EPA Ground Water Issue

Natural Attenuation of Hexavalent Chromium in Groundwater and Soils

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Introduction

Chromium is an important industrial metal used in diverse products and processes (Nriagu, 1988a, b). At many locations, Cr has been released to the environment via leakage, poor storage, or improper disposal practices (Palmer and Wittbrodt, 1991; Calder, 1988). Within the environment, Cr is found primarily in two oxidation states: Cr(VI) and Cr(III). Cr(VI) is relatively mobile in the environment and is acutely toxic, mutagenic (Bianci et al., 1983; Beyersmann et al., 1984; Bonatti et al., 1976; Paschin et al., 1983), teratogenic (Abbasi and Soni, 1984), and carcinogenic (Mancuso and Hueper, 1951; Mancuso, 1951; Waterhouse, 1975; Yassi and Nieboer, 1988; One, 1988). In contrast, Cr(III) has relatively low toxicity (van Weerelt et al., 1964) and is immobile under moderately alkaline to slightly acidic conditions.

Concerns about the impact of chromium on human health and the environment require an evaluation of the potential risk of chromium entering the groundwater flow system and being transported beyond compliance boundaries. At sites where such potential exists, active remedial measures such as excavation or pump-and-treat have been undertaken. Experience at sites where pump-and-treat remediation of chromium-contaminated groundwater is currently underway suggests that, although it is feasible to remove high levels of chromium from the subsurface, as concentrations decrease it becomes more difficult to remove the remaining chromium (Wittbrodt and Palmer, 1992). While several new remedial technologies are being investigated, there is still concern about the cost of such remediation technology; and, at many sites, there is a debate about the need for expensive remediation.

Researchers have identified natural reductants that can transform the more toxic hexavalent form of chromium to the less toxic trivalent form. Under alkaline to slightly acidic conditions, this Cr(III) precipitates as a fairly insoluble hydroxide, thereby immobilizing it within the soil. Such **"natural attenuation"** of hexavalent chromium is of great interest because it suggests that strict water-quality standards do not have to be attained everywhere within and beneath the site. If natural attenuation does occur, pump-and-treat remediation could desist after the most contaminated groundwater has been removed, even if the maximum contaminant level (MCL) has not be achieved. Under certain circumstances, expensive remedial measures may not even be necessary.

In this paper, what is known about the transformation of chromium in the subsurface is explored. This is an attempt to identify conditions where it is most likely to occur, and describe soil tests that can assist in determining the likelihood of natural attenuation of Cr(VI) in soils.

The Geochemistry of Chromium

Chromium exists in oxidation states ranging from +6 to -2, however, only the +6 and +3 oxidation states are commonly encountered in the environment. Cr(VI) exists in solution as monomeric ions $H_2CrO_4^0$, $HCrO_4^-$ (bichromate), and CrO_4^{2-} (chromate), or as the dimeric ion $Cr_2O_7^{2-}$ (bichromate)

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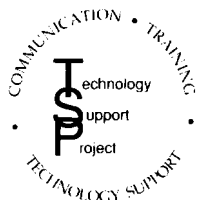
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(e.g. Palmer and Wittbrodt, 1991; Richard and Bourg, 1991). The monomeric species impart a yellow color to the water when the [Cr(VI)] is greater than 1 mg/L. Water that contains high levels of $Cr_2O_7^{2-}$ has an orange color.

The monomeric chromate species are related through a series of acid dissociation reactions

$$H_2CrO_4^0 \rightleftharpoons HCrO_4^- + H^+ \quad ; K,$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \quad ; K_2$$
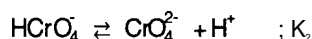
the pK values are -0.86 and 6.51, respectively (Allison et al., 1990). The bichromate is the result of the polymerization of the monomeric bichromate ions to form the dimer, $Cr_2O_7^{2-}$,

$$HCrO_4^- + HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + \& O \quad ; K_d$$
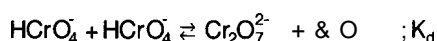
where pK_d is -1.54 (Allison et al., 1990). The relative concentration of each of these species depends on both the pH of the contaminated water (Fig. 1) and the total concentration of Cr(VI) (Fig. 2). Significant concentrations of $H_2CrO_4^0$ only occur under the extreme condition of pH c 1. Above pH 6.5, CrO_4^{2-} generally dominates. Below pH 6.5, $HCrO_4^-$ dominates when the Cr(VI) concentrations are low (<30 mM); but $Cr_2O_7^{2-}$ becomes significant when concentrations are greater than 1 mM, or it may even dominate when the total Cr(VI) concentrations are greater than 30 mM.

In the Cr(III)-H_2O system, Cr(III) exists predominantly as Cr^{3+} below pH 3.5. With increasing pH, hydrolysis of Cr^{3+} yields $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ (Rai, et al., 1987). At high concentrations, these ions impart a green color to the solution. Under slightly acidic to alkaline conditions, Cr(III) can precipitate as an amorphous chromium hydroxide.

Amorphous $Cr(OH)_3$ can crystallize as $Cr(OH)_3 \cdot 3H_2O$ or Cr_2O_3 (eskolaite) under different conditions (Swayambunathan et al., 1989). In the presence of Fe(III), trivalent chromium can precipitate as a solid solution. If the pH within the contaminant plume is between 5 and 12, the aqueous concentration of Cr(III) should be less than 1 μmole/L (<0.05 mg/L) (Fig. 3).

There are several mineral phases that contain Cr(VI) that may be present at chromium contaminated sites. Palmer and Wittbrodt (1990) identified $PbCrO_4$ (crocoite), $PbCrO_4 \cdot H_2O$ (iranite), and K_2CrO_4 (tarapacaite) in chromium sludge from a hardchrome plating facility. $CaCrO_4$ was found at a seepage face in a drainage ditch where there was high evaporation. Most of the contaminated groundwater was at equilibrium with $BaCrO_4$ (hashemite). $BaCrO_4$ forms a complete solid solution with $BaSO_4$ (Rai et al., 1988) and can be a major impediment to the remediation of chromium contaminated sites by pump-and-treat (Palmer and Fish, 1992; Wittbrodt and Palmer, 1992).
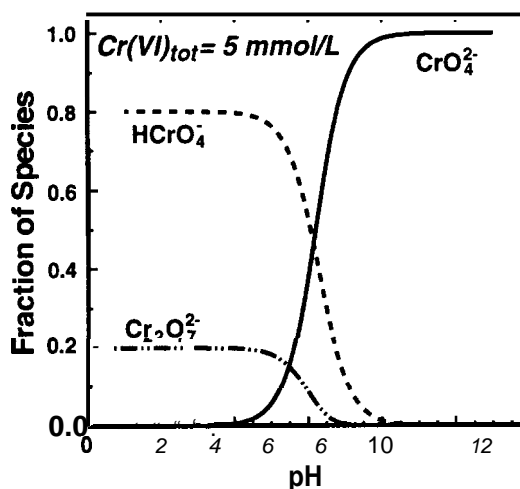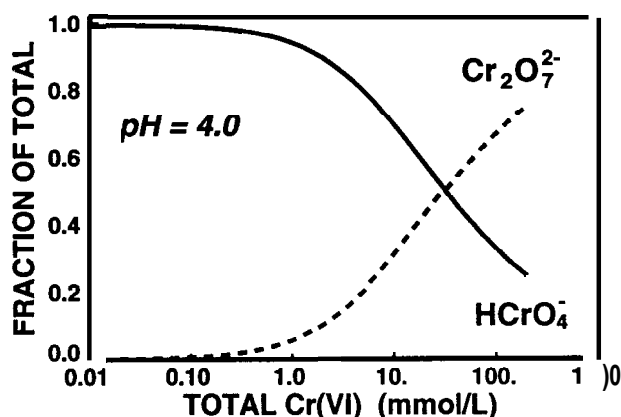

Figure 1. Distribution of Cr(VI) species as a function of pH.

Figure 2. Fraction of bichromate ($HCrO_4^-$) and bichromate ($Cr_2O_7^{2-}$) at pH 4 as a function of the total Cr(VI) concentration.

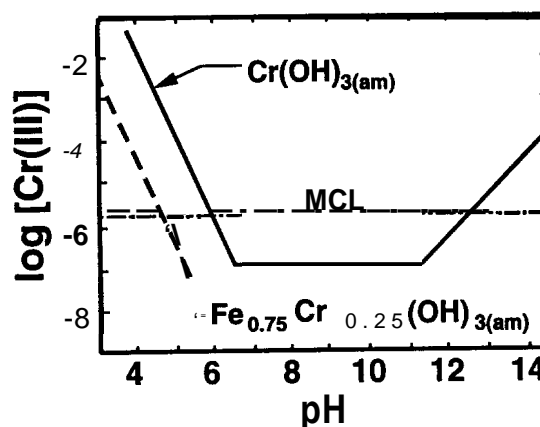Figure 3. Cr(III) concentration in equilibrium with $Cr(OH)_{3(am)}$ and $Fe_{0.75}Cr_{0.25}(OH)_3$, based on data from Rai et al., (1 987) and Sass and Rai (1987), respectively.

Reduction of Hexavalent Chromium

Cr(VI) is a strong oxidant and is reduced in the presence of electron donors. Electron donors commonly found in soils include aqueous Fe(II), ferrous iron minerals, reduced sulfur, and soil organic matter.

The reduction of Cr(VI) by ferrous iron can be written as

$$HCrO_4^- + 31\%^{2+} + 7H^+ + Cr^{3+} + 3Fe^{3+} + 4H_2O$$
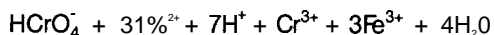
This reaction is very fast on the time scales of interest for most environmental problems with the reaction going to completion in less than 5 minutes even in the presence of dissolved oxygen (Eary and Rai, 1988). Only when the pH is greater than 10 or when PO_4 concentrations exceed 0.1 molar does the rate of oxidation of Fe^{2+} by dissolved oxygen exceed the rate of oxidation by Cr(VI) (Eary and Rai, 1988). When the pH of the groundwater is greater than 4, Cr(III) precipitates with the Fe(III) in a solid solution with the general composition $Cr_xFe_{1-x}(OH)_3$ (Sass and Rai, 1987; Amonette and Rai, 1990). If the reduction of Cr(VI) by Fe(n) is the only source of Fe(III) and Cr(III), a solid solution with the composition $Cr_{0.25}Fe_{0.75}(OH)_3$ forms via the reaction

$$HCrO_4^- + 3Fe^{2+} + 3H_2O + 5OH^- \rightarrow 4Cr_{0.25}Fe_{0.75}(OH)_3$$
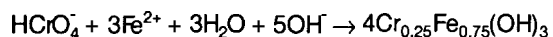
(Eary and Rai, 1988; Sass and Rai, 1987). The volubility of $Cr_xFe_{1-x}(OH)_3$ decreases as the mole fraction of Fe(III) in the solid increases. Therefore, if the pH is between 5 and 12, the concentration of Cr(III) is expected to be less than 10^{-6} molar.

Numerous minerals in geologic materials contain ferrous iron that is potentially available for the reduction of hexavalent chromium. These iron-containing minerals may be silicates, oxides, or sulfides. Common ferrous iron-containing silicates include olivine; pyroxenes such as augite and hedenbergite; the amphiboles hornblende, cummingtonite, and grunerite; micas such as biotite, phlogopite, and glauconite; chlorites, and the smectite nontronite. Iron oxides such as magnetite ($Fe^{2+}Fe_2^{3+}O_4$) contain iron as a major constituent, however, hematite ($Fe_2^{3+}O_3$) can contain small amounts of (FeO). in sulfide minerals such as pyrite (FeS_2), both the ferrous iron and the sulfide are active in reducing hexavalent chromium.

Lancy (1966) suggested that pyrite could be used for treating spent cooling waters that contain Cr(VI) as a corrosion inhibitor. He stated that the reduction of Cr(VI) occurs at the pyrite surface rather than in solution. Lancy (1966) found that reduction by pyrite occurred even in slightly alkaline solutions; however, the pyrite had to be continuously abraded to remove surface coatings. Blowes and Ptacek (1992) conducted batch tests in continuously agitated reaction vessels containing a solution of 18 mg/L Cr(VI) and pyrite both in the presence and in the absence of calcite. In the experiments that used both pyrite and calcite, 50% of the Cr was removed in less than 6.5 hours. Concentrations were < 0.05 mg/L after 20 hours.

Experiments conducted without the calcite attained 50% removal in 1 hour and concentrations were < 0.05 mg/L in less than 4 hours.

Cr(VI) reduction in the presence of iron oxides has been observed in several experiments. White and Hochella (1989) found that magnetite and ilmenite reduced Cr(VI) to Cr(III). The reduction of Cr(VI) in the presence of hematite (Fe_2O_3) was demonstrated by Eary and Rai (1989). They attribute the reduction to the presence of a small amount of an FeO component in the hematite. They suggest that reduction occurs in solution after the FeO component has been solubilized.

Reduction of Cr(VI) by ferrous iron-containing silicates has been reported. Eary and Rai (1989) suggest that the reduction of Cr(VI) in the presence of biotite occurs in solution rather than at the mineral surface. They observed an increase in the rate of reduction when their suspensions were spiked with Fe^{3+}. They explain their results with the mechanism proposed by White and Yee (1985) in which Fe^{3+} is reduced at the mineral surface by the reaction

$$[Fe(n), K^+]_{biotite} + Fe^{3+} \rightarrow [Fe(III)]_{biotite} + K^+ + Fe^{2+}$$
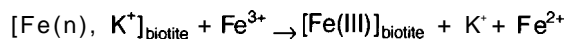
where the ions in the brackets denote ions within the crystal structure of biotite. To maintain charge balance, K^+ is released to solution as the iron in the crystal structure is oxidized. The Cr(VI) in solution is then reduced by the Fe^{2+}. The Fe^{3+} resulting from this reduction reaction is then adsorbed to the surface of the biotite where it is again reduced to Fe^{2+}, thus setting up a cycle that ultimately results in the reduction of more Cr(VI) than is stoichiometrically possible for the amount of iron that is in solution.

There are some key experimental difficulties in studying groundwater/mineral interactions such as those just described that have some bearing on the transfer of knowledge to the field. Although the processes can in some cases be interpreted from the data on mineral reactions, the rates themselves may be quite useless. A key difficulty in studying mineral reactions in the laboratory is that the rate of the reaction depends on how the solid phase was prepared. For example, if the samples are ground and simply washed before use, microparticles can adhere to the larger grain surfaces. These microparticles have greater specific surface area and can react at a much faster rate than the larger size particles. Such experimental artifacts were observed in weathering studies of pyroxenes (Schott et al., 1981).

Another important reductant in soils is organic matter. In fact, bichromate reduction has been used as a wet combustion method for the determination of soil organic carbon (Walkley and Black, 1934). Bichromate can react with soil organic carbon according to

$$2Cr_2O_7^{2-} + 3C^0 + 16H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$$
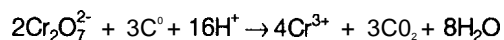
The Cr^{3+} may hydrolyze and precipitate as Cr-hydroxide or it may bind to the remaining soil organic carbon. Much of the soil organic carbon is present as soil humic and fulvic acids. Redox reaction with these materials has been demonstrated for several redox reactive species. Reduction of Cr(VI) by soil humic and fulvic acids has been demonstrated by Bartlett and Kimble (1 976), Bloomfield and Pruden (1980), Goodgame et al. (1984), Boyko and Goodgame (1986), and Stollenwerk and Grove (1985). The rate of reduction of Cr(VI) decreases with increasing pH (Fig. 4), increases with the increasing initial Cr(VI) concentration, and increases as the concentration of soil humic substance increases. At neutral pH, many weeks may be required for the Cr(VI) to be completely reduced Cr(VI).

In addition to these abiotic reduction pathways, Cr(VI) can be reduced by microbes in the subsurface (Martin et al., 1994). Both aerobic and anaerobic reduction by microbes have be observed, however, the latter is more common. The mechanisms for Cr(VI) by these microbes is not well known. It may be part of a detoxification mechanism that occurs intracellularly. Alternatively, the chromate may be utilized as a terminal electron acceptor-as part of the cell' s-metabolism. A third possibility is that reduction is an extracellular reaction with excreted waste products such as H_2S. In addition to two strains of Gram-positive bacteria, Martin et al., (1994) found a fungus in contaminated soil that was capable of reducing Cr(VI) under anaerobic conditions.
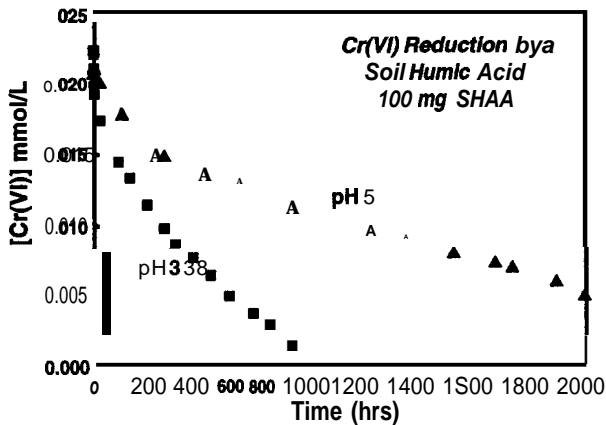
Figure 4. Reduction of Cr(VI) in a suspension of 100 mg/L soil humic acid (SHA) at pH 3 and 5 (Wittbrodt and Palmer, in preparation).

Oxidation of Cr(III)

Any evaluation of the natural attenuation of Cr(VI) must consider the potential oxidation of the Cr(III) to the toxic Cr(VI) form. In contrast to the numerous pathways for the reduction of Cr(VI), there are very few mechanisms for the oxidation of Cr(III). Only two constituents in the environment are known to

oxidize Cr(III) to Cr(VI): dissolved oxygen and manganese dioxides (MnO_2) (Eary and Rai, 1987). Studies of the reaction between dissolved oxygen and Cr(III) revealed very little (Schroeder and Lee, 1975) or no (Eary and Rai, 1987) oxidation of Cr(III) even for experiments conducted at pH as great as 12.5 for 24 days. Therefore, the transformation of Cr(III) by dissolved oxygen is not likely to bean important mechanism for the oxidation of Cr(III).

Oxidation of Cr(III) has been observed in several soils and sediments. The oxidation of the Cr(III) can be relatively slow requiring several months (Fig. 5). For example, Palmer and Wittbrodt (1 990) monitored Cr(VI) concentrations in batch tests using three different geologic media from a site in Corvallis, OR. They observed increases in Cr(VI) concentrations over a 300-day period with Cr(VI) concentrations becoming as great as 7 mg/L in one experiment. Bartlett and Kimble (1976) did not observe oxidation of Cr(III) in their dried soils but Bartlett and James (1979, 1983a) did observe oxidation in soils that were maintained in a moist state.
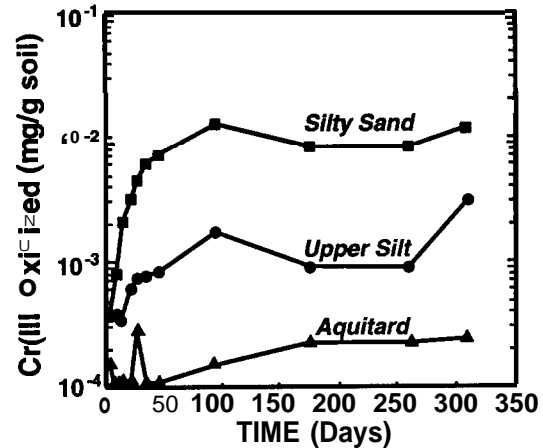
Figure 5. Cr(III) oxidized to Cr(VI) in a suspension of Willamette silt loam.

Bartlett and James (1979) observed a correlation between the amount of Cr(III) oxidized by soils and the amount of hydroquinone-reduced manganese in soils and suggested the oxidation of Cr(III) is the result of interaction with manganese dioxides. This hypothesis has been experimentally verified using ß-MnO_2 or pyrolusite (Eary and Rai, 1987) and δ-MnO_2 (Fendorf and Zasoski, 1992; Riser and Bailey, 1992). There is an increase in the rate and amount of Cr(III) oxidation as pH decreases, and the surface area to solution volume increases. Experimental results indicate that the oxidation follows the reaction

$$CrOH^{2+} + 1.5 \text{ δ-}MnO_2 \rightarrow HCrO_4^- + 1.5Mn2+$$
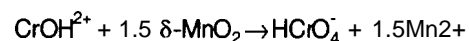
Significant oxidation of Cr(III) was observed in less than 1 hour (Fendorf and Zasoski, 1992) and continued for more than 600 hours (Eary and Rai, 1987). Eary and Rai (1987) developed an empirical rate law for the oxidation of Cr(III) by

β-MnO$_2$; however, the zero point charge for this phase is quite different than birnessite which is more commonly found in soils. Therefore, this rate law may not be applicable to manganese dioxides in soils.

Perspective on the Natural Attenuation of Cr(VI)

If hexavalent chromium can be reduced and immobilized in the subsurface as a result of interaction with naturally existing reductants, then expensive remedial measures may not be required at certain sites. In principle, the natural attenuation of Cr(VI) in the subsurface is feasible. There are several natural reductants that can transform Cr(VI) to Cr(III). If the pH of the contaminant plume is between about 5 and 12, Cr(III) precipitates as Cr(OH)$_3$ or as part of a solid solution with Fe(III), thereby keeping Cr(III) concentrations below 1 μmole/L (0.05 mg/L). Whether or not natural attenuation at a particular site is a viable option depends on the characteristics of both the aquifer and the contaminant plume under investigation.

The potential reductants of Cr(VI) include aqueous species, adsorbed ions, mineral constituents, and organic matter. When a contaminant plume containing hexavalent chromium enters the subsurface, it displaces the groundwater containing the dissolved reductants. There is little mixing of the waters containing the reducing agents and the Cr(VI)-contaminant plume. What mixing does occur will be driven by molecular diffusion at the front of the plume or from the edges of the plume and diffusion from lower permeability lenses containing relatively immobile water. Thus, aqueous reductants such as Fe^{2+} are not going to be important in reducing hexavalent chromium. Mixing of reductants and Cr(VI) in the plume are going to occur primarily though the interactions of the plume with the immobile soil matrix. Such interactions include desorption of reductants such as Fe^{2+} from mineral surfaces, direct and indirect surface redox reactions between Cr(VI) and the mineral surfaces, and reduction by soil organic matter. Thus, it is the soil matrix that is most important with regards to redox transformations of chromium in the subsurface. This argument is further supported by studies that clearly demonstrate that groundwater contributes less that 1 % of the oxidation capacities (equivalents of Cr oxidized per gram of soil) and reduction capacities (equivalents of Cr reduced per gram of soil) of aquifer systems while the soil matrix contributes the remaining fraction (Barcelona and Helm, 1991). Thus, any discussion of redox transformations of chromium in the subsurface must focus on the soil matrix.

Three key factors must be addressed in considering the potential use of natural attenuation of Cr(VI) in the subsurface. Firstly, the reduction capacity of the aquifer, R$_c$, must be great enough to reduce all of the Cr(VI) that passes through it. If X$_c$ is the distance from the source to the point of compliance (Fig. 6), the total mass of Cr(VI) from the source, MO, must be less than the total mass of Cr(VI), M$_r$, that can be reduced by the aquifer material between the source and XC:

$$M_o < M_r = x_c A \rho_b R_c \qquad (1)$$

where A is the cross-sectional area of the plume normal to the direction of groundwater flow and ρ_b is the dry bulk density of the aquifer. As X$_c$ increases, the mass of Cr(VI) that can be reduced increases. A key difficulty in applying this criterion is in providing a reasonable estimate of M$_o$. In the absence of other reactions such as adsorption or precipitation, the minimum rate of movement of the Cr(VI) front through the aquifer, v$_{min}$, computed by assuming the reductant reacts instantaneously with the Cr(VI), is

$$v_{min} = \frac{v_w}{1 + \frac{\rho_b}{\theta_v} \frac{R_c}{C.}} \qquad (2)$$

where ρ_b and θ_v are the dry bulk volumetric water content of the porous medium, V$_w$ is the velocity of the groundwater, and C$_o$ is the concentration of the chromium in the contaminant plume.
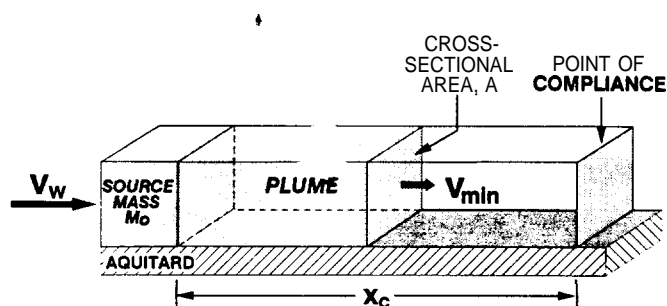
Figure 6. Cr-plume moving from the source area to the point of compliance. The initial Cr(VI) concentration in the source area is MO, vw is the groundwater velocity, v$_{min}$ is the velocity of the Cr(VI) front assuming instantaneous reduction of the Cr(VI), and X$_c$ is the distance from the source area to the point of compliance.

The second key factor in the application of natural attenuation of Cr(VI) is the rate of reduction relative to the rate of advective transport in the subsurface. The time for the reduction reaction to decrease the concentration from its initial concentration, CO, to some target concentration, C$_s$, such as a drinking water standard, should be less than the residence time of the contaminated water in the portion of the aquifer between the source of the Cr(VI) and the point of compliance. For example, if the rate of reduction of Cr(VI) follows a first-order rate equation

$$\frac{dC}{dt} = -kC \qquad (3)$$

the time for the concentration of Cr(VI) to decrease from C. to C$_s$ must be less than the residence time of the contaminated parcel of water within the aquifer

$$\ln(C_o / C_s) < \frac{x_c}{v_w} \qquad (4)$$

If natural attenuation is to be a viable option, this criterion must be met. Difficulties in utilizing this criterion arise in applying the appropriate rate equation and obtaining the pertinent rate coefficients.

A third factor concerning the natural attenuation of $Cr(VI)$ is the possible oxidation of $Cr(III)$ to the more toxic **hexavalent** form. While contamination is actively entering the subsurface, conditions may favor the reduction of $Cr(VI)$ to $Cr(III)$. After the source of the active contamination is removed, however, chemical parameters within the aquifer, particularly pH, may be altered. Under the new conditions, oxidation of $Cr(III)$ may be favored. Thus, soil containing $Cr(III)$ formed during the active contamination phase may become a source of $Cr(VI)$.

Both oxidation and reduction of chromium are occurring simultaneously within the subsurface as part of a geochemical cycle. As the $Cr(III)$ is oxidized to $Cr(VI)$ by manganese dioxides in the soil, $Cr(VI)$ can be reduced to $Cr(III)$ by some **reductant** such as soil organic carbon or pyrite. The rate of change in $[Cr(VI)]$ $(d[Cr(VI)]/dt)$ is the sum of the rate of reduction of $Cr(VI)$, R_{red}, and the rate of oxidation of $Cr(III)$, R_{ox}:

$$\frac{d[Cr(VI)]}{dt} = \left[\frac{[Cr(VI)]}{dt}\right]_{red} + \left[\frac{[Cr(VI)]}{dt}\right]_{ox} = R_{red} + R_{ox} \qquad (5)$$

If a soil initially contains both $Cr(VI)$ and $Cr(III)$, then $[Cr(VI)]$ increases when $R_{red} + R_{ox} > 0$ and decreases when $R_{red} + R_{ox} < O$. Ultimately, the $[Cr(VI)]$ will reach a steady state, i.e., $d[Cr(VI)]/dt = O$. At this time, the rate of loss of $Cr(VI)$ via reduction is balanced by the rate of production by the oxidation of $Cr(III)$:

$$-R_{red} = R_{ox} \qquad (6)$$

Wittbrodt and Palmer (1 994) suggest that the reduction of $Cr(VI)$ by soil **fulvic** acid can be represented by

$$R_{red} = -k_{red} X_e^{-1} [HCrO_4^-][SHS][H^+]^p \qquad (7)$$

where $[SHS]$ is the concentration of soil **humic** substance and X_e denotes the equivalent fraction of the **humic** substance that has been oxidized. Fendorf and Zasoski (1992) suggest that $CrOH^{2+}$ is the reactive species in the oxidation of $Cr(III)$ by MnO_2. For illustrative purposes, assume that the oxidation reaction follows a rate equation of the form

$$R_{ox} = k_{ox} [CrOH^{2+}] [A/V]^m [H^+]^n \qquad (8)$$

where (A/V) denotes the surface area of the MnO_2 per unit volume of solution. If we further assume that the solution is equilibrated with $Cr(OH)_{3(am)}$, then

$$R_{ox} = k_{ox} (K/K_w^2)(A/V)^m [H+]^n +' \qquad (9)$$

where K_w is the dissociation constant for H_2O and K is the equilibrium constant for the reaction

$$Cr(OH)_{3(am)} \rightleftharpoons Cr(OH)^{2+} + 2(OH^-)$$
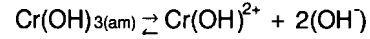
Equating R_{ox} with $-R_{red}$ and rearranging the terms yields

$$[HCrO_4^-] = \frac{k_{ox}}{k_{red}} \frac{K}{K_w^2} X_e \frac{(A/V)^m}{[SHS]} [H^+]^{n+2-p} \qquad (lo)$$

Although some of the specific points of rate equations presented here are debatable, equation 10 does illustrate aspects of natural attenuation in soils that contain both a **reductant** and MnO_2. The key point is that as long as the supply of **reductant** and MnO_2 have not been significantly depleted, $[HCrO_4^-]$ does not converge to zero with increasing residence time within the aquifer as one would expect for a first order reaction that only considers reduction of $Cr(VI)$. Rather, $[HCrO_4^-]$ converges to some steady-state concentration that is $> O$ that may or may not be above the MCL. This steady-state concentration increases with increasing k_{ox}/k_{red}, and $(A/V)^m/[SHS]$ and it varies with pH. Thus, in principle, if the rate equations are correct and all of the parameters are known, one could calculate the **steady-state** $Cr(VI)$ concentration and determine if natural attenuation could achieve compliance goals. Studies of the kinetics of these coupled processes needs be done to verify the general forms of the rate equations and to determine the appropriate rate coefficients.

Determining the Potential for Natural Attenuation

If "natural attenuation" is to be considered an alternative to expensive remediation efforts, additional characterization is required to demonstrate that the expectations are likely to be met. There is no single test that can tell us if natural attenuation of $Cr(VI)$ will occur at a particular site. Several tests are briefly described which have been utilized to address key factors affecting $Cr(VI)$ transport in the subsurface and describe how the results can be utilized in determining the potential for the natural attenuation of $Cr(VI)$ in the subsurface.

Ideally, it must be demonstrated that 1) there are natural **reductants** present within the aquifer, 2) the amount of $Cr(VI)$ and other reactive constituents do not exceed the capacity of the aquifer to reduce them, 3) the rate of $Cr(VI)$ reduction is greater than the rate of transport of the aqueous $Cr(VI)$ from the site, 4) the $Cr(III)$ remains immobile, and 5) there is no net oxidation of $Cr(III)$ to $Cr(VI)$. Some of these criteria are relatively simple while others require additional tests and interpretation. Additional tests that will be required include tests of the oxidizing and reducing capacities of the aquifer.

Mass of Cr(VI) at the Source

It must be demonstrated that the amount of Cr(VI) in the aquifer does not exceed the capacity of the soil for reducing this chromium. Therefore an important first step in evaluating the potential for natural attenuation is to determine the mass of Cr(VI) in the soil. Chromium exists in the subsurface either in solution or in association with the solid phase. Cr(VI) in solution can be determined by the diphenylcarbazide (DPC) method (APHA, 1989). Aqueous samples are most often obtained from monitoring wells. Alternatively, water separated from the soil matrix either by centrifugation or by squeezing. The pH of these waters should be measured to determine if it is within the proper range (5.5 to 12) to insure the Cr(III) concentrations are less than 1 μM (0.05 mg/L).

Cr(VI) associated with the soil matrix maybe adsorbed to mineral surfaces (particularly iron oxides) or precipitated as chromate minerals. There is no precise method for determining each of these fractions of Cr(VI); nonetheless, determinations have been made using sequential extractions. An initial water extraction serves to remove remaining pore water and dissolve highly soluble chromium minerals present in the soil or that may have precipitated as the result of evaporation during sample handling and storage. This water extraction also removes some adsorbed ions.

Following the water extraction, a phosphate extraction is used as a measure of the "exchangeable" chromate in the soil (Bartlett and James, 1988). The test is conducted by adding phosphate to the soil and equilibrating for 24 hours. The water is then separated from the slurry and Cr(VI) is measured by the DPC method (Bartlett and Kimble, 1976; Bartlett and James, 1988c). The increase in the chromate concentration is the amount of "exchangeable" chromate. Amacher and Baker (1982) found optimal extraction using 0.01 M monobasic potassium phosphate (KH_2PO_4). James and Bartlett (1983b) used a solution of 0.005 M KH_2PO_4 and 0.05 M K_2HPO_4 to yield a pH of 7.2. James and Bartlett (1983b) stated that doing the extraction at pH 7.2 is preferred because there is less likelihood of chromate reduction than at lower pH. However, decreasing the pH of the soil slurry can result in dissolution of $BaCrO_4$ from the soil. Moreover, if the pH of the soil water was initially low, then increasing the pH to 7.2 can cause precipitation of $BaCrO_4$, thereby complicating the interpretation of the results. When the soil water is not equilibrated with $BaCrO_4$, the phosphate extraction method of James and Bartlett (1983b) primarily measures the amount of adsorbed Cr(VI) in the soil. The phosphate removes chromate by both directly competing for the adsorption sites in the soil and indirectly (in some cases) by increasing the pH.

$BaCrO_4$ is a likely chromate mineral phase that can be a source of Cr(VI) in contaminated aquifers. There is no direct test for $BaCrO_4$ in soils, however, when the groundwater is equilibrated with this phase and the source of the Ba^{2+} is entirely from the clays in the natural soil, the maximum amount of $BaCrO_4$ in the aquifer is equal to the ammonium acetate exchangeable Ba^{2+} (Thomas, 1982) in background

soils. For example, Palmer and Wittbrodt (1990) found that the amount of exchangeable Ba^{2+} was useful in estimating the number of pore volumes required to flush Cr(VI) from soil columns.

At many sites, the total Cr(VI) associated with the soil matrix is the sum of the $BaCrO_4$ and the PO_4-extractable Cr(VI). This sum, S, is often reported in units of mass per gram of soil. The total concentration of Cr(VI) in the soil, $Cr(VI)_{tot}$ is the sum of the aqueous Cr(VI) and the matrix associated Cr(VI), S, which can be reported in common units of mass per unit volume of water by

$$Cr(VI)_{tot} = [Cr(VI)] + \frac{1000\,\rho_b}{0,} S \qquad (11)$$

where the dry bulk density of the soil, ρ_b, is in g-cm^{-3}. The total mass of Cr(VI) in the site soils can then be estimated by integrating the concentrations over the volume of contaminated soil.

Mass of Cr(III) in the Subsurface

If all of the chromium that entered the soil was Cr(VI), then demonstrating the presence of Cr(III) in the soil would prove that reduction is occurring. The mass of Cr(III) in the soil can provide a measure of the amount of reduction that has occurred. Although proof of chromate reduction is necessary, it is not sufficient for demonstrating that natural attenuation will adequately protect the environment.

The total amount of Cr(III) present in the soil is the sum of the mass in solution as well and mass associated with the solid phase. Total chromium in solution can be determined by atomic absorption spectrophotometry (AAS) or inductively coupled plasma spectroscopy (ICP). When total chromium is statistically greater than Cr(VI), Cr(III) can be simply determined by difference.

The amount of Cr(III) associated with the soil matrix has ostensibly been determined using several techniques. An ammonium oxalate (0.1 M) extraction serves to remove amorphous hydroxides of Cr, Fe, and Al (Ku et al., 1978; Borggaard, 1988). Bartlett (1991) suggests that a K, H-citrate extraction provides a measure of the Cr(III) that is potentially removable by low molecular weight organic molecules. A dithionate-citrate-bicarbonate (DCB) extraction is conducted by adding 0.3 M sodium citrate and 0.1 M sodium bicarbonate to the soil sample and heating to 80°C for 20 minutes. One gram of sodium dithionate is then added and the soil slurry is stirred for another 15 minutes. The DCB extraction removes the crystalline forms of the Cr-, Fe-, and Al-oxyhydroxides (Ku et al., 1978; Borggaard, 1988). The dithionate reduces crystalline iron (goethite) in the soil and Cr, Fe, and Al are complexed by the citrate. In addition to the Cr(III) oxyhydroxides, the DCB method also extracts sparingly soluble Cr(VI) mineral phases such as $BaCrO_4$, thereby complicating interpretation of the results. Bartlett (1991) uses

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40 mL per gram of soil of 0.7 M NaOCl solution (undiluted laundry bleach) at pH 9.5 to extract chromium. The slurry is placed in a boiling water bath for 20 minutes before the liquid is separated and Cr is determined by AAS or ICP. This method is useful in determining total chromium in the soil because it readily oxidizes and removes Cr(III) that is not removed by other methods.

Identification of Potential Reductants

The presence of Cr(III) in the soil maybe indicative of active reduction in the soil, or it may be the result of the neutralization of acidic waters containing Cr(III) with subsequent precipitation of chromium hydroxides. Therefore, identification of specific reductants within the aquifer is warranted. The identification of some potential reductants at a site can be fairly simple in some cases. For example, pyrite (FeS_2), a common constituent in many geological materials, is readily identifiable by its visual characteristics. Other mineral phases capable of reducing Cr(VI) can be identified using classical petrographic techniques or powder x-ray diffraction. Scanning electron microscopy (SEM) can be utilized to identify crystallite morphology. SEMS equipped with energy dispersive x-ray spectroscopy can also provide information about the elemental composition of these crystallite. Electron diffraction patterns obtained from transmission electron microscopes provide crystallographic information. Such electron microscopy methods can, however, be relatively expensive. A fairly simple and inexpensive test for organic carbon can provide a measure of the amount of carbon available for reduction of Cr(VI). Knowledge of the specific reductant within the aquifer is useful in determining the time scale for the reduction of Cr(VI) based on studies that are reported in the literature. Soils containing iron sulfides or organic matter are more likely to reduce Cr(VI) on the time scales of interest than soils containing ferrous iron silicates.

Reduction Capacity of the Aquifer

Adequate protection of the environment by natural attenuation of Cr(VI) requires that the soil possess a large enough reducing capacity to reduce all the hexavalent chromium in the source area. Several measures for predicting reduction of Cr(VI) in soil are presented by Bartlett and James (1 988) and Bartlett (1991). A measure of the maximum amount of Cr(VI) that can be reduced per unit mass of aquifer, the **"total Cr(VI) reducing capacity"**, can be obtained using the classical Walkley-Black method for determining soil organic carbon (Bartlett and James, 1988). In this method, 2 to 3 grams of soil are reacted with a mixture of 1 N $K_2Cr_2O_7$ in IN H_2SO_4 for 30 minutes (Walkley and Black, 1934; Nelson and Sommers, 1982; Bartlett and James, 1988). The Cr(VI) concentration is measured using the diphenylcarbazide (DPC) method (APHA, 1989) and the decrease in the mass of Cr(VI) in the reaction vessel per gram of soil used in the test is the reduction capacity. Although this method of determining soil organic carbon has its limitations (e.g. Nelson and Sommers, 1982), it is a direct measure of how much Cr(VI) can be reduced by a soil at extreme acid concentrations. Variations on this method

use heat or a combination of heat and pressure (Nelson and Sommers, 1982). Barcelona and Helm (1991) used a modified closed-tube chemical oxygen demand procedure (U.S. EPA, 1979) to determine reduction capacities.

The extreme conditions of pH and temperature used in the total Cr(VI) reducing capacity test may yield a greater reducing capacity than would be available under most environmental conditions. The **"available reducing capacity"** test of Bartlett and James (1988) determined the reduction capacity by reacting about 4 to 5 grams of moist soil in a solution of 10 mM H, PO, and $K_2Cr_2O_7$ for 18 hours. The H_3PO_4 is added to buffer the pH and to compete with the Cr(VI) for the adsorption sites. When KH_2PO_4 is used Bartlett and James referred to it as the **"reducing intensity".** These tests are designed to determine the reducing capacity at pH values more likely to be encountered in the field. However, in long term reduction tests at near neutral pH, Palmer and Wittbrodt (unpublished data) observed reduction occurring after 250 days (Fig. 7). Such long-term reduction tests are not practical at most waste sites.
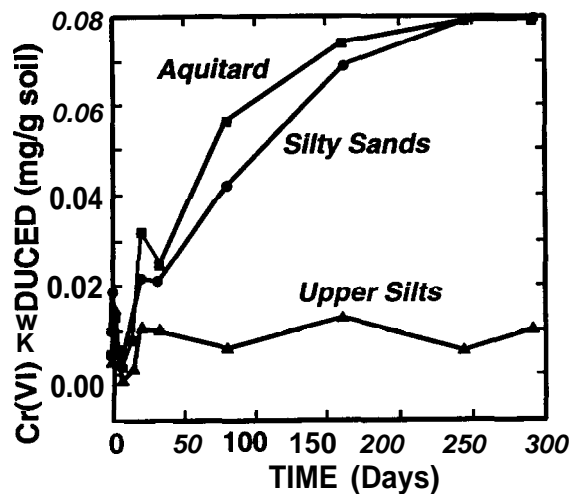

Figure 7. Cr(VI) reduced to Cr(III) in Willamette silt loam.

Oxidation Capacity

A potential limitation to the use of natural attenuation of Cr(VI) in soil is the oxidation of the Cr(III) to Cr(VI) by MnO_2. If the oxidizing capacity of the soil is greater than the reduction capacity, then as the chromium is cycled in the soil it could exhaust the soil reductant and be oxidized and ultimately mobilized in the soil. It is important, therefore, to determine the capacity of the aquifer to oxidize Cr(III).

Bartlett and James (1988) suggest a relatively simple test for the amount of Cr(III) that can be oxidized by a soil. The method involves adding 2.5 grams of soil to a solution containing 25 ml of 1 mM $CrCl_3$. After shaking for 15 minutes, a solution of KH_2PO_4 . K_2HPO_4 is added to the reaction vessel, the slurry centrifuged or filtered, and the Cr(VI)

measured using the DPC method. Moist soils should be used in these tests. Drying the soils alters the surfaces of the manganese dioxides making them less reactive (Bartlett and James, 1979).

Barcelona and Helm (1991) used a solution of chromous (Cr(II)) ion to measure the oxidation capacity of soils. They added about 1 g of soil to cuvettes containing the Cr(II) solution. The work was performed in a glove box to prevent oxygen from reacting with the Cr(II). The cuvettes were sealed, shaken, and allowed to react for 2 hours. The samples were centrifuged and the Cr(II) measured spectrophotometrically. The loss of Cr(II) is then used as a measure of the oxidation capacity of the soils.

Each of these methods has some problems. Palmer and Wittbrodt (unpublished data) conducted oxidation tests similar to the Bartlett and James (1 988) method except that the concentration of Cr(VI) was monitored over nearly a year. Cr(VI) concentrations in these tests continued to increase up to 100 days and may have been continuing after 300 days. For one soil, the short-term oxidation test of Bartlett and James underestimated the amount of oxidation obtained in the long-term tests by more than an order of magnitude. It is not clear in the Barcelona and Helm method whether the Cr(II) is being oxidized to Cr(III) or Cr(VI) or some combination of the two. If both products are forming, the results are more difficult to interpret.

If the only mechanism for the oxidation of Cr(III) in soils is oxidation by manganese oxides, then using extraction methods specifically designed for this purpose may be a good way of determining the oxidation capacity of the soils. One very simple extraction technique (Chao, 1972; Gambrell and Patrick, 1982) utilizes 0.1 M hydroxylamine hydrochloride ($NH_2OH . HCl$) in 0.1 M HNO_3. About 0.5 g of soil are added to 25 mL $NH_2OH . HCl$ of the solution and shaken for 30 minutes and the Mn concentration is measured. The number of moles of Cr(III) that can be oxidized is then computed by dividing the number of moles of Mn^{2+} per gram of soil obtained in the extraction by 1.5. The hydroxylamine hydrochloride test is fast, easy, and specifically targets the phase that promotes the oxidation of Cr(III).

Rates of Oxidation and Reduction

Key factors in the suitability of natural attenuation as an option for chromium contaminated soils are the rates of oxidation and reduction of chromium. This information is the most difficult to obtain. Scientists are only now learning about the form of the applicable rate equations and the appropriate rate coefficients that may apply. Such kinetic studies are an area where research has lagged behind the practical need for the information. While rates can be obtained from the technical literature, one must be careful to use rates of reduction for materials that are most likely controlling the Cr(VI) reduction in the site soil. In addition, because the rates depend on the concentration (surface area per liter of solution) of the

reductant and pH, it is important to obtain rate coefficients that were acquired under conditions similar to those at the site. Many rate studies have considered only a limited set of conditions such as a single pH value or one reductant concentration. Consequently, the reported rate coefficients are apparent values that are strictly valid only under the conditions of the experiment. Thus, the experimental factors must be taken into account before the rate coefficients can be applied to field problems.

When MnO_2 is present, Cr(III) maybe oxidized back to Cr(VI) and the net rate of reduction will be less than that obtained from experiments that only utilize reductants. Further, many rate experiments are conducted in stirred reactors that can abrade reactive surfaces. In soils, the rate of reaction may become surface limited as adsorbed ions and precipitates cover the reactive surfaces.

One method of obtaining the net rate of reduction is through tests on uncontaminated soils obtained from the site. These soils should be similar to those through which the contaminant plume will be migrating. Cr(VI) can be added to the soil slurry and the Cr(VI) concentrations monitored over time. The reaction vessels must exclude light to prevent photoreduction reactions and the slurry must have the same pH as the contaminant plume. A key limitation to such experiments is that they require several months to a year to complete.

Estimating Reduction from Monitoring Well Data

In principle, Cr(VI) reduction can be estimated from the decrease in the mass of Cr(VI) in the aquifer (e.g., Henderson, 1994). The key difficulty in such an approach is to estimate the mass of Cr(VI) using the aqueous concentrations. The total mass of Cr(VI) in the aquifer is the sum of the mass that is in solution, the mass that is adsorbed to the aquifer matrix, and the mass that is precipitated within the aquifer. The mass of Cr(VI) in solution is obtained by integrating the Cr(VI) concentrations over the volume of the contaminated aquifer

$$M_{aq} = \theta_v CV \qquad (12)$$

where V is the volume of aquifer containing a plume with a Cr(VI) concentration of C.

The mass of Cr(VI) adsorbed to the soil matrix, M_{ads}, can be computed from the adsorption isotherm. For example, if Cr(VI) follows a Langmuir isotherm, then over a volume of aquifer, V, with constant aqueous Cr(VI) concentration, C, M_{ads} can be computed as

$$M_{ads} = \rho_b \left[\frac{S_{max} K_{ads} C}{1 + K_{ads} C} \right] V(1 - \theta_v) \qquad (13)$$

where K_{ads} is the Langmuir adsorption constant, S_{max} is the maximum amount of contaminant that can be adsorbed to the soil.

There is no unique amount of Cr(VI) precipitate for a given hexavalent chromium concentration. Therefore it is impossible to estimate mass of this fraction of Cr(VI) is the subsurface using only the measured concentrations in monitoring wells. Thus, natural attenuation of Cr(VI) from mass balances using monitoring well data can only be used when it can be reasonably demonstrated the Cr(VI) precipitates cannot form within the aquifer.

Even when it is demonstrated that the formation of precipitates within the aquifer is unlikely, there are inherent problems with any monitoring system that can create uncertainties in the estimated mass of Cr(VI) during a sampling round. In the three-dimensional flow field, the highest concentrations from one sampling period may migrate between the discrete monitoring points of the next sampling round. The undetected mass is not included in the total mass estimates in the second sampling round and may be mistakenly interpreted as mass loss due to Cr(VI) reduction.

Summary

Under certain conditions, toxic Cr(VI) can be reduced to the less toxic Cr(III) in soils and precipitated as an insoluble hydroxide phase. The possibility of relying on such "natural attenuation" of Cr(VI) is attractive because of the great expense of remediating chromium contaminated sites. Before such an option is adopted, however, it should be demonstrated that natural attenuation is likely to occur under the specific conditions at the site being investigated.

If natural attenuation is to be considered a viable option for chromium contaminated sites, then ideally, it must be demonstrated that 1) there are natural reductants present within the aquifer, 2) the amount of Cr(VI) and other reactive constituents do not exceed the capacity of the aquifer to reduce them, 3) the time scale required to achieve the reduction of Cr(VI) to the target concentration is less than the time scale for the transport of the aqueous Cr(VI) from source area to the point of compliance, 4) the Cr(III) will remain immobile, and 5) there is no net oxidation of Cr(III) to Cr(VI). The most difficult information to obtain is the time scales for the reduction and oxidation of chromium in the soil.

Demonstrating Cr(VI) reduction in aquifer by mass balances that rely primarily on the aqueous concentrations from monitoring well networks are valid only if it is demonstrated that Cr(VI) precipitates are not forming in the aquifer. The monitoring network must be sufficiently dense that estimates of Cr(VI) are accurate.

Several soil tests are described that are useful in determining the mass of Cr(VI) and Cr(III) in the source areas and the reduction and oxidation capacities of the aquifer materials. Some simple conceptual models are presented whereby this information, combined with knowledge of the residence time of the chromium between the source and the point of compliance can be used to determine the feasibility of natural attenuation

of Cr(VI). The major limitation to this approach is the lack of information about the rate of oxidation and reduction of chromium under conditions likely to encountered by plumes emanating from chromium sources. Without better information about these rate processes under a wider range of conditions with respect to pH, the use of the natural attenuation option for contaminated soils will continue to be a highly debated issue.

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