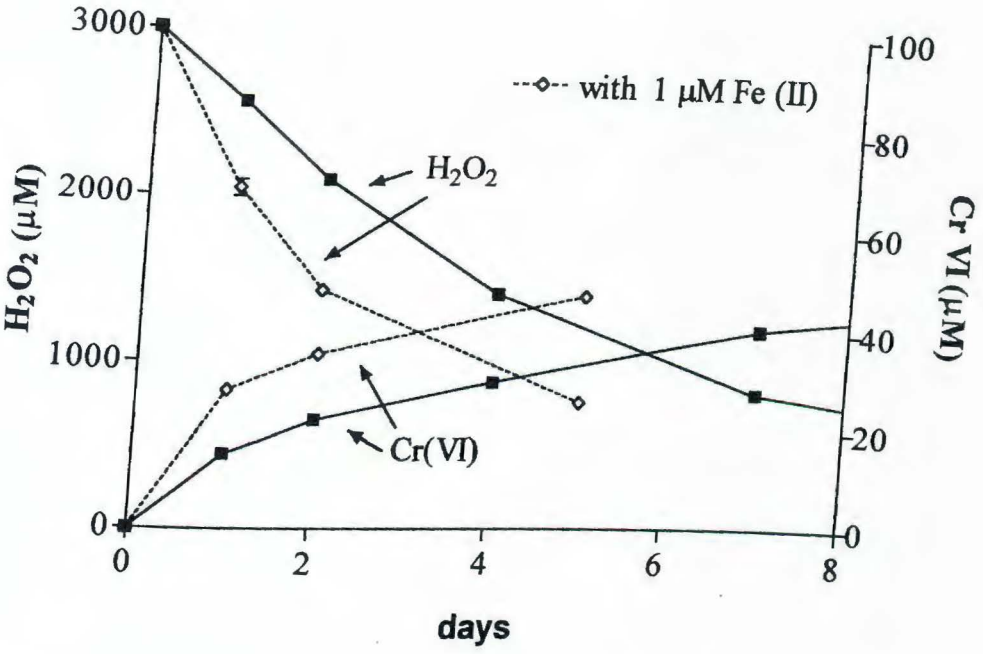
The addition of small (1 μM) amounts of Fe(II) to the same Cr(III)/H_2O_2 and Cr(VI)/H_2O_2 systems resulted in significantly enhanced Cr(III) oxidation, and less Cr(VI) reduction/complex formation coupled with quicker Cr(VI) recovery (Figures 3-8 a-b). Not surprisingly, H_2O_2 dismutation rates increase in both systems.

DISCUSSION

Cr(III)/H_2O_2 Interactions

The oxidation of aged solutions of Cr(III) shown across a range of OH^-/Cr ratios (Figure 3-1) can be attributed to the addition of H_2O_2. Evidence that eliminates O_2 as a potential oxidant in the system is provided by experiments that showed sparging Cr(III) (2:1 OH^-/Cr ratio) reactant solutions for 30 min with N_2 before adding H_2O_2 had no significant effect on oxidation rates (see Appendix Figure A-5). Sparging Cr(III) solutions with O_2 showed a similarly slight effect when compared to the same experiments done without sparging (Figure 3-2b).

One problem inherent in studying the Cr(III)/H_2O_2 system is in characterizing the initial reactant solutions of Cr(III). Ligand displacement reactions of hexacoordinate Cr(III) complexes are slow, with half times in the range of several hours (Cotton and Wilkinson, 1988). In aqueous systems, the resulting kinetic inertness of oxygen in the first Cr(III) coordination shell gives rise to two Cr(III) chemistries, a fast one and a slow one. The fast chemistry involves protonation, deprotonation and hydrogen bonding in response to the system pH, whereas the slow chemistry involves the formation of covalent OH bridges between Cr(III) atoms, giving



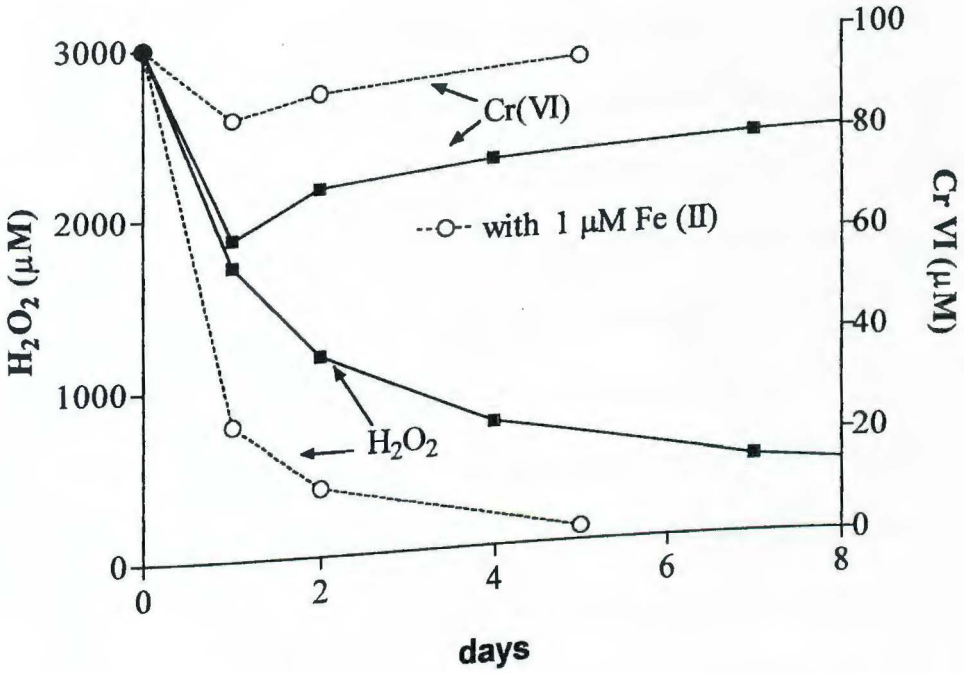
Cr(VI) (μM), H_2O_2 (μM) and pH for samples without Fe(II)

days	Cr(VI)		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	0.0	0.0	3000	3000	4.73	4.73
1.0	14.9	14.9	2594	2560	4.44	4.44
2.0	21.8	21.8	2109	2091	4.39	4.39
4.0	30.1	28.9	1411	1416	4.35	4.36
7.0	40.0	40.7	826	829	4.18	4.17
15.0	58.8	59.4	243	246	4.05	4.05

Cr(VI) (μM), H_2O_2 (μM) and pH for samples with 1μM Fe(II)

days	CrVI		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	0.0	0.0	3000	3000	4.57	4.57
1.0	27.5	28.1	1997	2102	4.22	4.23
2.0	34.7	35.3	1462	1405	4.21	4.19
5.0	46.9	46.9	793	739	4.14	4.13

Figure 3-8a. Reaction of 100 μM aged, hydrolyzed (2:1 OH^-/Cr) Cr(III) and 3000 μM H_2O_2 in 0.01 M $NaNO_3$ with and without the addition of 1.0 μM $FeSO_4$. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM.



Cr(VI) (μM), H_2O_2 (μM) and pH for samples without Fe(II)

days	CrVI		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	100.0	100.0	3000	3000	4.06	4.06
1.0	61.7	62.9	1715	1702	4.68	4.69
2.0	71.6	71.6	1157	1180	4.58	4.58
4.0	75.8	75.8	724	729	4.43	4.49
7.0	79.4	79.4	456	456	4.35	4.34
15.0	87.2	87.2	166	164	4.27	4.28

Cr(VI) (μM), H_2O_2 (μM) and pH for samples with 1μM Fe(II)

days	CrVI		peroxide		pH	
	Y1	Y2	Y1	Y2	Y1	Y2
0.0	100.0	100.0	3000	3000	4.06	4.06
1.0	86.7	85.4	753	817	4.24	4.24
2.0	89.5	91.4	436	363	4.18	4.18
5.0	96.5	94.0	45	112	4.11	4.13

Figure 3-8b. Reaction of 100 μM Cr(VI) and 3000 μM H_2O_2 in 0.01 M $NaNO_3$ with and without the addition of 1 μM $FeSO_4$. Analytical uncertainty for H_2O_2 determination is 2%, and experimental error for Cr(VI) is ± 0.5 μM.

rise to oligomers and polymers. Coordinative inertness of ligands surrounding Cr(III) allow a variety of oligomers to persist for weeks to months in solution (Stunzi and Marty, 1983). The "fast" and "slow" Cr(III) chemistries are interdependent: lability of $Cr(H_2O)_6^{3+}$ has been shown to increase upon deprotonation. Xu et al. (1985) measured water exchange rates for $CrOH(H_2O)_5^{2+}$ that were 75 times faster than those for $Cr(H_2O)_6^{3+}$ ($k_{ex} = 2.4 \times 10^{-6}\ s^{-1}$ at 298.15 K). Rate increases of 50-200 fold in the dimerization of $Cr(H_2O)_6^{3+}$ were observed for each additional deprotonation step (Rotzinger et al., 1986). Deprotonation (or increasing OH^-/Cr ratios in solution species) therefore corresponds to increased rates of condensation or oligomer formation.

Cr(III) oligomers from dimer to hexamer begin to form within minutes in aqueous solutions (Stunzi and Marty, 1983). The particular mixture of oligomers present in a Cr(III) solution will depend on temperature, time, pH, Cr(III) concentrations, concentrations of added OH^-, extent of stirring, and whether solutions were formed from the deprotonation of $Cr(H_2O)_6^{3+}$ or the protonation of $Cr(OH)_4^-$ (Spiccia and Marty, 1986; Spiccia et al., 1987; Spiccia et al., 1988). Stunzi and Marty developed a technique using acidification and ion exchange separation of Cr(III) solutions (as well as amorphous Cr(III) solids) to identify the fully protonated forms of Cr(III) oligomers: the blue-purple monomer $Cr^{3+}(aq)$, the greenish-blue dimer $Cr(OH)_2Cr^{4+}(aq)$, the green trimer $Cr_3(OH)_4^{5+}(aq)$, and the olive tetramer $Cr_4(OH)_6^{6+}(aq)$. In each case, H_2O molecules complete the presumed octahedral, six-coordinate first coordination sphere of each Cr center. Stirring, time, local OH^-

concentrations and Cr(III) concentrations all increase the extent of higher oligomer formation (Spiccia and Marty, 1986). The tendency of oligomers to coagulate increases with increasing pH, and they flocculate as OH^-/Cr approaches 3:1, forming an amorphous solid. Above pH 13, a deep green solution forms, presumably an extensively polymerized "$Cr(OH)_4^-$", considering the increased lability of its highly deprotonated form (Spiccia et al., 1988).

Characterizing Cr(III) solutions involves distinguishing between "fresh" and "aged" systems, where fast or slow Cr(III) chemistry respectively prevails. In fresh solutions of aqueous Cr(III) the monomer $Cr^{3+}(aq)$ successively deprotonates as OH^-/Cr ratios increase to form monomers $CrOH^{2+}$, $Cr(OH)_2^+$, and $Cr(OH)_3^0$. An "active" $Cr(OH)_3(s)$ precipitates in fresh systems, and, unlike the amorphous $Cr(OH)_3(s)$, it does not contain bridging hydroxide ligands. Its units are linked through hydrogen bonds between OH^- and H_2O ligands of adjacent Cr(III) centers, and it produces only the monomer $Cr^{3+}(aq)$ upon acidification (Spiccia and Marty, 1986). Its solubility is significantly higher than that of amorphous $Cr(OH)_3(s)$. Values of log K determined for its dissolution:

$$Cr(OH)_3(s) + 2H^+ \rightleftharpoons CrOH^{2+} + 2H_2O \qquad (3.1$$

are 8.0 for the "active" precipitate (von Meyenburg et al., 1973) vs. 5.78 for the amorphous solid (Rai et al., 1987). The active precipitate will revert in time and at ambient temperatures to a more amorphous phase (Spiccia and Marty, 1986).

Figure 3-9 shows speciation diagrams constructed from equilibrium data representing: a) a "fresh" monomeric system (acid dissociation constants taken from

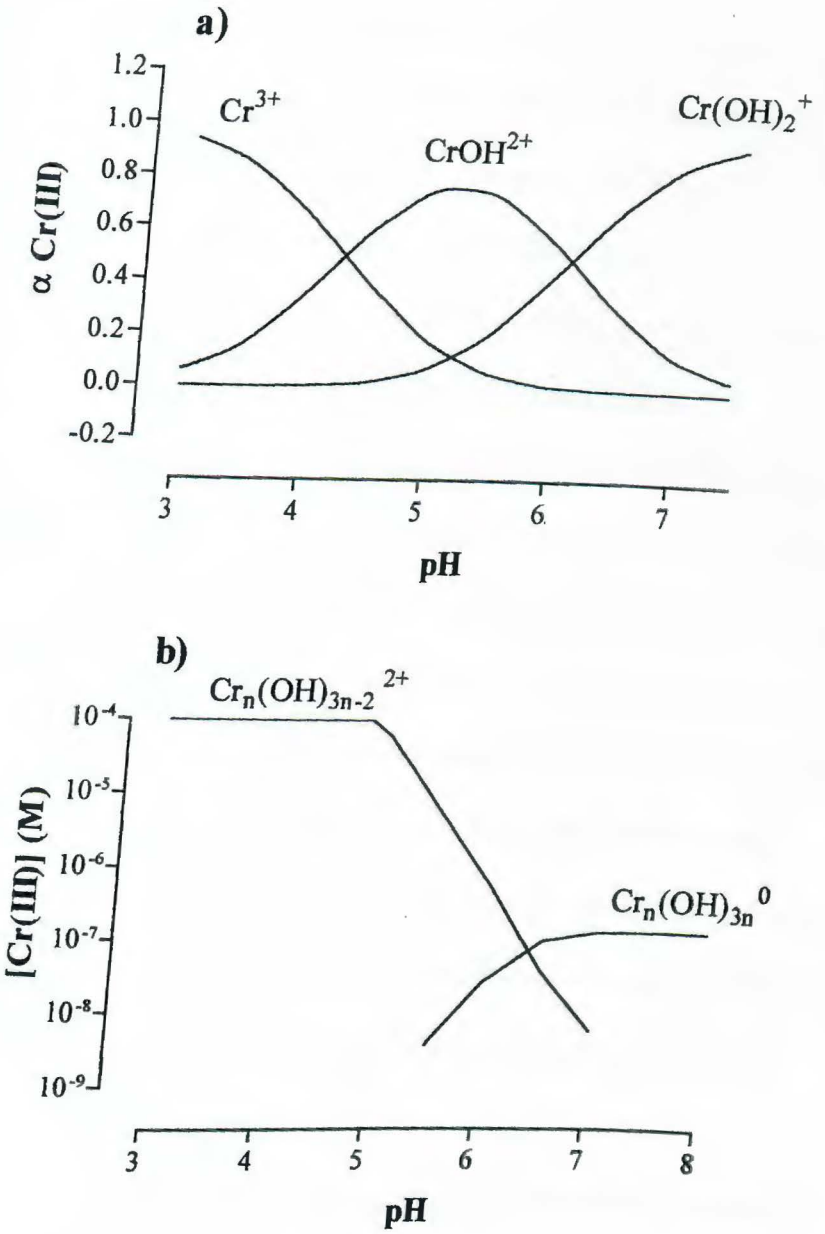


Figure 3-9. Speciation diagrams for Cr(III) in aqueous systems a) representing a "fresh" or monomer system. At $\Sigma Cr(III) = 10^{-6}$ M, saturation with respect to active $Cr(OH)_3(s)$ is not reached in this pH range (based on equilibrium data for soluble Cr(III) species from Stunzi and Marty (1983) and solubility data for active $Cr(OH)_3(s)$ from von Meyenburg et al., 1973) b) representing an "aged" system or oligomer mixture. At $\Sigma Cr(III) = 10^{-4}$ M saturation with respect to amorphous polymeric $Cr(OH)_3^0$ is reached at pH 4.8 (based on equilibrium data from Rai et al., 1987).

Rotzinger et al., 1986, and based on Stunzi and Marty (1983) data); and b) an "aged" system containing a mixture of aqueous Cr(III) oligomers in equilibrium with amorphous Cr(III) solids. The "aged" system is based on data provided by Rai et al. (1987) that has become the basis for much of the Cr thermodynamic data reported in the literature (e.g. Ball and Nordstrom, 1998). The equilibrium model of Rai and co-workers identified $CrOH^{2+}$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ as the Cr(III) species which account for Cr(III) solubilities across the pH range from 4-14. Their data indicated that the only significant Cr(III) species found in solution between pH 3-6 was $CrOH^{2+}$, based on a 2:1 slope that resulted from plotting log [Cr(III)] vs. pH in that pH range. They therefore concluded that multimers (e.g. $Cr(OH)_2Cr^{4+}$, $Cr_3(OH)_4^{5+}$) were not present in the aqueous phase. Spiccia (1988) predicted that experimental conditions used by Rai would produce oligomers, and applied his separation technique for oligomers on Cr(III) systems as prepared in Rai et al. (1987). He found the aqueous phase to consist almost completely (>98%) of multinuclear species, and made the point that Rai's conclusions were based on the charge, not the nuclearity of the Cr(III) species being measured.

Since Spiccia's technique for determining oligomers used an acidification step before separation, all the oligomers became protonated. They might have been present in a deprotonated form as $Cr_n(OH)_{3n-2}^{2+}$ in Rai's solutions. A structure for $Cr_n(OH)_{3n-2}^{2+}$ such as the linear configuration depicted in Figure 3-10 could account for the 2+ charge prevailing in Rai's system, as well as charges assigned to the multinuclear compounds (e.g. $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, $Cr_4(OH)_6^{6+}$) by Spiccia and co-workers,

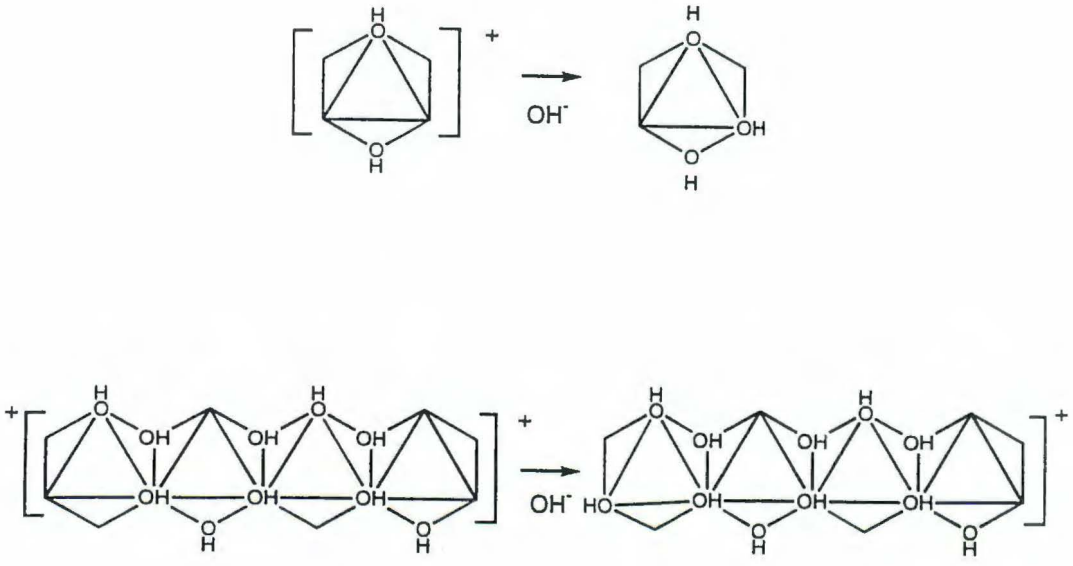


Figure 3-10. Proposed pre-equilibrium step to the oxidation of Cr(III) by H_2O_2 :

a) in a "fresh" system: $Cr(OH)_2^+ + OH^- \rightleftharpoons Cr(OH)_3^0$

b) in an "aged system": $Cr_n(OH)_{3n-2}^{2+} + OH^- \rightleftharpoons Cr_n(OH)_{3n-1}^+$

Each octahedron represents the inner coordination sphere surrounding a single Cr(III) atom. Matrix points not occupied by an OH ligand are occupied by H_2O.

where non bridging OH groups would be protonated under the acidic conditions in which they are separated. The 2+ charge on a polynuclear $Cr_n(OH)_{3n-2}^{2+}$ could be expected to be distributed on opposite ends of the molecule, as indicated in Figure 3-10.

The aged Cr(III) solutions used in this study, prepared while stirring with dropwise addition of dilute NaOH, and equilibrated for at least a week, undoubtably contained a mixture of oligomers, and are best described using the speciation data for an "aged" system (Figure 3-9). The pH of solutions with OH^-/Cr ratios up to 2.75 remained below pH 5.2. Assuming a 2+ charge for the solution species, the low pH at these OH^-/Cr ratios also supports the presence of oligomers, because solution pH would have been much higher if the $CrOH^{2+}$ monomer were the predominant species.

Some deprotonation appears to be necessary for the oxidation of Cr(III) by H_2O_2, as none occurred at pH 3 (Figure 3-2a) where the $Cr^{3+}(aq)$ monomer is the prevalent species. The rate of oxidation by 100 μM H_2O_2 (Figure 3-1) reached a maximum at the 2:1 OH^-/Cr ratio, above that ratio $Cr_n(OH)_{3n}^{0}$ (aq) oligomers possibly began to form and flocculate up to the 3:1 OH^-/Cr ratio, impeding oxidation by limiting access to deprotonated OH groups as they became buried in floc. At OH^-/Cr ratios over 3, further deprotonation may have caused increasing rates of Cr(III) oxidation by H_2O_2. Oxidation of octahedral Cr(III) to tetrahedral Cr(VI) requires a change in coordination number from 6 to 4, a change that may be facilitated by the increased lability that accompanies deprotonation.

Pettine and Millero (1990) determined the rate constant for the oxidation of

Cr(III) by H_2O_2 to be: $\log k = 8.13-2.17/T$ for the rate law:

$$-d[Cr(III)]/dt = k\,[Cr(III)][H_2O_2][OH^-] \qquad (3.2$$

where the rate is in M/min and T is in ^{0}C. They used dilute (1.9 μM) Cr(III) solutions buffered to 7.4-8.5. In this pH range they found a linear relationship between $k^{-2/3}$ and aging time of Cr(III) reactant solutions. Their rate constant was determined by extrapolating the line back to zero time, thus correcting for aging effects that slowed the oxidation reaction. We can therefore conclude theirs approximates a "fresh" system as described in Figure 3-9. Using the speciation diagram for the "fresh" system and the solubility constant for the "active" $Cr(OH)_3(s)$ (equation 3.1), it is predicted that saturation would not be reached in the fresh system at pH 7.5 at Cr concentrations used in Pettine and Millero's experiments. It follows that the predominant species in their system is the monomer $Cr(OH)_2^+$, and their rate law becomes:

$$-d[Cr(III)]/dt = k\,[Cr(OH)_2^+][H_2O_2][OH^-] \qquad (3.3$$

The case may then be made that $Cr(OH)_3^0$ is the active species in Pettine and Millero's experiments. Their rate law can be interpreted as involving a pre-equilibrium step:

$$Cr(OH)_2^+ (aq) + OH^- \rightleftharpoons Cr(OH)_3^0 (aq) \qquad (3.4$$

where $[Cr(OH)_2^+][OH^-] = [Cr(OH)_3^0]/K$. K is calculated from equilibrium constants from Rotzinger et al. (1986) and Rai et al., (1987) to be $10^{8.2}$, and substitution into Pettine and Millero's rate law produces:

$$-d[Cr(III)]/dt = (k/K)\,[Cr(OH)_3^0][H_2O_2] \qquad (3.5$$

where $k/K = 10^{0.39}$, within reason for a bimolecular mechanism.

It may be further hypothesized that a similar mechanism applies to the oxidation

of Cr(III) by H_2O_2 in the aged systems used in the present study. Figure 3-2b shows the oxidation of 100 μM Cr(III) (at 2:1 OH^-/Cr) by 3000 μM H_2O_2. If average concentrations from day 0 to day 1 of the oxidation are applied to Pettine and Millero's rate law (equation 3.2), a rate is calculated (1.03×10^{-8} M/min) that corresponds exactly to the measured initial rate of oxidation. As we are taking $Cr_n(OH)_{3n-2}^{2+}$ to be the predominant species in our 2:1 OH^-/Cr system, one interpretation of the correspondence of our measured rate to Pettine and Millero's rate law is that oligomers in our system become activated toward oxidation by deprotonation by an OH^- at one end of the molecule, behaving near an active site like $CrOH_2^+$. A diagrammatic comparison of the deprotonation of aged and fresh species is made in Figure 3-10. I postulate that once a terminal Cr(III) center is deprotonated, it becomes more labile and subject to oxidation by H_2O_2. Pettine and Millero's rate law for our aged system then becomes:

$$-d[Cr(III)]/dt = k\,(1/n)\,[Cr_n(OH)_{3n-2}^{2+}][H_2O_2][OH^-] \qquad (3.6$$

Measured and calculated rates diverge somewhat due to the factor 1/n where $1<n<6$, and to corrections to thermodynamic data from different sources obtained at various ionic strengths, but still fall within an order of magnitude of one another.

In this work, during oxidation, measured pH values decreased across the range of OH^-/Cr ratios (Figure 3-1), consistent with the oxidation of Cr(III) by H_2O_2:

$$3H_2O_2 + 2Cr^{3+} + 2H_2O \rightleftharpoons 2HCrO_4^- + 8H^+ \qquad (3.7$$

$$3H_2O_2 + 2CrOH^{2+} \rightleftharpoons 2HCrO_4^- + 6H^+ \qquad (3.8$$

$$3H_2O_2 + Cr_2(OH)_2^{4+} \rightleftharpoons 2HCrO_4^- + 6H^+ \qquad (3.9$$

$$3H_2O_2 + Cr_2(OH)_4^{2+} \rightleftharpoons 2HCrO_4^- + 4H^+ + 2H_2O \quad (3.10$$

$$3H_2O_2 + 2Cr(OH)_2^+ \rightleftharpoons 2HCrO_4^- + 4H^+ + 2H_2O \quad (3.11$$

$$3H_2O_2 + 2Cr(OH)_4^- \rightleftharpoons 2CrO_4^{2-} + 2H^+ + 6H_2O \quad (3.12$$

Production of H^+ relative to production of Cr(VI) at 17 days exceeds stoichiometric ratios. For example at $OH^-/Cr = 0$, 25 times as much H^+ is produced as Cr(VI), compared to the 4:1 ratio expected from equation (3.7), at $OH^-/Cr = 2$, 11 times as much H^+ is produced as Cr(VI), compared to the 2:1 ratios expected from equations (3.10) or (3.11).

Another process in this system that could generate extra H^+ is the further polymerization of Cr(III) species during oxidation. For example, if, as a result of the oxidation of the terminal Cr(III) center in an oligomer, a $Cr_{n-1}(OH)_{3n-4}^+$ species was produced, it could bond with another multimer (e.g.):

$$H_2O + Cr_3(OH)_8^+ + Cr_2(OH)_4^{2+} \rightleftharpoons Cr_5(OH)_{13}^{2+} + H^+ \quad (3.13$$

to produce H^+. An additional H^+ for each Cr(VI) produced still does not account for total H^+ generated during oxidation. It should be kept in mind that other reactions may complicate these systems as the oxidation of Cr(III) proceeds, including reduction of Cr(VI) by H_2O_2, or the formation of peroxochromium complexes and their subsequent interaction with H_2O_2.

As OH^- levels increase beyond the development of solid floc at OH^-/Cr ratio 3:1, Cr(III) becomes soluble once again as "$Cr(OH)_4^-$". Rai et al. (1987) obtained $\log K = -18.3$ for:

$$Cr(OH)_3(s) + H_2O \rightleftharpoons Cr(OH)_4^-(aq) + H^+ \quad (3.14$$

This would suggest that the concentration of soluble Cr(III) in the initial 4:1 solution (pH ~10) was in the region of 10^{-8} M, and that the oxidation of Cr(III) by peroxide (equation 3.12) enhanced chromium solubility under alkaline conditions.

Figures 3-2 a-c show how H_2O_2 behavior varied markedly with pH in the presence of Cr(III). Peroxide standards prepared at pH 3, 4.5, and 10 in 0.01 M $NaNO_3$ retained consistent absorbance readings in the course of experiments and showed no catalytic disappearance of H_2O_2 in the absence of Cr.

Beck et al. (1991) noted no catalytic destruction of high levels of H_2O_2 (3M) added to Cr(III) nitrate in "weakly acidic solution," and those results correspond to results in Figure 3-2a, at pH 3, where no catalytic destruction of H_2O_2 is observed. This suggests that the presence of Cr(VI) plays a critical role in the catalytic destruction of H_2O_2.

The observation that the rate of chromium oxidation in the OH^-/Cr 4:1 system (Figure 3-2c) appears to level off at about one week, while peroxide levels are still high, could be an indication that an intermediate species, such as the tetraperoxochromium(V) complex could be forming initially, contributing to the dismutation of the peroxide, and slowly decomposing back to chromate over time. At the end of four weeks, about 92% of the Cr was present in the system as Cr(VI). Similarly, intermediate species such as the violet diperoxochromium(VI) or the chromium(V) peroxo species detected by Zhang and Lay (1998) (see Chapter 1) could be forming in the midrange pH solution, once chromium begins to be oxidized. The formation of persistent peroxochromium complexes may also explain the changing

pattern in the behavior of [Cr(VI)] and pH when levels of H_2O_2 above 1500 μM are applied to Cr(III) (Figure 3-3a).

Cr(VI)/H_2O_2 Interactions

As with the Cr(III)/H_2O_2 system, the Cr(VI)/H_2O_2 interaction depended strongly on pH, and its behavior changed significantly across a relatively narrow pH range. In three systems from pH 4-5 (Figure 3-4 a-c), application of H_2O_2 to Cr(VI) initially caused Cr(VI) to disappear, reach a minimum level within hours, then reappear over days. Cr(VI) is either being reduced and reoxidized, or forming a peroxochromium(VI) complex that reverts to $HCrO_4^-$ as H_2O_2 levels decline.

At minimum Cr(VI) levels, the ratio of H^+ used to Cr(VI) consumed is 1.5-1.6 for all three solutions, in contrast to the 4:1 ratio observed at pH 3 which corresponded to complete reduction of chromium to hexaaquochromium(III):

$$2HCrO_4^- + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 3O_2 + 8H_2O \qquad (3.15$$

A closer fit is the reduction to $Cr_n(OH)_{3n-2}^{2+}$:

$$nHCrO_4^- + (3n/2)H_2O_2 + (n+2)H^+ \rightarrow Cr_n(OH)_{3n-2}^{2+} + (n+2)H_2O + (3n/2)O_2 \qquad (3.16$$

Formation of polymers as Cr(VI) is reduced consumes H^+ per atom of Cr in the ratio (n+2)/n which has a maximum value of 3 for a monomer and a minimum value at of 1 for a large polymer. Measured pH changes correspond to $n \approx 4$ in this scheme. Cr(III) oligomers could be subsequently reoxidized to Cr(VI), as in equation (3.10). The pe-pH diagram in Chapter 1 (Figure 1-2) further illustrates how, as H_2O_2 diminishes and pH increases to around pH 5 during reduction of Cr(VI) to Cr(III), Cr(VI) will become

stable with respect to H_2O_2, while Cr(III) could continue to be oxidized by H_2O_2 even at low H_2O_2 concentrations.

Using pH changes to consider the formation of peroxochromium complexes, we observe that the violet peroxochromium complex that has been shown to form in this pH range (Witt and Hayes, 1982; Dickman and Pope, 1994), does not require protons to form:

$$HCrO_4^- + 2H_2O_2 \rightleftharpoons [Cr^{VI}O(O_2)_2OH]^- + 2H_2O \qquad (3.16$$

Subsequent reduction to the Cr(V) species postulated by Zhang and Lay (1998) would also not require protons:

$$[Cr^{VI}O(O_2)_2OH]^- + H_2O_2 \rightleftharpoons [Cr^{V}O(O_2)_2OH_2]^- + HO_2\cdot \qquad (3.17$$

However, if this complex lost one of its peroxo ligands to form the monoperoxochromium(V) species Zhang and Lay suggested would form at low H_2O_2/Cr levels, it would account for two protons:

$$[Cr^{V}O(O_2)_2OH_2]^- + H_2O + 2H^+ \rightleftharpoons [Cr^{V}O(O_2)OH_2]^+ + H_2O_2 \qquad (3.18$$

If about half of the hydroperoxyl radical formed in (3.17) were deprotonated:

$$HO_2\cdot \rightleftharpoons O_2\cdot^- + H^+ \qquad (3.19$$

($pK_a = 4.8$) (Wardman and Candeias, 1996) the 1.5 ratio of H^+ used to Cr(VI) consumed could fit the sequence (3.16)-(3.19). The slow reoxidation of a monoperoxo chromium(V) species could account for the reappearance of $HCrO_4^-$, and the eventual lowering of pH back to starting levels:

$$[Cr^{V}O(O_2)OH_2]^+ + H_2O_2 \rightleftharpoons HCrO_4^- + OH\cdot + H_2O + 2H^+ \qquad (3.20$$

completing a Haber Weiss type of cycle between Cr(VI) and Cr(V).

Attempts to determine initial rate constants for the disappearance of Cr(VI) in solutions with different initial $[H_2O_2]$ (Figure 3-5 a-b) were thwarted by the complicated behavior of H_2O_2, which oscillated as it decreased over the first hours of the reaction (Figure 3-6a). The observed H_2O_2 oscillation, unless it was the unlikely result of the oxidation of H_2O, also provides evidence for the formation of a peroxochromium species that releases H_2O_2, as in equation (3.18).

After the initial two days, solutions at initial 3000 and 4500 μM H_2O_2 showed congruent behavior, and data points taken between day three and day seven for these two solutions, when H_2O_2 decomposition rates have slowed, give consistent values for a postulated equilibrium constant (Figure 3-11):

$$K = [Cr^*] [Cr(VI)]^{-1} [H_2O_2]^{-1} [H^+]^{-1} = 12.3 \pm 0.3 \times 10^6 M^{-2} \qquad (3.21$$

This would describe an equilibrium condition between $HCrO_4^-$ and Cr*, a chromium monoperoxo complex requiring one proton to form. The data points do not give consistent values for an equilibrium constant :

$$K = [Cr^*] [Cr(VI)]^{-1} [H_2O_2]^{-2} \qquad (3.22$$

where Cr* would describe a diperoxo Cr(VI) complex (Perez-Benito and Arias, 1997).

Unlike the systems at given initial Cr(VI) and H_2O_2, where pH was varied, the proton requirement during the initial consumption of Cr(VI) in the experiments which vary initial $[H_2O_2]$ is not consistent, ranging from a 1.4 to 2.4 ratio of H^+ used to Cr(VI) consumed, indicating a change in reaction mechanism as absolute levels of peroxide change.

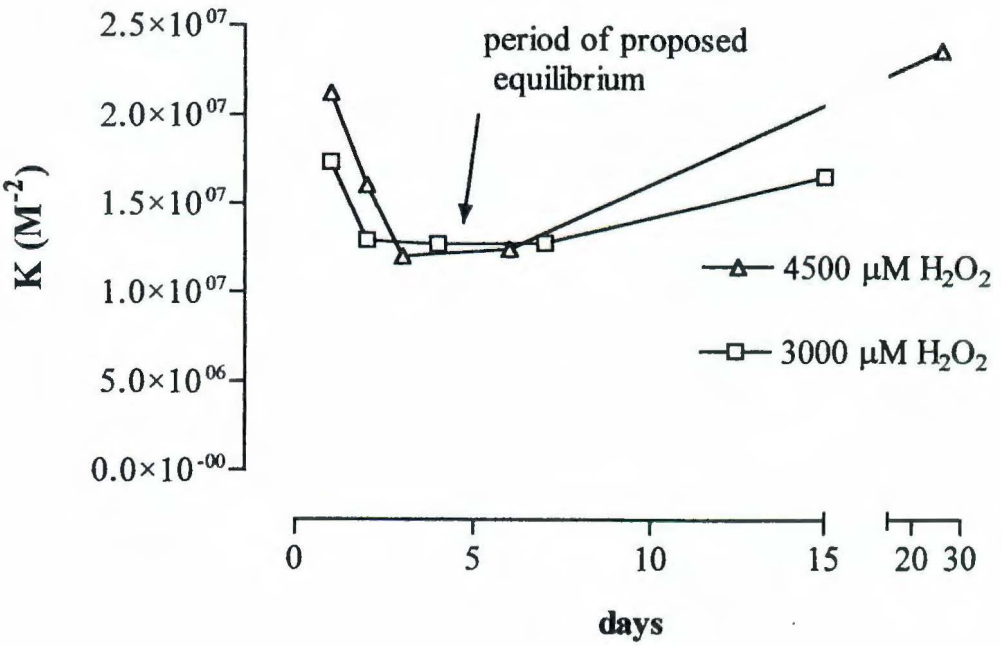


Figure 3-11. K vs. sampling time for the reaction of 100 μM Cr(VI) with different concentrations of H_2O_2. K calculated as $K = [Cr^*] [Cr(VI)]^{-1} [H_2O_2]^{-1} [H^+]^{-1}$, where Cr* = 100 μM - [Cr(VI)], and represents a chromium monoperoxo complex. Data from Table 3-1.

Effects of Adding Methanol or Fe(II)

The inhibition of Cr(III) oxidation over time where methanol is added to a Cr(III) system (Figure 3-7a) suggests that methanol is donating electrons to species which form as a result of Cr(III) oxidation and which additionally contribute to the further oxidation of Cr(III) in the system. The inhibition of Cr(VI) recovery observed by adding methanol to the Cr(VI) system likewise suggests that methanol is interacting with intermediate species that would otherwise either reoxidize to or dissociate as $HCrO_4^-$. Interestingly, a similar decrease in Cr(VI) concentration (22-26 μM) is produced by the addition of methanol in both the Cr(III) and Cr(VI) systems. Direct interaction of Cr(VI) and methanol (e.g. the formation of a methanol-Cr(VI) ester) is precluded, however, by unchanging [Cr(VI)] in the presence of methanol and the absence of H_2O_2 (Figure 3-7b). Further, an ester formation with an intermediate diperoxo complex (e.g. $Cr^{VI}O(O_2)_2OH^-$) would be expected to produce different equilibrium concentrations of $HCrO_4^-$ with 9.0 mM methanol and with 3.0 mM methanol, which is not the case.

Conversely, addition of a relatively small amount of Fe(II) (1 μM) enhanced Cr(III) oxidation, increased rates of H_2O_2 dismutation, and inhibited the initial disappearance of Cr(VI) (Figures 3-8a and 3-8b). Hydroxyl radicals, which would be produced via a Fe(II)/H_2O_2 Fenton interaction, have been previously shown to oxidize Cr(III) (Buxton et al, 1997) and most likely account for the enhanced levels of Cr(VI) in both systems.

SUMMARY

Despite the complexity of the chromium/peroxide system, a number of observations may be made about its characteristic behavior under environmentally relevant conditions. Peroxide will oxidize soluble, hydrolyzed Cr(III) at pH 4.5 and above and is capable of enhancing the oxidative dissolution of $Cr_n(OH)_{3n}^{0}$ under alkaline conditions. There is evidence that peroxochromium compounds form and persist in the presence of Cr(VI) under mid range pH conditions and at mM H_2O_2 levels. The evidence includes [H_2O_2] oscillations in the presence of Cr(VI) at mid-range pH, and erratic [Cr(VI)] and pH behavior at H_2O_2 levels over 1500 μM. These H_2O_2 levels are much higher than peroxide levels that would naturally occur, but much lower than proposed remediation levels (see Chapter 4). Changes in pH in aqueous Cr(VI)/H_2O_2 systems point toward a chromium(V) monoperoxo species as a likely candidate for a persistent, slowly decomposing peroxochromium intermediate species. However, these same pH changes also support an interpretation of Cr(VI) reduction to a $Cr_n(OH)_{3n-2}^{2+}$ oligomer, and its subsequent reoxidation as conditions become thermodynamically favorable at diminished H_2O_2 concentrations. Hexavalent chromium can be expected to behave as a catalyst toward H_2O_2 in soils, and enhance their oxidative capacity while helping to dissipate high levels of applied H_2O_2.

Chapter 4

Chromium-Peroxide Interactions and Implications for the Use of Hydrogen Peroxide to Remediate Biorefractory Organic Waste

In 1998, EPA undertook field scale demonstrations of several innovative technologies to clean up biorefractory organic contamination in groundwater, sediment and soil (U.S. EPA, 1998). One of these was *in situ* chemical oxidation, and included the subsurface application of high concentrations of hydrogen peroxide combined with an iron catalyst (Fenton's reagent) to produce oxidation of an extensive variety of organic wastes via hydroxyl radicals. Given the prevalence of chromium as a soil contaminant in industrial waste sites, and the possibility of its presence in sites where Fenton remediation is being considered, the impact of high levels of H_2O_2 on its mobility and toxicity needs to be assessed. The current study of Cr/H_2O_2 interactions undertaken with soils and aqueous systems lends some insight into the possible ramifications of using H_2O_2 in the presence of chromium.

In the current study, experiments were done using single applications of H_2O_2 made to soils or aqueous systems in concentrations that varied from 100 μM to 100 mM. These levels of H_2O_2 are low compared to those being tested for Fenton remediation, and could correspond to lingering effects of H_2O_2 treatment after much of it has been dissipated in the soil, or to H_2O_2 levels commonly considered for supplying dissolved oxygen to enhance bioremediation (Pardieck et al., 1992). Although the level of H_2O_2 application will vary at a site depending on contaminant levels, subsurface characteristics and pre-application laboratory testing, H_2O_2 application levels as high as 50% (17 M) have been reported by EPA. Many of the Fenton treatment preparations have been patented (e.g. Geo-Cleanse®, consisting of H_2O_2 and ferrous sulfate; ISOTEC℠, consisting of H_2O_2 and a proprietary iron complex added as a catalyst; and

Clean-OX®, consisting of H_2O_2, and an iron catalyst in acid), so that exact knowledge of the nature of the treatment is unavailable. Higher H_2O_2 application levels sustained over days or weeks may magnify effects on chromium that have been observed in the current work. At the outset, however, a consideration of the possible impact of H_2O_2 on Cr in soils should be accompanied by a consideration of the possibly significant effects that Cr could have on H_2O_2 applied in the field.

Chromium catalyzes H_2O_2 decay. Figure 4-1 shows that at 1 M application levels, H_2O_2 will both oxidize Cr(III) and reduce Cr(VI) across the entire pH range. In particular wherever there is ambient Cr(VI) in a waste site, or the possibility of Cr(VI) resulting from the H_2O_2 oxidation of Cr(III), Cr will affect the longevity of H_2O_2 in the subsurface, and the distance that it can be pumped from injection wells. Because the action of Cr(VI) on H_2O_2 is catalytic, small amounts of Cr(VI) can destroy large amounts of H_2O_2.

When H_2O_2 is applied as Fenton's reagent, the purpose of Fe(II) is to similarly work as a catalyst, providing the powerful oxidizing capacity of $OH^{\cdot}$ radicals, and producing innocuous H_2O_2 decomposition products (H_2O and O_2). Since Cr(VI) has been shown to oxidize Fe(II) (Eary and Rai, 1988; James, 1994; Buerge and Hug, 1998, Seaman et al., 1999), it is possible that Cr(VI) might interfere with the Fenton remediation chemistry by destroying Fe(II) and becoming the dominant pathway for H_2O_2 decomposition. The $FeOOH/Fe^{2+}$ reduction line shown in Figure 4-1 shows that below pH 3, 10^{-4} M Fe(II) will not act as a reductant toward Cr(VI). The Fe reduction line will rise as Fe(II) concentrations decrease, increasing the pH at which it would not

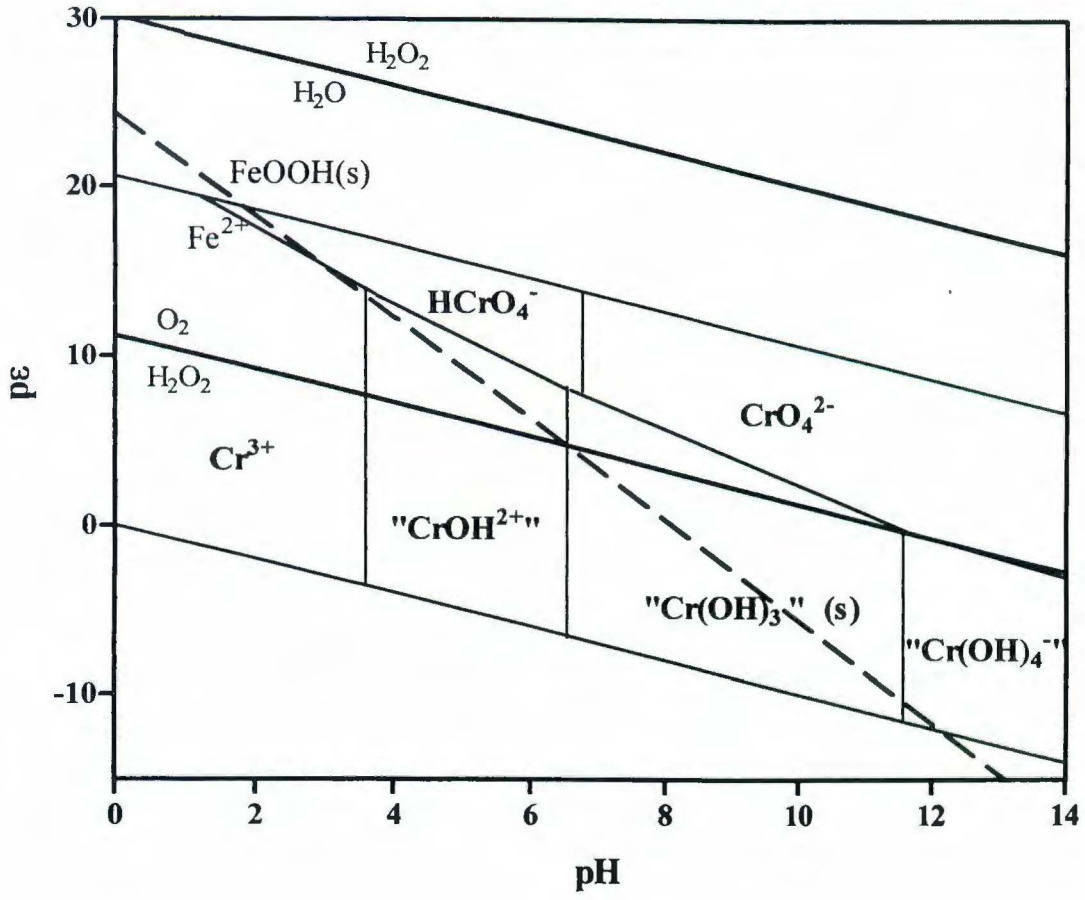


Figure 4-1. Stability diagram for aged aqueous Cr(III) and Cr(VI) species. Solid lines depicting H_2O_2/H_2O and O_2/H_2O_2 redox couples predict H_2O_2 could behave as an oxidant toward Cr(III) as well as a reductant toward Cr(VI) at all pHs. The dashed line represents the FeOOH(s)/Fe^{2+} couple, and predicts Fe^{2+} will not reduce Cr(VI) below pH 3, at these concentrations. From Cr data compiled by Ball and Nordstrom, 1998; H_2O_2 and Fe data from Woods and Garrells, 1987. Activity of H_2O_2 1.0 M, activities of other aqueous species = 10^{-4} M, activities of $Cr(OH)_3$(s), FeOOH(s) and H_2O(l) = 1. P_{O_2} = 0.21 atm.

reduce Cr(VI). Applied in catalytic amounts, and in acidic treatment solutions (as generally indicated in some of the patent descriptions) Fe(II) could be stable with respect to Cr(VI) during the treatment process. Experiments in this work done at pH 4-5 showed increases in Cr(VI) levels in the presence of μM Fe(II) and mM H_2O_2, demonstrating that Fe(II) in those circumstances was not oxidized by Cr(VI) and, in fact, enhanced Cr(III) oxidation.

Due to its catalytic effect on H_2O_2, Cr(VI) would probably also enhance H_2O_2 oxidation of organic co-contaminants. Experiments with methanol show that Cr(VI) levels in the Cr/H_2O_2 system are depressed in the presence of methanol, under conditions in which Cr(VI) and methanol do not react alone. In this case, methanol, rather than Cr(III) (or another Cr(V, IV) intermediate), could be acting as a reductant in the catalytic cycle, as in a peroxidase mechanism.

Possible effects of H_2O_2 on Cr, depending on reaction conditions, include oxidation of Cr(III) to Cr(VI), reduction of Cr(VI) to Cr(III), and the formation of peroxochromium complexes that may be more hazardous than Cr(VI) alone (Aiyar et al., 1991; Shi et al., 1999). Although the reduction of Cr(VI) by H_2O_2 appears to proceed more rapidly than its oxidation at the mid range pH (4-5) found in some Cr-contaminated sites (e.g. plating waste sites), as H_2O_2 diminishes below mM levels, Cr(VI) becomes thermodynamically stable with respect to H_2O_2, first at high pH and then at lower pH. An initial quenching of Cr(VI) concentrations by applications of H_2O_2 above pH 4 could result in a reappearance of Cr(VI), either due to its reduction and reoxidation, or to the decomposition of peroxochromium complexes that form at

high H_2O_2 levels (over 1-2 mM) and revert to soluble Cr(VI) as H_2O_2 concentrations drop.

The response of different Cr-elevated soils to peroxide was shown to vary widely, depending on the Cr deposition process, pH, and the reducing or oxidizing environment of the site. The nature of Cr(III) at a site will affect its ability to be oxidized by H_2O_2. For example, peroxide was shown to oxidize Cr(III) to Cr(VI) in the surface horizon of a plating waste site that contained high levels (6%) of total Cr, but did not oxidize Cr(III) in a serpentine soil with naturally elevated Cr(III). Chromium at the plating waste site was discharged as Cr(VI), and Cr(III) present in the site was reduced relatively recently and was present mainly in the form of amorphous Cr (hydr)oxides. In contrast, Cr(III) at the serpentine site, was present in a more crystalline form as chromite, or incorporated into a serpentine mineral such as antigorite. Chromium(III) was also oxidized in the high pH, low organic matter environment of an ore processing residue soil, where enhanced Cr(VI) levels from a single H_2O_2 application were sustained for several days. In contrast, Cr(III) in a tannery waste site soil was not oxidized by applications up to 0.1M H_2O_2, probably due to the highly reducing environment at that site caused by high levels of animal organic waste and wetland conditions. High levels of organic matter, however, were not necessarily an indication that Cr(III) would not be oxidized by peroxide: the plating waste site had more soil organic matter than the tannery site, yet Cr(III) was readily oxidized in its surface horizon. Soil organic matter was probably the cause of a rapid return of Cr(VI) to ambient levels after a single application of H_2O_2, although a

sustained application of H_2O_2 would probably counter the reducing effect of organic matter.

High levels of H_2O_2 could have a negative impact on the nature of Cr contamination at certain kinds of waste sites, rendering greater quantities of it mobile in its toxic, hexavalent form. The effect is minimized if Cr(III) is principally in an insoluble form. High pH (9-11) or low pH (4-5) environments could render Cr(III) reactive to H_2O_2 and initiate the generation of Cr(VI).

From the point of view of the hazard caused by Cr(VI), H_2O_2 remediation should not be used near Cr electroplating waste sites or sites containing Cr ore processing residues. Sites containing high levels of newly reduced Cr(III) or with soil conditions that support ambient soluble Cr(III) would be especially at risk. Soluble Cr(VI) should be carefully monitored in any other site containing Cr to which high levels of H_2O_2 are being continuously applied.

Appendix

Table A-1. XRD data from COPR soil.

[ssCOPR.RAW] COPR soil from melanie												Peak ID Report
SCAN: 10.0/70.0/0.02/1.2(sec), Cu(40kV,30mA), I(max)=937, 07/22/99 18:21												
PEAK: 17-pts/Parabolic Filter, Threshold=3.0, Cutoff=0.1%, BG=3/1.0, Peak-Top=Summit												
NOTE: Intensity = Counts, 2T(0)=0.0(°), Wavelength to Compute d-Spacing = 1.54056A(Cu/K-alpha1)												
#	2-Theta	d(A)	Intensity	I%	Phase ID	d(A)	I%	h	k	l	2-Theta	Delta
1	14.105	6.2738	72	7.8								
2	18.455	4.8036	73	7.9								
3	19.800	4.4802	45	4.9								
4	20.821	4.2628	231	24.9	Quartz	4.2550	16.0	1	0	0	20.859	0.039
5	21.982	4.0401	73	7.9								
6	22.975	3.8678	85	9.2	Calcite	3.8538	9.9	0	1	2	23.059	0.084
7	23.704	3.7504	39	4.2								
8	24.080	3.6927	31	3.3								
9	26.582	3.3505	927	100.0	Quartz	3.3435	100.0	1	0	1	26.639	0.057
10	27.471	3.2441	80	8.6								
11	27.807	3.2057	147	15.9								
12	28.181	3.1640	177	19.1								
13	29.399	3.0356	453	48.9	Calcite	3.0345	100.0	1	0	4	29.409	0.010
14	30.206	2.9563	91	9.8								
15	31.497	2.8381	66	7.1	Calcite	2.8422	1.9	0	0	6	31.450	-0.047
16	33.036	2.7092	62	6.7								
17	35.539	2.5239	215	23.2		2.4944	13.9	1	1	0	35.975	0.059
18	35.916	2.4983	117	12.6	Calcite	2.4569	9.0	1	1	0	36.543	-0.017
19	36.560	2.4558	230	24.8	Quartz							
20	37.874	2.3736	38	4.1								
21	39.012	2.3069	43	4.6		2.2815	8.0	1	0	2	39.464	-0.095
22	39.559	2.2762	796	85.9	Quartz	2.2361	4.0	1	1	1	40.299	0.114
23	40.185	2.2422	22	2.4	Quartz	2.1277	6.0	2	0	0	42.449	0.067
24	42.382	2.1309	111	12.0	Quartz	2.0940	14.9	2	0	2	43.166	0.026
25	43.140	2.0952	104	11.2	Calcite	1.9799	4.0	2	0	1	45.792	0.132
26	45.660	1.9853	75	8.1	Quartz	1.9269	6.4	0	2	4	47.125	0.164
27	46.960	1.9333	44	4.7	Calcite	1.9269	6.4	0	2	4	47.125	-0.281
28	47.406	1.9161	122	13.2	Calcite	1.9116	18.5	0	1	8	47.526	-0.109
29	47.634	1.9075	70	7.6	Calcite	1.8747	19.4	1	1	6	48.519	0.078
30	48.441	1.8776	139	15.0	Calcite							
31	48.924	1.8602	90	9.7								
32	49.181	1.8510	67	7.2								
33	49.405	1.8432	77	8.3		1.8180	13.0	1	1	2	50.138	0.017
34	50.121	1.8185	246	26.5	Quartz							
35	53.738	1.7044	25	2.7		1.6717	4.0	2	0	2	54.873	-0.068
36	54.941	1.6698	54	5.8	Quartz	1.6592	2.0	1	0	3	55.323	0.170
37	55.154	1.6639	32	3.5	Quartz	1.6083	1.0	2	1	0	57.234	-0.006
38	57.239	1.6081	103	11.1	Quartz	1.5415	9.0	2	1	1	59.958	0.057
39	59.901	1.5429	151	16.3	Quartz							
40	60.351	1.5324	24	2.6		1.5249	5.1	2	1	4	60.681	-0.043
41	60.724	1.5239	42	4.5	Calcite							
42	60.724	1.5239	42	4.5		1.4728	1.9	1	2	5	63.066	0.223
43	62.843	1.4775	81	8.7	Calcite							

Table A-2. XRD data from Connecticut plating waste soil.

[ssCONN(0-14).RAW] Connecticut soil, 0-14 cm												Peak ID Report
SCAN: 10.0/70.0/0.02/1.2(sec), Cu(40kV,30mA), I(max)=967, 07/22/99 19:30												
PEAK: 13-pts/Parabolic Filter, Threshold=3.0, Cutoff=0.1%, BG=3/1.0, Peak-Top=Summit												
NOTE: Intensity = Counts, 2T(0)=0.0(°), Wavelength to Compute d-Spacing = 1.54056A(Cu/K-alpha1)												
#	2-Theta	d(A)	Intensity	I%	Phase ID	d(A)	I%	h	k	l	2-Theta	Delta
1	10.453	8.4557	54	5.7								
2	12.296	7.1921	75	8.0	Chlorite Ia	7.1659	100.0	0	0	2	12.342	0.045
3	12.550	7.0475	94	10.0								
4	18.167	4.8792	43	4.6								
5	18.295	4.8452	70	7.4								
6	18.564	4.7756	28	3.0	Chlorite Ia	4.7773	74.0	0	0	3	18.558	-0.007
7	19.879	4.4627	40	4.2	Chlorite Ia	4.5130	34.9	-1	1	1	19.655	-0.224
8	20.779	4.2712	291	30.9	Quartz	4.2550	16.0	1	0	0	20.859	0.080
9	20.942	4.2383	158	16.8	Chlorite Ia	4.2407	10.7	1	-1	1	20.930	-0.012
10	23.622	3.7632	62	6.6								
11	25.556	3.4827	60	6.4	Chlorite Ia	3.5031	15.2	-1	1	3	25.405	-0.151
12	26.658	3.3411	943	100.0	Quartz	3.3435	100.0	1	0	1	26.639	-0.019
13	27.493	3.2416	58	6.2								
14	27.915	3.1935	72	7.6								
15	28.060	3.1773	102	10.8	Chlorite Ia	3.1456	4.6	1	-1	3	28.349	0.289
16	29.692	3.0063	56	5.9	Chlorite Ia	2.9832	5.0	-1	1	4	29.927	0.235
17	30.891	2.8923	50	5.3								
18	31.043	2.8785	46	4.9	Chlorite Ia	2.8664	10.7	0	0	5	31.177	0.134
19	34.893	2.5692	49	5.2	Chlorite Ia	2.5901	11.9	1	-3	1	34.603	-0.290
20	35.087	2.5555	57	6.0	Chlorite Ia	2.5572	1.9	-1	1	5	35.062	-0.024
21	35.234	2.5451	56	5.9	Chlorite Ia	2.5489	3.4	-1	3	2	35.180	-0.054
22	35.700	2.5129	32	3.4								
23	36.699	2.4468	58	6.2	Chlorite Ia	2.4476	1.6	1	-3	2	36.686	-0.013
24	38.958	2.3100	38	4.0	Chlorite Ia	2.3059	0.3	-2	2	1	39.029	0.071
25	39.478	2.2807	154	16.3	Quartz	2.2815	8.0	1	0	2	39.464	-0.014
26	39.676	2.2698	70	7.4	Chlorite Ia	2.2674	8.9	1	-3	3	39.719	0.044
27	40.241	2.2392	36	3.8								
28	40.305	2.2358	34	3.6	Quartz	2.2361	4.0	1	1	1	40.299	-0.006
29	42.460	2.1272	89	9.4	Quartz	2.1277	6.0	2	0	0	42.449	-0.011
30	45.602	1.9876	56	5.9	Chlorite Ia	1.9880	0.9	2	-2	3	45.593	-0.009
31	45.779	1.9804	79	8.4	Quartz	1.9799	4.0	2	0	1	45.792	0.013
32	48.763	1.8659	56	5.9	Chlorite Ia	1.8720	0.5	0	-2	7	48.596	-0.168
33	50.159	1.8172	248	26.3	Quartz	1.8180	13.0	1	1	2	50.138	-0.021
34	50.658	1.8005	34	3.6	Chlorite Ia	1.7993	2.3	0	-4	5	50.696	0.037
35	52.778	1.7331	150	15.9	Chlorite Ia	1.7318	2.8	-3	1	0	52.819	0.041
36	53.261	1.7185	49	5.2	Chlorite Ia	1.7250	6.6	1	3	6	53.042	-0.219
37	54.834	1.6728	80	8.5	Chlorite Ia	1.6739	27.4	-1	-3	7	54.795	-0.039
38	55.004	1.6681	69	7.3	Chlorite Ia	1.6704	15.2	0	-2	8	54.921	-0.083
39	55.004	1.6681	69	7.3								
40	59.981	1.5410	126	13.4	Quartz	1.5415	9.0	2	1	1	59.958	-0.023
41	60.356	1.5323	28	3.0								
42	65.850	1.4172	24	2.5	Quartz	1.4184	1.0	3	0	0	65.784	-0.066
43	66.493	1.4050	19	2.0	Chlorite Ia	1.4049	1.7	-1	-3	9	66.498	0.005

Table A-3. XRD data from Serpentine soil.

[ssSoldier's Delight.RAW] Soldiers Delight 53-75 cm												Peak ID Report
SCAN: 10.0/70.0/0.02/1.2(sec), Cu(40kV,30mA), I(max)=2139, 07/26/99 15:43												
PEAK: 17-pts/Parabolic Filter, Threshold=3.0, Cutoff=0.1%, BG=3/1.0, Peak-Top=Summit												
NOTE: Intensity = Counts, 2T(0)=0.0(°), Wavelength to Compute d-Spacing = 1.54056A(Cu/K-alpha1)												
#	2-Theta	d(A)	Intensity	I%	Phase ID	d(A)	I%	h	k	l	2-Theta	Delta
1	12.181	7.2598	2129	100.0	Antigorite 6M	7.3000	100.0	0	0	1	12.114	-0.067
2	12.498	7.0767	482	22.6	Antigorite 6M	6.9500	6.0	-2	0	1	12.727	0.229
3	17.804	4.9777	100	4.7								
4	19.713	4.4999	34	1.6								
5	19.899	4.4582	42	2.0								
6	19.998	4.4363	54	2.5								
7	20.859	4.2550	452	21.2	Quartz	4.2557	21.0	1	0	0	20.856	-0.003
8	21.341	4.1600	111	5.2								
9	21.478	4.1339	83	3.9								
10	21.772	4.0787	43	2.0								
11	22.015	4.0341	57	2.7	Antigorite 6M	4.0100	2.0	9	0	1	22.150	0.134
12	24.698	3.6017	1129	53.0	Antigorite 6M	3.6300	75.0	0	0	2	24.502	-0.196
13	25.254	3.5237	80	3.8	Antigorite 6M	3.5100	6.0	-11	0	1	25.354	0.100
14	26.700	3.3360	2035	95.6	Quartz	3.3439	100.0	1	0	1	26.636	-0.064
15	27.583	3.2312	96	4.5								
16	27.729	3.2145	101	4.7								
17	27.979	3.1863	179	8.4								
18	28.607	3.1178	25	1.2								
19	29.604	3.0150	42	2.0								
20	29.813	2.9944	63	3.0								
21	31.337	2.8521	43	2.0								
22	33.119	2.7026	39	1.8								
23	33.409	2.6799	37	1.7								
24	34.707	2.5825	60	2.8	Antigorite 6M	2.5900	1.0	-7	3	1	34.604	-0.104
25	34.981	2.5629	67	3.1	Antigorite 6M	2.5700	2.0	7	3	1	34.882	-0.100
26	35.521	2.5252	147	6.9	Antigorite 6M	2.5200	18.0	13	2	1	35.597	0.075
27	36.542	2.4569	165	7.8	Quartz	2.4570	6.7	1	1	0	36.541	-0.001
28	36.931	2.4319	73	3.4								
29	37.243	2.4123	134	6.3	Antigorite 6M	2.4200	10.0	0	0	3	37.120	-0.123
30	37.792	2.3785	36	1.7	Antigorite 6M	2.3900	3.0	-14	0	2	37.603	-0.189
31	37.815	2.3771	47	2.2								
32	39.519	2.2785	134	6.3	Quartz	2.2817	6.6	0	1	2	39.461	-0.058
33	40.398	2.2309	105	4.9	Quartz	2.2368	2.9	1	1	1	40.286	-0.112
34	41.600	2.1691	41	1.9	Antigorite 6M	2.1670	5.0	7	4	0	41.643	0.043
35	41.980	2.1504	46	2.2	Antigorite 6M	2.1500	5.0	16	0	2	41.988	0.008
36	42.575	2.1217	169	7.9	Antigorite 6M	2.1260	1.0	-9	1	3	42.485	-0.091
37	45.520	1.9911	50	2.3								
38	45.801	1.9795	101	4.7	Quartz	1.9800	2.7	0	2	1	45.789	-0.012
39	50.200	1.8158	221	10.4	Antigorite 6M	1.8150	6.0	-1	0	4	50.225	0.025
40	51.296	1.7796	29	1.4	Antigorite 6M	1.7810	4.0	-1	1	4	51.252	-0.043
41	53.027	1.7255	58	2.7								
42	53.301	1.7173	39	1.8								
43	53.562	1.7095	33	1.6								

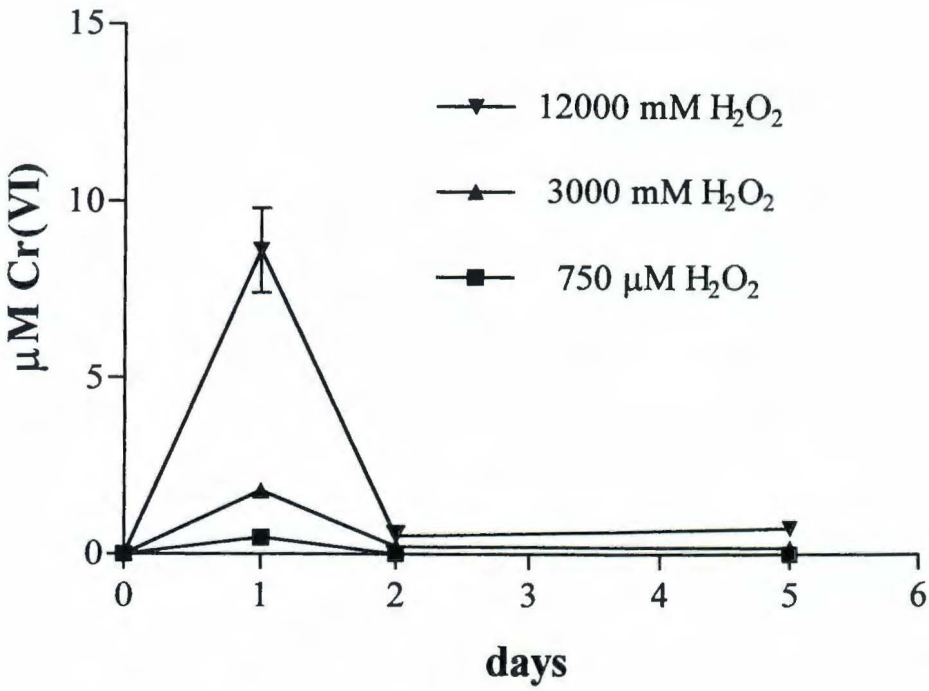


Figure A-1. Oxidation of Cr(III) in Connecticut plating waste soil (14-40 cm) after single applications of different concentrations of H_2O_2. Soil amended with 100 µM Cr(III) prepared with 2:1 OH^-/Cr ratio.

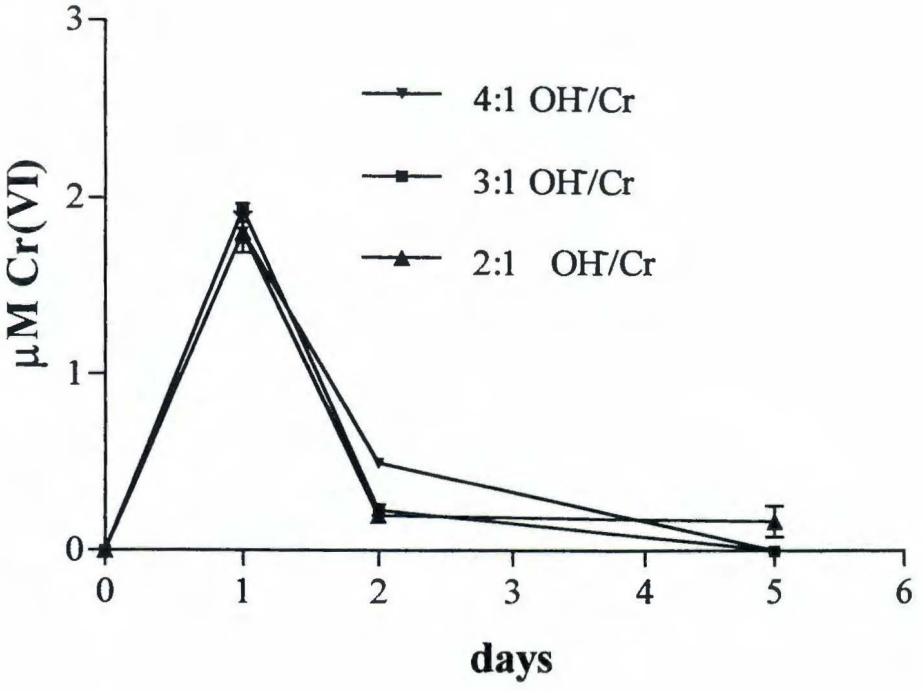


Figure A-2. Oxidation of Cr(III) in Connecticut plating waste soil (14-40 cm) after a single application of 3.00 mM H_2O_2. Soil amended with 100 µM Cr(III) prepared with different OH^-/Cr ratios.

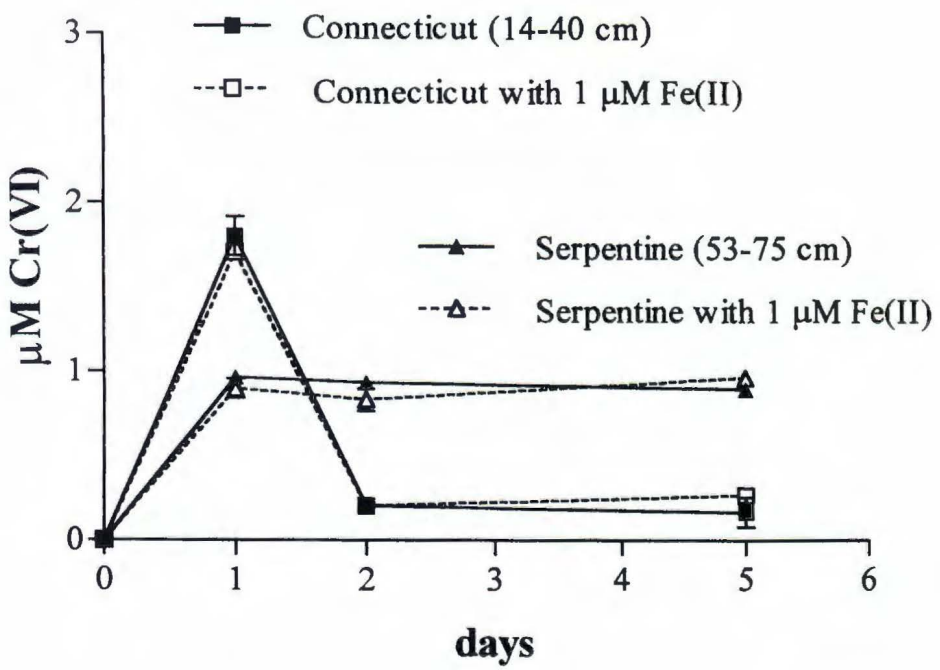


Figure A-3. Oxidation of Cr(III) in two soils after a single application of 3.00 mM H_2O_2. Soils amended with 100 μM Cr(III) prepared with 2:1 OH^-/Cr ratio. Applications of H_2O_2 were made with and without 1.0 μM $FeSO_4$.

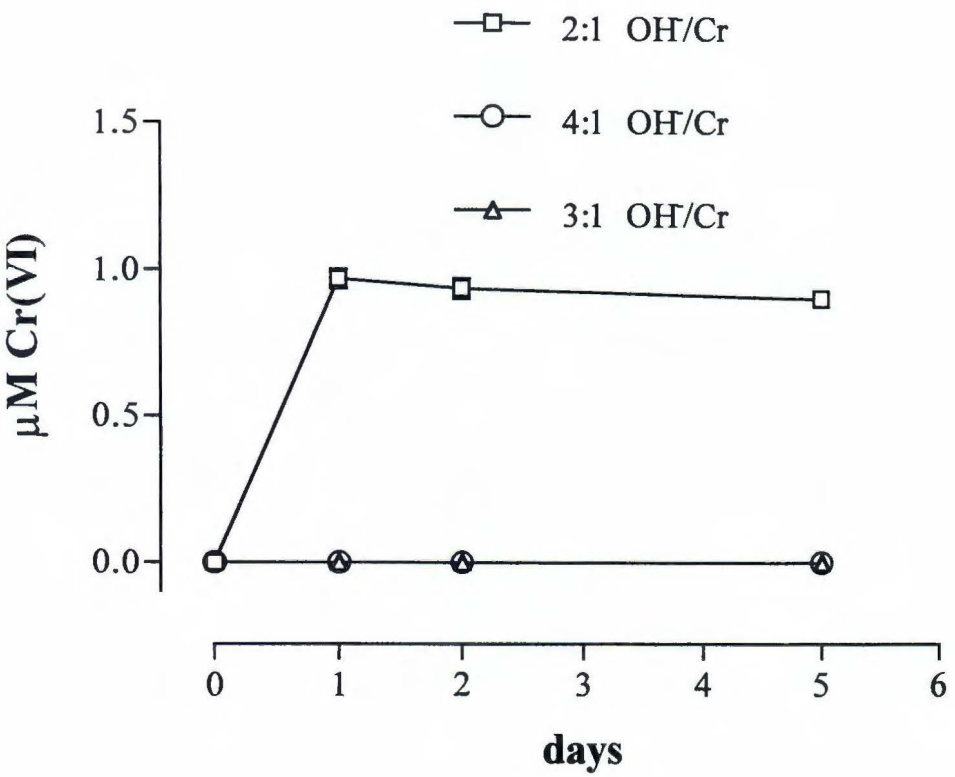


Figure A-4. Oxidation of Cr(III) in Serpentine soil (53-75 cm) after a single application of 3.00 mM H_2O_2. Soil amended with 100 µM Cr(III) prepared with different OH^-/Cr ratios.

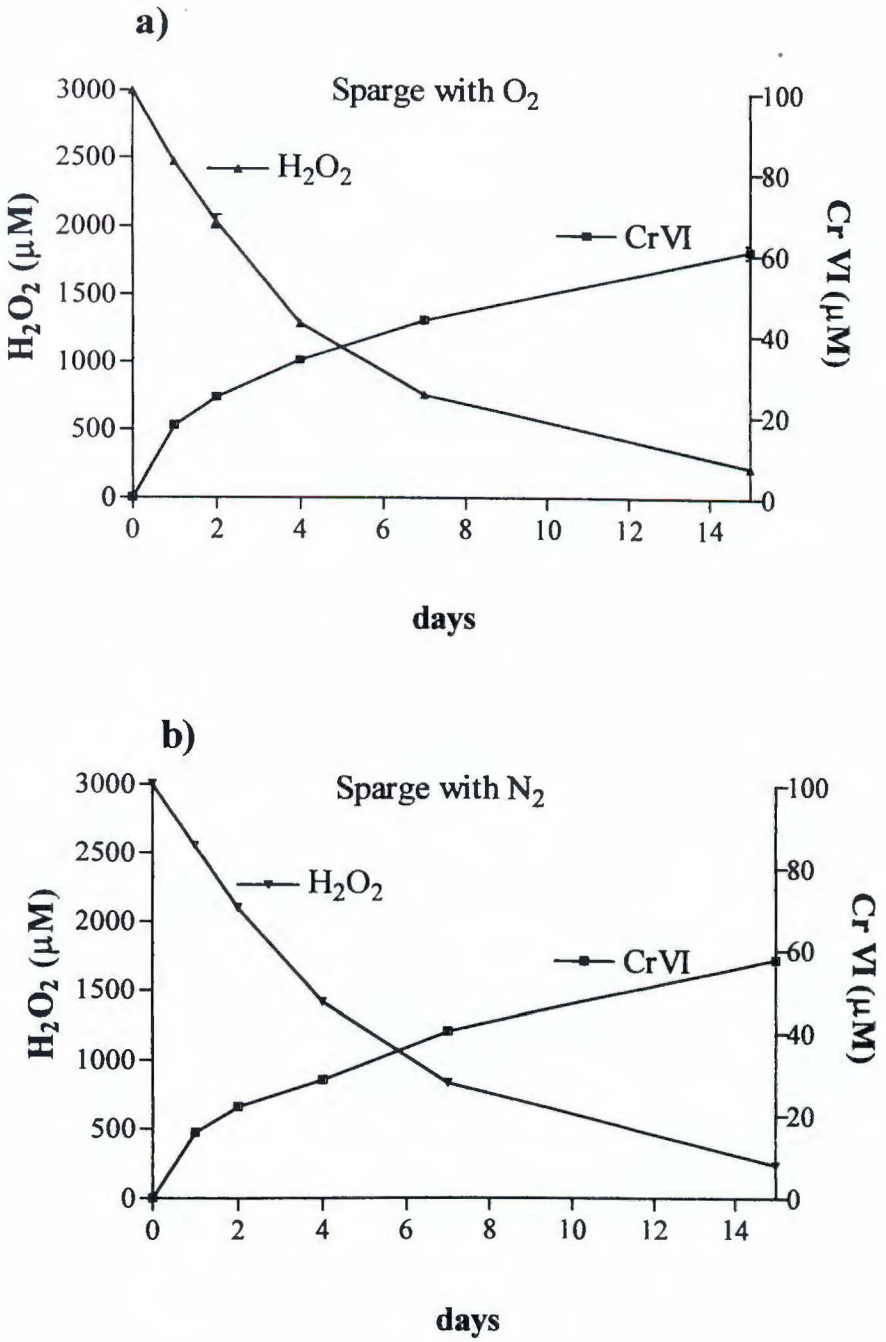


Figure A-5. Interaction of 100 μM Cr(III) (prepared with 2:1 OH^-/Cr ratio) and 3.00 mM H_2O_2 after a) sparging 30 min with O_2 and b) sparging 30 min with N_2.

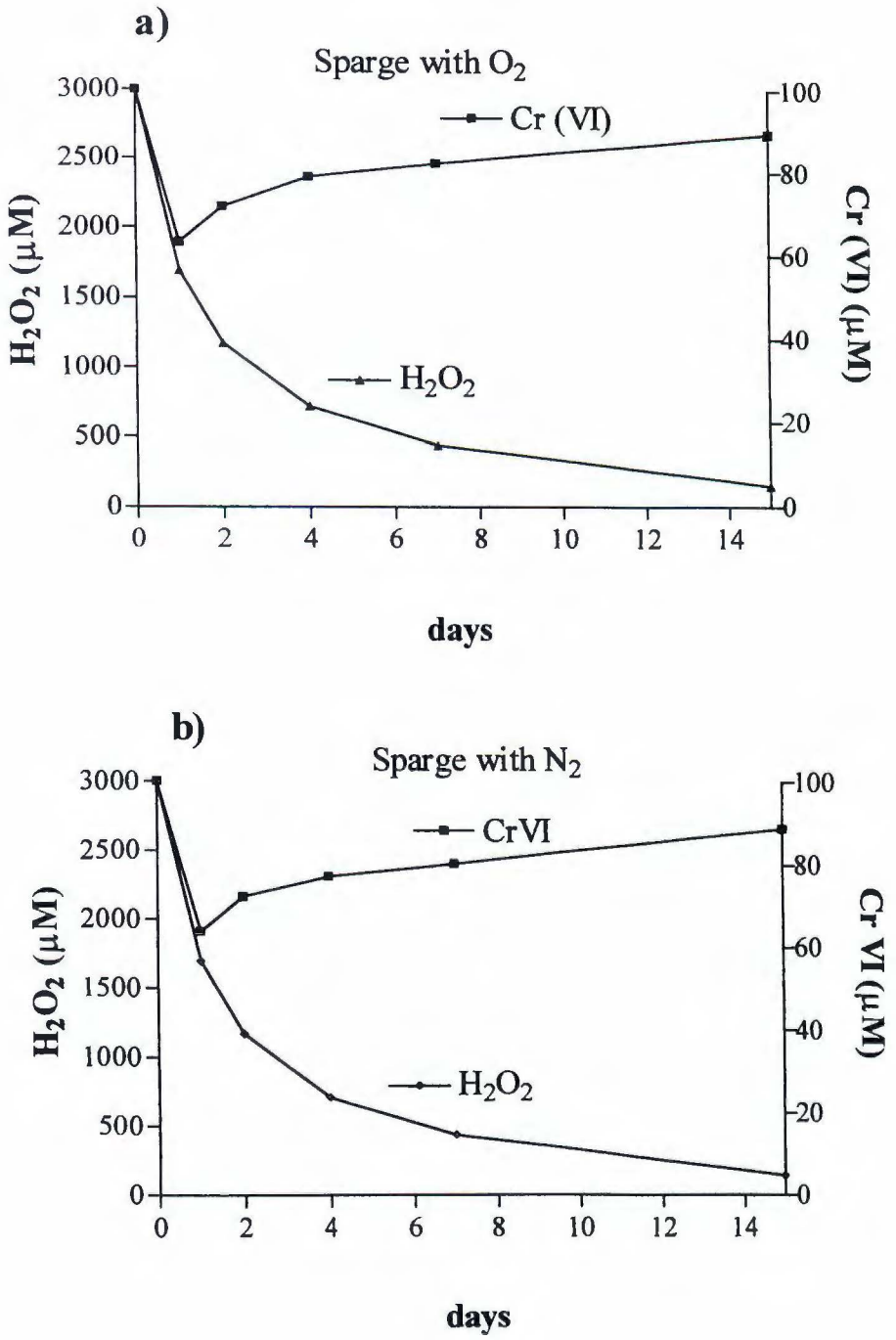


Figure A-6. Interaction of 100 μM Cr(VI) and 3.00 mM H_2O_2 at pH 4.0 after a) sparging 30 with O_2 and b) sparging 30 min with N_2.

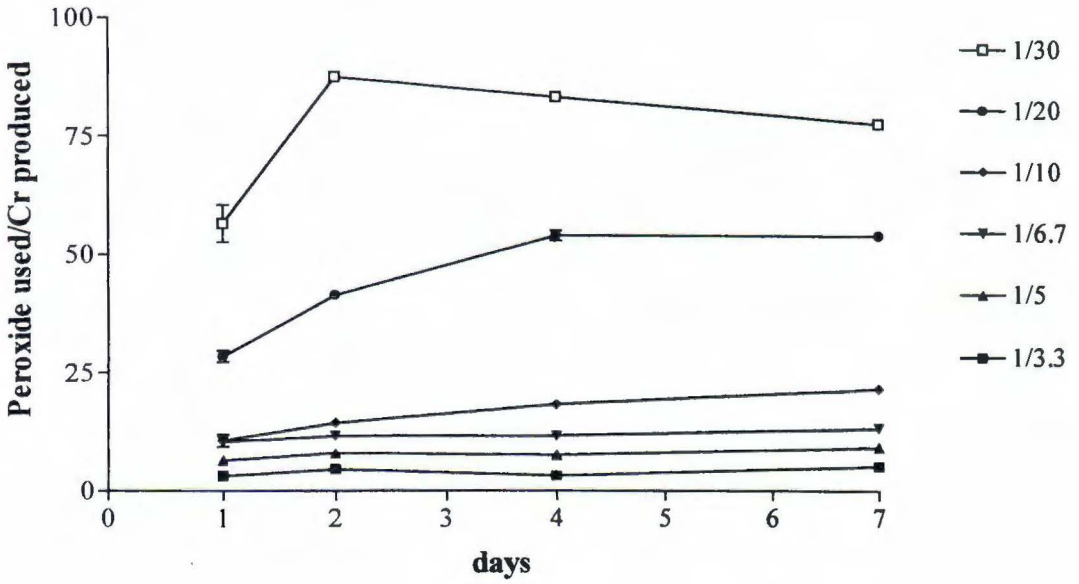


Figure A-7. Ratio of H_2O_2 used to Cr(VI) produced from 100 μM Cr(III) (prepared with 2:1 OH^-/Cr ratio) for different initial concentrations of H_2O_2. Different initial H_2O_2 concentrations given as Cr(III)/H_2O_2 ratios.

REFERENCES

Aiyar, J., Berkovits, H.J., Floyd, R.A. and Wetterhahn, K.E. (1991) Reaction of chromium (VI) with glutathione or with hydrogen peroxide: Identification of reactive intermediates and their role in chromium(VI)-induced DNA damage. Environ. Health Perspect. 92: 53-62.

Ball, J.W. and Nordstrom, D.K. (1998) Critical evaluation and selection of standard state thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides and hydroxides. J. Chem. Eng. Data 43: 895-918.

Baloga, M.R. and Earley, J.E. (1961) The kinetics of the oxidation of Cr(III) to Cr(VI) by hydrogen peroxide. J. Am. Chem. Soc. 83: 4906-4909.

Baron, D. and Palmer, C.D. (1996) Solubility of $KFe_3(CrO_4)_2(OH)_6$ at 4 to35° C. Geochim. Cosmochim. Acta 60, 3815-3824.

Baron, D., Palmer, C.D. and Stanley, J.T. (1996) Identification of two iron-chromate precipitates in a Cr(VI)-contaminated soil. Environ. Sci. Technol. 30, 964-968.

Bartlett, R.J. (1991) Chromium cycling in soils and water: Links, gaps, and methods. Environ. Health Perspect. 92: 17-24.

Bartlett, R.J. and James, B.R. (1979) Behavior of chromium in soils: III. Oxidation. J. Environ. Qual. 8: 31-35.

Bartlett, R.J. and James, B.R. (1980) Studying air-dried, stored soil samples - some pitfalls. Soil Sci. Soc. Am. J. 44: 721-724.

Baxendale, J.H. (1952) Decomposition of hydrogen peroxide by catalysts in homogenous aqueous solution. Adv. Catal. IV: 31-87.

Baxendale, J.H. (1955) Oxidation of Benzene by Hydrogen Peroxide, University of Notre Dame Press, Notre Dame, IN, p34.

Beck, M.T., Nagy, I.P. and Székely, G. (1991) Oscillatory kinetics and mechanism of the chromate catalyzed decomposition of hydrogen peroxide. Int. J. Chem. Kinet. 23: 881-896.

Bielski, B.H.J., Cabelli, D.E. and Arudi, R.L. (1985) Reactivity of $HO_2^{\bullet}/O_2^{\bullet-}$ radicals in aqueous solution. J. Phys. Chem. Ref. Data 14: 1041-1100.

Bowman, R.A. (1988) A rapid method to determine total phosphorus in soils. Soil Sci. Soc. Am. J. 52: 1301-1304.

Brown, S.B., Jones, P. and Suggett, A. (1970) Recent developments in the redox chemistry of peroxides. In: Progress in Inorganic Chemistry Vol. 13, pp. 159-203.

Buerge, I.J. and Hug, S.J. (1998) Influence of organic ligands on chromium (VI) reduction by iron (II). Environ. Sci. Technol. 32: 2092-2099.

Burke, T., Fagliano, J., Goldoft, M., Hazen, R.E., Iglewicz, R. and McKee, T. (1991) Chromite ore processing residue in Hudson County, New Jersey. Environ. Health Perspect. 92: 131-137.

Buxton, G.V. and Djouder, F. (1996) Disproportionation of Cr V generated by the radiation-induced reduction of Cr VI in aqueous solution containing formate: A pulse radiolysis study. J. Chem. Soc., Faraday Trans. 92: 4173-4176.

Buxton, G.V., Djouder, F., Lynch, D.A. and Malone, T.N. (1997) Oxidation of Cr III to Cr VI initiated by $OH\cdot$ and $SO_4^{\cdot-}$ in acidic aqueous solution. J. Chem. Soc., Faraday Trans. 93: 4265-4268.

Calder, L.M. (1988) Chromium contamination of groundwater. In: Chromium in the Natural and Human Environments (Nriagu, J.O. and Niebor, E., Eds.), pp. 215-229, John Wiley, New York.

Carberry, J.B. (1994) Enhancement of bioremediation by partial preoxidation. In Remediation of Waste Contaminated Soils (Wise, D. and Trantolo, D., Eds.), pp. 543-596.

Chernikov, S. (1998) Chromate Reduction in Soils and Simple Systems by Humic Substances and a Variety of Organic Materials, Ph.D. Dissertation, University of Maryland, Dept of Natural Resource Science, College Park.

Chiu, A., Chiu, N., Shi, X.L., Beaubier, J. and Dalal, N.S. (1998) Activation of a procarcinogen by reduction: Cr6+-> Cr5+-> Cr4+-> Cr3+ a case study by electron spin resonance (ESR/PMR). Environmental Carcinogenesis & Ecotoxicology Reviews-Part C of Journal of Environmental Science and Health 16, 135-148.

Cohen, M.D., Kargacin, B., Klein, C.B. and Costa, M. (1993) Mechanism of chromium carcinogenicity and toxicity. Crit. Rev. Toxicol. 23: 255-281.

Cooper, W.J. and Zika, R.G. (1983) Photochemical formation of hydrogen peroxide in surface and ground waters exposed to sunlight. Science 220: 711-712.

Cotton, F.A. and Wilkinson, G. (1988) Advanced Inorganic Chemistry, 5th Edition, John Wiley & Sons, New York.

Cranston, R.E. and Murray, S.W. (1978) The determination of chromium species in natural waters. Anal. Chim. Acta 99: 275-282.

Cremer, D. (1983) General and theoretical aspects of the peroxide group. In The Chemistry of Peroxides (Patai, S., Ed.), pp. 1-84, John Wiley & Sons, New York.

Davis, A., Kempton, J.H. and Nicholson, A. (1994) Groundwater transport of arsenic and chromium at a historical tannery, Woburn, Massachusetts, U.S.A. Applied Geochem. 9: 569-582.

Davis, A. and Olsen, R.L. (1995) The geochemistry of chromium migration and remediation in the subsurface. Ground Water 33: 759-768.

DeFlora, S., Bagnasco, M., Serra, D. and Zanacchi, P. (1990) Genotoxicity of chromium compounds: A review. Mutation Res. 238: 99-172.

Deng B. and Stone, A.T. (1996) Surface catalyzed chromium(VI) reduction: Reactivity comparisons of different organic reactants and different oxide surfaces. Environ. Sci. Technol. 60: 99-106.

Dickman, M.H. and Pope, M.T. (1994) Peroxo and superoxo complexes of chromium, molybdenum, and tungsten. Chem. Rev. 94: 569-584.

Dorfman, L.M. and Adams, G.E. (1973) Reactivity of the hydroxyl radical. National Bureau of Standards Rep. NSRDS-NBS-46 NBS, Washington, D.C.

Duke, F.R. and Haas, T.W. (1961) The homogeneous base-catalyzed decomposition of hydrogen peroxide. J. Phys. Chem. 65: 304-306.

Eary, L.E. and Rai, D. (1987) Kinetics of chromium (III) oxidation to chromium (VI) by reaction with manganese dioxide. Environ. Sci. Technol. 21: 1187-1193.

Eary, L.E. and Rai, D. (1988) Chromate removal from aqueous wastes by reduction with ferrous iron. Environ. Sci. Technol. 22: 972-977.

El-Wakil, E.M. (1986) Studies on Some Chemical Properties of Some Egyptian Soils: Decomposition of Hydrogen Peroxide by Torrifluvents, Ph.D. dissertation, University of Tanta, Egypt.

Elovitz, M.S. and Fish, W. (1995) Redox interactions of Cr(VI) and substitutes phenols: products and mechanism. Environ. Sci. Technol. 29: 1933-1943.

Elprince, A.M. and Mohamed, W.H. (1992) Catalytic decomposition kinetics of aqueous hydrogen peroxide and solid magnesium peroxide by birnessite. Soil Sci. Soc. Am. J. 56: 1784-1788.

Evans, D.F. and Upton, M.J. (1985) Studies on singlet oxygen in aqueous solution, Part 4. The 'spontaneous' and catalyzed decomposition of hydrogen peroxide. J. Chem. Soc. Dalton Trans. 2525-2529.

Fendorf, S.E. and Zasoski, R.J. (1991) Chromium oxidation by d-MnO_2 - Characterization. Environ. Sci. Technol. 26: 79-85.

Fendorf, S.E., Zasoski, R.J. and Burau, R.G. (1993) Competing metal ion influences on chromium (III) oxidation by birnessite. Soil Sci. Soc. Am. J. 57: 1508-1515.

Fendorf, S., Eick, M.J., Grossi, P. and Sparks, D.L. (1997) Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. Environ. Sci. Technol. 31: 315-320.

Fenton, H.J.H. (1894) Oxidation of tartaric acid in the presence of iron. J. Chem. Soc. 65: 899-910.

Frew, J.E., Jones, P. and Scholes, G. (1983) Spectrophotometric determination of hydrogen peroxide and organic hydroperoxides at low concentrations in aqueous solutions. Anal. Chim. Acta 155: 139-150.

Funahashi, S., Uchida, F. and Tanaka, M. (1978) Reactions of hydrogen peroxide with metal complexes. 3. Thermodynamic and kinetic studies on the formation, dissociation, and decomposition of peroxochromium (VI) complexes in acid media. Inorg. Chem. 17: 2784-2789.

Gancy, A.B. and Wamser, G.A. (1976) Suppression of water pollution caused by solid wastes containing chromium compounds. U.S. Patent No. 3,981,965 .

Greenwood, N.N. and Earnshaw, A. (1994) Chemistry of the Elements, Pergamon Press, New York.

Haber, F. and Weiss, J. (1934) The catalytic decomposition of hydrogen peroxide by iron salts. Proc. R. Soc. London A147: 332-351.

Herbert, D. and Pinsent, J. (1948) Crystalline bacterial catalase. Biochem. J. 43: 193-202.

Ho, C.L., Shebl, M.A. and Watts, R.J. (1995) Development of an injection system for in situ catalyzed peroxide remediation of contaminated soil. Haz. Waste & Haz. Materials 12: 15-25.

Holm, T.R., George, G.K. and Barcelona, M.J. (1987) Fluorometric determination of hydrogen peroxide in groundwater. Anal. Chem. 59: 582-586.

House, D.A. (1997) Advances in Inorganic Chemistry, Vol. 44 Vol. 44, pp. 341-373.

Inada, Y. and Funahashi, S. (1997) Laboratory stopped-flow XAFS apparatus. Structure determination of the short-lived peroxochromium intermediate formed during reduction process of chromate(VI) ion by hydrogen peroxide. Zeitschrift Fur Naturforschung Section B-a Journal of Chemical Sciences 52, 711-718.

Itoh, M., Nakamura, M., Suzuki, T., Kawai, K., Horitsu, H. and Takamizawa, K. (1996) Mechanism of chromium (VI) toxicity in Escherichia coli: Is hydrogen peroxide essential in Cr(VI) toxicity? J. Biochem. (Tokyo) 117: 780-786.

JADE: software for XRD spectra identification. (1999) Materials Data, Inc., Livermore CA.

James, B.R. (1994) Hexavalent chromium solubility and reduction in alkaline soils enriched with chromite ore processing residue. J. Environ. Qual. 23: 227-233.

James, B.R. (1996a) The challenge of remediating chromium contaminated soil. Environ. Sci. Technol. 30: 248A-251A.

James, B.R. (1996b) Chromium Oxidation and Reduction Chemistry in Soils: Relevance to Chromate Contamination of Groundwater of the Northeastern United States, Research proposal submitted to the Maryland Water Resources Research Center.

James, B.R. and Bartlett, R.J. (1983a) Behavior of chromium in soils. V. Fate of organically complexed Cr(III) added to soil. J. Environ. Qual. 12: 169-172.

James, B.R. and Bartlett, R.J. (1983b) Behavior of chromium in soils. VII. Adsorption and reduction of hexavalent forms. J. Environ. Qual. 12: 177-181.

James. B.R., Petura, J.C., Vitale, R.J. and Mussoline, G.R. (1995) Hexavalent chromium extraction from soils: a comparison of five methods. Environ. Sci. Technol. 29: 2377-2381.

James. B.R., Petura, J.C., Vitale, R.J. and Mussoline, G.R. (1997) Oxidation-reduction chemistry of chromium: Relevance to the regulation and remediation of chromate-contaminated soils. J. Soil Contamination 6(6): 569-580.

Jennette, K. (1979) Chromate metabolism in liver microsomes. Biol. Trace Elem. Res. 1: 55-62.

Johnson, C.A. and Xyla, A.G. (1991) The oxidation of chromium (III) to chromium (VI) on the surface of manganite (g - MnOOH). Geochim. Cosmochim. Acta 55: 2861-2866.

Katz, S.A. and Salem, H. (1994) The Biological and Environmental Chemistry of Chromium, VCH Publishers, New York.

Kawanishi, S., Inoue, S. and Sano, S. (1986) Mechanism of DNA cleavage induced by sodium chromate(VI) in the presence of hydrogen peroxide. J. Biol. Chem. 261: 5952-5958.

Kieber, R.J. and Helz, G.R. (1992) Indirect photoreduction of aqueous chromium (VI). Environ. Sci. Technol. 26: 307-313.

Kläning, U.K. (1958) Photoinduced oxidations of alcohols by acid chromate. Acta Chem. Scan. 12: 576-577.

Kläning, U.K. (1977) Photoinduced oxidation of propan-2-ol by acid chromate. J. Chem. Soc., Faraday Trans. 73: 434-455.

Kontchou, C.Y. and Blondeau, R. (1990) Isolation and characterization of hydrogen peroxide producing *Aerococcus* sp. from soil samples. FEMS Microbiol. Lett. 68: 323-328.

Kortenkamp, A., Oetken, G. and Beyersmann, D. (1990) The DNA cleavage induced by chromium (V) complex and by chromate and glutathione is mediated by activated oxygen species. Mutat. Res. 232: 155-161.

Manceau, A. and Charlet, L. (1992) X-ray absorption spectroscopic study of the sorption of Cr (III) at the oxide-water interface - Molecular mechanism of Cr (III) oxidation on Mn oxides. J. Colloid Interface Sci. 148: 425-442.

Mattuck, R. (1994) The Role of Wetlands in the Immobilization of Chromium Contamination, Master's Thesis, University of Connecticut-Storrs (Tech. Rep. ERI-94.05).

Melhorn, R.J., Buchanan, B.B. and Leighton, T. (1994) Bacterial chromate reduction and product characterization. In: Emerging Technology for Bioremediation of Metals (Mean, J.L. and Hinchee, R.E., Eds.), Lewis Publishers, Boca Raton, Florida.

Nakayasu, K., Fukushima, M., Sasaki, K., Tanaka, S. and Nakamura, H. (1999) Comparative studies of the reduction behavior of chromium(VI) by humic substances and their precursors. Environ. Toxicol. Chem. 18: 1085-1090.

National Research Council (1990) Recommended Dietary Allowances, 10th Ed.,Committee on Dietary Allowances, Food and Nutrition Board, National Academy of Sciences, Washington, D.C.

Nikolaidis, N.P., Robbins, G.A., Scherer, M., McAninch, B., Binkhorst, G., Asikainen, J. and Suib, S.L. (1994) Verical distribution and partitioning of chromium in a glaciofluvial aquifer. Ground Wat. Monit. Remed.

Nriagu, J. and Niebor, E. (1988) Chromium in the Natural and Human Environments, J. Wiley, Series in Advances in Environmental Science and Technology, V 20, NY.

Palmer, C.D. and Wittbrodt, P.R. (1991) Processes affecting the remediation of chromium contaminated sites. Environ. Health Perspect. 92: 25-40.

Palmer, C. and Puls, R. (1994) Natural attenuation of hexavalent chromium in groundwater and soils. USEPA, Office of Research and Development, Office of Solid Waste and Emergency Response. EPA/540/S-94/505.

Pardieck, D.L., Bouwer, E.J. and Stone, A. (1992) Hydrogen peroxide use to increase oxidant capacity for in situ bioremediation of contaminated soils and aquifers: A review. Journal of Contaminant Hydrology 9: 221-242.

Perez-Benito, J.F. and Arias, C. (1997) A kinetic study of the chromium(VI) hydrogen peroxide reaction. Role of the diperoxochromate(VI) intermediates. Journal of Physical Chemistry A.. 101, 4726-4733.

Pettine, M., La Noce, T., Liberatori, A. and Loreti, L. (1988) Hydrogen peroxide interference in the determination of chromium(VI) by the diphenylcarbazide method. Anal. Chim. Acta 209: 315-319.

Pettine, M. and Millero, F.J. (1990) Chromium speciation in seawater: the probable role of hydrogen peroxide. Limnol. Oceanogr. 35: 730-736.

Pettine, M., Millero F.J. and La Noce, T. (1991) Chromium (III) interactions in seawater through its oxidation kinetics. Mar. Chem. 34: 29-46.

Pignatello, J.J. and Baehr, K. (1994) Ferric complexes as catalysts for "Fenton" degradation of 2,4-D and metolachlor in soil. J. Environ. Qual. 23: 365-370.

Powell, R.M., Puls, R.W., Hightower, S.K. and Sabatini, D.A. (1995) Coupled iron corrosion and chromate reduction: mechanisms for subsurface remediation. Environ. Sci. Technol. 29: 1913-1922.

Price, D., Worsfold, P.J. and Mantoura, R.F.C. (1992) Hydrogen peroxide in the marine environment: Cycling and methods of analysis. Trends Anal. Chem. 11: 379-383.

Rabenhorst, J.E., Foss, J.E. and Fanning, D.S. (1982) Genesis of Maryland soils formed from serpentinite. Soil Sci. Soc. Am. J. 46: 607-616.

Rai, D., Sass, B. and Moore, D.A. (1987) Chromium (III) hydrolysis constants and solubility of chromium (III) hydroxide. Inorg. Chem. 26: 345-349.

Ravikumar, J.X. and Gurol, M. (1994) Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand. Environ. Sci. Technol. 28: 394-400.

Rotzinger, F.P., Stünzi, H. and Marty, W. (1986) Early stages of the hydrolysis of chromium(III) in aqueous solution. 3. Kinetics of dimerization of the deprotonated aqua ion. Inorg. Chem. 25: 489-495.

Sass, B.M. and Rai, D. (1987) Solubility of amorphous chromium(III)-iron(III) hydroxide solid solutions. Inorg. Chem. 26: 2228-2232.

Schumb, W.C., Satterfield, C.N. and Wentworth, R.L. Hydrogen Peroxide, Reinhold, New York p 759.

Seaman, J.C., Bertsch, P.M. and Schwallie, L. (1999) In situ Cr(VI) reduction within coarse-textured, oxide-coated soil and aquifer systems using Fe(II) solutions. Environ. Sci. Technol. 33, 938-944.

Seinfeld, J.H. (1986) Atmospheric Chemistry and Physics of Air Pollution, Wiley-Interscience, NY p 739.

Shi, X.L., Chiu, A., Chen, C.T., Halliwell, B., Castranova, V. and Vallyathan, V. (1999) Reduction of chromium(VI) and its relationship to carcinogenesis. Journal of Toxicology and Environmental Health-Part B-Critical Reviews 2, 87-104.

Shi, X.L. and Dalal, N.S. (1989) Chromium (V) and hydroxyl radical formation during the glutathione reductase-catalyzed reduction of chromium (VI). Biochem. Biophys. Res. Commun. 163: 627-634.

Shi, X.L. and Dalal, N.S. (1990) Evidence for a Fenton-type mechanism for the generation of OH• radicals in the reduction of Cr(VI) in cellular media. Arch. Biochem. Biophys. 281: 90-95.

Shi, X.L. and Dalal, N.S. (1993) Generation of free radicals from hydrogen peroxide and lipid hydroperoxides in the presence of Cr(III). Arch. Biochem. Biophys. 302: 294-299.

Shi, X.L., Leonard, S.S., Liu, K.J., Zang, L.Y., Gannett, P.M., Rojanasakul, Y., Castranova, V. and Vallyathan, V. (1998) Cr(III)-mediated hydroxyl radical generation via Haber-Weiss cycle. J. Inorg. Biochem. 69, 263-268.

Silvester, E., Charlet, L. and Manceau, A. (1995) Mechanism of chromium (III) oxidation by Na-buserite. J. Phys. Chem. 99: 16662-16669.

Skoog, D.A., West, D.M. and Holler, F.J. (1994) Analytical Chemistry, 6th Ed., Pp. 305-327, Saunders College Pub., Philadelphia.

Soil Survey of Windham County, C. (1981) USDA, Soil Conservation Service, U.S. Govt. Print. Off.

Spain, J.C., Milligan, J.D., Downey, D.C. and Slaughter, J.K. (1989) Excessive bacterial decomposition of H_2O_2 during enhanced biodegradation. Ground Water 27: 163-167.

Spiccia, L. (1988) Solubility of chromium(III) hydroxides. Inorg. Chem. 27: 432-434.

Spiccia, L. and Marty, W. (1986) The fate of "active" chromium hydroxide, $Cr(OH)_3 \times 3H_2O$, in aqueous suspension. Study of the chemical changes involved in its aging. Inorg. Chem. 25: 266-271.

Spiccia, L., Marty, W. and Giovanoli, R. (1988) Hydrolytic trimer of chromium(III). Synthesis through chromite cleavage and use in the preparation of the "active" trimer hydroxide. Inorg. Chem. 27: 2660-2666.

Spiccia, L., Stoeckli-Evans, H., Marty, W. and Giovanoli, R. (1987) A new "active" chromium(III) hydroxide: $Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4\text{-}2H_2O$. Inorg. Chem. 26: 474-482.

Spitalsky, E. (1907) Catalysis by means of chromic acid and its salts I. Z. Anorg. Allg. Chem. 53: 184.

Spitalsky, E. (1908) Catalysis by means of chromic acid and its salts II. Z. Anorg. Allg. Chem. 56: 72.

Stearns, D.M. and Wetterhahn, K.E. (1994) Reaction of chromium (VI) with ascorbate produces chromium (V), chromium (IV) and carbon based radicals. Chem. Res. Toxicol. 7: 219-230.

Stearns, D.M. and Wetterhahn, K.E. (1997) Intermediates produced in the reaction of chromium (VI) with dehydroascorbate cause single-strand breaks in plasmid DNA. Chem. Res. Toxicol. 10: 271-278.

Stunzi, H. and Marty, W. (1983) Early stages of the hydrolysis of chromium (III) in aqueous solution 1. Characterization of a tetrameric species. Inorg. Chem. 22: 2145-2150.

Suthersan, S.S. (1997) Remediation Engineering Design Concepts, CRC Lewis Publishers, New York pp. 215-236.

Tyre, B.W., Watts, R.J. and Miller, G.C. (1991) Treatment of four biorefractory contaminants in soils using catalyzed hydrogen peroxide. J. Environ. Qual. 20: 832-838.

Tyrpin, L.R. (1998) Using a Thermodynamically Based Approach to Assess the Redox Status and Predict the Valence State of Chromium in Simple, Aqueous Systems and Chromium Enriched Soils, Master's Thesis, University of Maryland, College Park, MD.

U.S. EPA (1981) Interim report on the groundwater quality of east and north Woburn, Massachusetts. USEPA Contract No. 68-01-6056, TDD F1-8010-04B, Washington, D.C.

U.S. EPA (1998) In situ remediation technology: in situ chemical oxidation. USEPA, Office of Research and Development, Office of Solid Waste and Emergency Response, Technology Innovation Office. EPA/542/S-98/008.

Vitale, R.J., Mussoline, G.R., Rinehimer, K.A., Petura, J.C. and James, B.R. (1997) Extraction of sparingly soluble chromate from soils: Evaluation of methods and E(h)-pH effects. Environ. Sci. Technol. 31, 390-394.

von Meyenburg, U., Široký, O. and Schwarzenbach, G. (1973) Die deprontonierung von metallaquoionen II: Aquochrom(III)-ion. Zur struktur activer chromhydroxide. Helv. Chim. Acta 56: 1099.

Wagner, D.P., Fanning, D.S., Foss, J.E., Patterson, M.S. and Snow, P.A. (1982) In Acid Sulfate Weathering (Kittrick, J.A., Ed.), pp. 109-125, Special Publication No. 10; Soil Science Society of America , Madison, WI.

Wardman, P. and Candeias, L.P. (1996) Fenton chemistry, an introduction. Radiat. Res. 145: 523-531.

Watts, R.J., Udell, M.D., Kong, S.H. and Leung, S.W. (1999) Fenton-like soil remediation catalyzed by naturally occurring iron minerals. Environmental Engineering Science 16, 93-103.

Watts, R.J., Udell, M.D. and Monsen, R.M. (1993) Use of iron minerals in optimizing the peroxide treatment of contaminated soils. Water Environ. Res. 65: 839-844.

Watts, R.J., Udell, M.D., Rauch, P.A. and Leung, S. (1990) Treatment of pentachlorophenol-contaminated soils using Fenton's reagent. Haz. Waste & Haz. Materials 7: 335-345.

Weng, C.H., Huang, C.P., Allen, H.E., Cheng, A.H.D. and Sanders, P.F. (1994) Chromium leaching behavior in soil derived from chromite ore processing waste. Sci. Total Environ. 154, 71-86.

Witt, S.N. and Hayes, D.H. (1982) Kinetics and mechanism of the formation of violet peroxychromate in aqueous solution. Inorg. Chem. 21: 4014-4016.

Wittbrodt, P.R. and Palmer, C.D. (1996) Reduction of Cr(VI) by soil humic acids. Eur. J. Soil Sci. 47: 151-162.

Woods, T.L. and Garrels, R.M. (1987) Thermodynamic Values at Low Temperature for Natural Inorganic Materials: An Uncritical Summary, Oxford University Press, Oxford.

Xu, F.G., Krouse, R. and Swaddle, T.W. (1985) Conjugate base pathway for water exchange on aqueous chromium(III): variable-pressure and -temperature kinetic study. Inorg. Chem. 24: 267-270.

Zepp, R.G., Faust, B.C. and Hoigne, J. (1992) Hydroxyl radical formation in aqueous reaction (pH3-8) of iron(II) with hydrogen peroxide: The phot-Fenton reaction. Environ. Sci. Technol. 26: 313-319.

Zhang, L.B. and Lay, P.A. (1996) EPR spectroscopic studies of the reactions of Cr(VI) with L-ascorbic acid, L-dehydroascorbic acid, and 5,6-O-isopropylidene-L-ascorbic acid in water. Implications for chromium (VI) genotoxicity. J. Am. Chem. Soc. 118, 12624-12637.

Zhang, L.B. and Lay, P.A. (1998) EPR spectroscopic studies on the formation of chromium (V) peroxo complexes in the reaction of Cr(VI) with hydrogen peroxide. Inorg. Chem. 37, 1729-1733.