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Processes Affecting the Remediation of Chromium-Contaminated Sites

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The remediation of chromium-contaminated sites requires knowledge of the processes that control the migration and transformation of chromium. Advection, dispersion, and diffusion are physical processes affecting the rate at which contaminants can migrate in the subsurface. Heterogeneity is an important factor that affects the contribution of each of these mechanisms to the migration of chromium-laden waters. Redox reactions, chemical speciation, adsorption/desorption phenomena, and precipitation/dissolution reactions control the transformation and mobility of chromium. The reduction of Cr^{VI} to Cr^{III} can occur in the presence of ferrous iron in solution or in mineral phases, reduced sulfur compounds, or soil organic matter. At neutral to alkaline pH, the Cr^{III} precipitates as amorphous hydroxides or forms complexes with organic matter. Cr^{III} is oxidized by manganese dioxide, a common mineral found in many soils. Solid-phase precipitates of hexavalent chromium such as barium chromate can serve either as sources or sinks for Cr^{VI}. Adsorption of Cr^{VI} in soils increases with decreasing chromium concentration, making it more difficult to remove the chromium as the concentration decreases during pump-and-treat remediation. Knowledge of these chemical and physical processes is important in developing and selecting effective, cost-efficient remediation designs for chromium-contaminated sites.

Introduction

Chromium is an important industrial metal used in the manufacture of many diverse products including alloys, chemicals, and refractories (*1,2*). Approximately 58% of the chromium used in the United States is for metallurgical purposes such as the manufacture of ferrous and nonferrous alloys. Another 23% is produced by the chemical industry for use in pigments, electroplating, leather tanning, fungicides, corrosion inhibitors in cooling water and drilling muds, wall paper, photographic films, magnetic tapes, printing inks, and many other products. Chromium is also used as a catalyst in the synthesis of many organic chemicals. The manufacture of refractories such as chromite and chrome-magnesite bricks accounts for an additional 18% of U.S. utilization of chromium.

Many minerals contain high percentages of chromium, however, chromite ($FeCr_2O_4$) is the only economically important ore mineral. Although chromium is extremely important to U.S. industry, virtually none of it is currently mined within the U.S. Currently, the principal sources of this ore are deposits in South Africa, Zimbabwe, and Finland (*3*). However, from 1828 to 1850, chromite deposits in Maryland were the world's main source of this ore (*4*). Between the early 1900s and 1970, much of the imported ore was processed in New Jersey.

Processing of the ore for the manufacture of Cr^{VI} compounds involves roasting the ore with soda ash (Na_2CO_3) and lime. The material is then leached with water to remove the soluble Na_2CrO_4. This process may be repeated a second time to recover additional Cr^{VI}. At the end of the process there is a waste residue or "mud" that contains $CaCrO_4$, calcium aluminochromate ($3CaO{\cdot}Al_2O_3{\cdot}CrO_4$), tribasic calcium chromate [$Ca_3(CrO_4)_2$], and basic ferric chromate [$Fe(OH)CrO_4$] that dissolve in and add hexavalent chromium to percolating waters (*5*).

Chromium can enter the environment by several natural processes as well as from human activities. For example, naturally elevated levels of hexavalent chromium have been found in Paradise Valley, Arizona (*6*). Chromate and dichromate mineral phases have been found in the Atacama Desert in Chile (*7*). This paper focuses on the processes that affect the remediation of sites contaminated by chromium as a result of human activities associated with manufacturing and ore processing. Knowledge of these physical and chemical processes is required if efficient and cost-effective

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remediation of chromium-contaminated sites is to be attained.

Chromium-Contaminated Sites

Leakage, poor storage, and improper disposal practices at manufacturing and ore processing facilities have released chromium to the environment, causing contamination of groundwater and surface water (*8*). For example, 27 Superfund sites for which Records of Decision had been signed before 1987 report chromium as being a potential problem (*9*). One of most widely known cases of groundwater contamination by chromium is the Nassau County site on Long Island, New York (*10–15*). The source of the chromium contamination was a recharge basin used for the disposal of solutions from an aircraft plant. Discharge of untreated wastes occurred between 1941 and 1949. The concentration of Cr^{VI} in the discharged water is believed to have been approximately 40 mg/L. A treatment plant was installed in 1949 that reduced concentrations, but they remained as high as 35 mg/L. A thin and elongated plume of Cr^{VI} migrated 1300 m down gradient from the waste disposal basins, where it then discharged into Massapequa Creek. The chromium appeared to be migrating with the same velocity as the groundwater. This is surprising because the pH of the groundwater is in the range of 4.6 to 6.2 and some adsorption of the Cr^{VI} is expected.

In contrast to the nearly conservative behavior of Cr^{VI} at the Long Island site, a plume of chromium-contaminated water emanating from a tailings pond in Telluride, Colorado, was found to move at a rate only one-tenth the groundwater velocity (*16,17*). The aquifer material was sand and gravel, and the pH of the groundwater was approximately 6.8. Adsorption and extraction tests that have been conducted on the soils are discussed below.

Very high levels of groundwater contamination by hexavalent chromium have occurred at the United Chrome Products site in Corvallis, Oregon (*18*). The United Chrome Products site was a hard chrome plating facility that operated from 1956 until May, 1985. Between 1956 and 1975, a dry well was used to dispose of floor drippings, washings, and product rinsates. After operations ceased, it was discovered that the process tanks had been leaking directly to the groundwater. The contaminant plume is approximately 100 m in length, and the chromium-contaminated water has discharged into the local drainage system. Reported concentrations of hexavalent chromium in groundwater are as great as 14,600 mg/L (14.6 g/L). Soils contain as much as 25,900 mg/kg (2.6%) chromium. A pump-and-treat groundwater remediation system is currently in place, and as of June 1, 1990, an estimated 18,600 lbs of chromium have been removed from the subsurface (Randy Pratt, CH2M-Hill, personal communication). Geochemical characterization of the site is currently in progress to determine the specific chemical processes that limit the existing pump-and-treat system.

Several other locations around the country illustrate the variety of sites where chromium contamination can occur. For example, Frontier Hard Chrome (Vancouver, Washington) is another hard chrome plating facility that disposed of rinsates down a dry well (*19*). High levels of chromium have been found in a private well adjacent to the Palmetto Wood Preserving Site in Dixiana, South Carolina (*20*). This facility used fluoride-chromate-arsenate-phenol and acid-copper-chromate processes for treating wood. In Hudson County, New Jersey, waste "mud" from the processing of chromite ore had been used as "clean fill" for residential, commercial, and public buildings (*21*). This material contains as much as 2.5% Cr^{VI} and is believed to be responsible for the contamination of soils and waters in the area. The facilities that generated this material operated for 70 years. As many as 110 sites containing this waste mud have been identified. The total amount of chromium in the sites is estimated to be at least 160 million lbs.

In an effort to minimize the risk of exposure to the public, regulatory agencies are now demanding the cleanup of chromium-contaminated water and soils. The initial stages of such clean-up can often be accomplished in a relatively short period of time by removing potential contaminant sources, removing highly contaminated shallow soils, and in some cases installing a low permeability cap. In contrast, remediation of the subsurface is often an inexact process that can take many years and cost millions of dollars. If optimal remedial strategies are to be found for chromium-contaminated sites, then some understanding of the physical and chemical processes affecting the migration and chemical state of chromium is required.

Physical Processes Affecting Migration of Chromium in the Subsurface

The transport of a dissolved substance, such as chromium, in groundwater is often described in terms of the advection-dispersion equation, which is written in its one-dimensional form as:

$$D\partial^2 C / \partial x^2 - v_w \partial C / \partial x = \partial C / \partial t \pm \mathrm{RXN} \qquad (1)$$

where C is the concentration of the contaminant, v_w is the velocity of the groundwater, D is the dispersion coefficient, and RXN is a generalized term to represent chemical reaction terms. The rate and direction of migration of chromium, like any other dissolved contaminant, are influenced by hydraulics of groundwater flow. The velocity of a parcel of groundwater, v_w, is given by a modified form of Darcy's equation:

$$v_w = -(K / \theta_s)(dh / dx) \qquad (2)$$

where K is the hydraulic conductivity of the aquifer, dh/dx is the hydraulic gradient, and θ_s is the porosity of

the aquifer. These parameters can be obtained through several field and/or laboratory tests (*22,23*). Once they are known, one can, in principle, predict the rate and direction of movement of the groundwater. If extraction (injection) wells are present, the drawdown (rise) in the potentiometric surface due to groundwater withdrawal (injection) will be superimposed on the natural ground water gradient. Thus, the rate at which a parcel of water moves from a given location in the aquifer to another depends on *a)* the hydraulic conductivity of the aquifer, *b)* the porosity of the aquifer, *c)* the distance from the extraction (injection) well, *d)* the rate of groundwater withdrawal (injection), and *e)* the magnitude and direction of the natural groundwater gradient.

Dispersion is often a process that is invoked to describe the spreading of the solute concentrations about mean advective flow path. It is composed of velocity-dependent hydrodynamic component and a molecular diffusion component:

$$D = \alpha v_w + D_m \qquad (3)$$

where α is the longitudinal dispersivity parameter, and D_m is an effective molecular diffusion coefficient. Mathematical solutions of Eqs. (1) through (3) (subject to appropriate boundary conditions) have often been used in the past to argue that dispersion would cause substantial dilution of contaminant plumes. However, misinterpretation of the actual processes has led to apparently scale-dependent values of the dispersivity parameter (*24*). Carefully monitored field tests (*25–27*) have indicated that the dispersivity parameter and hence the dispersion coefficient is very small, that flow is predominantly advective, and that heterogeneities are a key factor controlling the concentrations of non-reactive, conservative tracers. Thus, a decline in concentrations of chromium in subsurface waters is not likely to be the result of hydrodynamic dispersion processes but is more likely the result of nonhydrodynamic processes such as molecular diffusion or chemical reactions.

Chemical Processes

Oxidation-Reduction and Chemical Speciation

Chromium exists in oxidation states ranging from 0 to +6. Under reducing conditions, Cr^{III} is the most thermodynamically stable form of the oxidation states (*28*); however, Cr^{VI} can remain metastable for long periods of time. At concentrations less than 10 mM or at neutral pH, Cr^{VI} exists as $H_2CrO_4^0$, $HCrO_4^-$ and CrO_4^{2-} that are involved in the acid dissociation reactions:

$$H_2CrO_4^0 \leftrightarrows H^+ + HCrO_4^- \qquad ; K_1$$

$$HCrO_4^- \leftrightarrows H^+ + CrO_4^{2-} \qquad ; K_2$$

that have pK values of 0.86 and 6.51, respectively (*29*). Thus, CrO_4^{2-} is predominant above pH 6.5, $H_2CrO_4^0$ predominates only if the pH is below 0.9, and $HCrO_4^-$ predominates in the pH range 0.9 to 6.5 (Fig. 1). Although these boundaries shift with ionic strength and temperature, they are reasonable demarcations between the dominant aqueous forms. Under acid conditions and for total concentrations of Cr^{VI} greater than 10 mM, $HCrO_4^-$ polymerizes to form dichromate, $Cr_2O_7^{2-}$ (*30*).

$$HCrO_4^- + HCrO_4^- \leftrightarrows Cr_2O_7^{2-} + H_2O \qquad ; K_d$$

with a pK of –1.54 (*29*). The dominance of the chromate ions ($HCrO_4^-$ and CrO_4^{2-}) in chromium-contaminated waters is recognized by the yellow color imparted to the water in concentrations above 1 mg/L. The presence of dichromate is seen as an orange color in contaminated water.

The predominant form of Cr^{III} in a Cr^{III}-H_2O system at pH less than 3 is Cr^{3+}. The hydrolysis of Cr^{III} with increasing pH has been recently reviewed and studied by Rai et al. (*31*). Their data suggest that the most important species are $CrOH^{2+}$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$, with $Cr(OH)_2^{2-}$ occurring in the very narrow pH band between 6.27 and 6.84 (Fig. 1). They found no evidence of polynuclear complexes of the form $Cr_m(OH)_n^{3m-n}$.

Cr^{III} can form complexes with several organic ligands and polymers (*32,33*). Cr^{III} remains in solutions containing citric acid and diethylenetriaminepentaacetic acid (DTPA) at much higher pH than in water (*33*). Similar tests with a reagent-grade fulvic acid resulted in a pre-

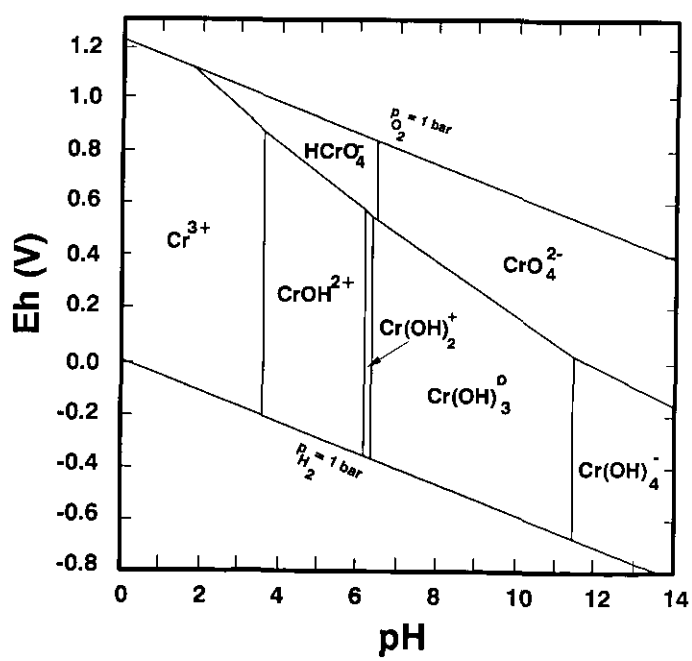

FIGURE 1. Eh-pH diagram for aqueous chromium species in a chromium-H_2O system. Based on data from Rai et al. (*31*), Wagman et al. (*99*), Hem (*100*), and Barner and Scheuerman (*101*).

cipitate believed to be a humic acid impurity. At higher concentrations of fulvic acid and in solutions of water-soluble soil organic matter, Cr^{III} was complexed and kept at elevated levels at higher pH than in pure water. Longer term tests with citrate show decreases in the Cr^{III} concentration with time. James and Bartlett (*33*) suggest that this is the result of the adsorption of the chromium-citrate followed by microbial degradation of the citrate.

Cr^{VI} is a strong oxidant and is reduced in the presence of electron donors such as Fe^{II}. The Cr^{VI} state is generally considered to pose the greatest human health risk because it is more toxic, more mobile, and more soluble than Cr^{III}. Therefore, the reduction of Cr^{VI} to Cr^{III} is an important process with regard to aquifer remediation. The transformation of Cr^{VI} to Cr^{III} within soils is likely to occur as a result of reduction by ferrous iron in solution; ferrous iron minerals; reduced sulfur compounds; or soil organic matter.

While the oxidation states of +3 and +6 are the most commonly encountered in the environment, Cr^{V} and Cr^{IV} are important intermediate states that influence the rate of reduction of the hexavalent form. Cr^{VI} does not always convert directly to Cr^{III} but may be initially reduced to either Cr^{V} or Cr^{IV}. Many reduction experiments follow a rate law for one-equivalent reducing agents that assumes that the concentration of Cr^{V} is a steady-state value, the rate of oxidation of Cr^{IV} to Cr^{V} is negligible, and the reduction of Cr^{V} to Cr^{IV} is the rate-limiting step (*30*). For two-equivalent reducing agents, the reduction of Cr^{VI} to Cr^{IV} is often the initial and rate-limiting step. Unfortunately, most of these rate laws have been developed for very high concentrations and extreme pH conditions, and their applicability to environmental conditions has yet to be explored.

The reduction of Cr^{VI} by ferrous iron can be described by the overall reaction:

$$Cr^{VI} + 3Fe^{II} \rightarrow Cr^{III} + 3Fe^{III}$$

This reaction appears to be appropriate for pH less than 10 and for PO_4 concentrations less than 0.1 mM. Above pH 10, the rate of oxidation of the ferrous iron by dissolved oxygen is greater than the rate of oxidation of ferrous iron by CrO_4. PO_4 is known to increase the rate of oxidation of Fe^{II} by dissolved oxygen (*34*). The Cr^{III} and Fe^{III} can hydrolyze, combine, and precipitate in a solid solution series (see next section). This reaction was found to be very rapid, with equilibrium being established in less than 5 min even in the presence of dissolved oxygen (*34*).

Fe^{II}_{aq} is not always present in significant concentrations in subsurface waters, however, a major source of Fe^{II} may be found in mineral phases that are present in the geologic units. For example, the minerals hematite (which contains some FeO) and biotite are capable of reducing Cr^{VI} (*35*). For both mineral phases, the reduction of the Cr^{VI} appears to be occurring in solution and not at the mineral surface itself. Therefore, the rate of reduction of the Cr^{VI} depends on the rate of dissolution of the FeO component in the mineral phases. For biotite, it is suggested that once the Fe^{II} has been oxidized, the resulting Fe^{III} reacts with the Fe^{II} in the mineral according to

$$[Fe^{II},K^+]_{biotite} + Fe^{3+} \rightarrow [Fe^{III}]_{biotite} + K^+ + Fe^{2+}$$

(*35,36*). This reaction can be driven by the continual oxidation of the Fe^{II} by Cr^{VI}. This Fe^{II}_{aq} ion is then available for the further reduction of Cr^{VI}. The resulting Fe^{III} is reduced at the surface of the biotite, continuing the cycle. The rate of reduction of Cr^{VI} by hematite and biotite increases with increasing ratio of surface area to solution volume and is greater under acid conditions than under neutral or alkaline conditions (*35*).

Other common mineral phases may be effective in reducing Cr^{VI} to Cr^{III} in the subsurface. For example, iron sulfides can be excellent sources of ferrous iron. The observation that iron in the octahedral sites of iron-rich smectite can be readily oxidized by O_2 and reduced by sodium dithionite ($Na_2S_2O_4$) (*37*) suggests that the octahedral iron may also reduce Cr^{VI}. Other phyllosilicates such as chlorite contain significant amounts of ferrous iron that may reduce Cr^{VI} in a manner similar to biotite.

Cr^{VI} can be reduced by sulfur compounds such as sulfide and sulfite. Although sulfide can reduce Cr^{VI}, studies indicate that ferrous iron must be present to act as a catalyst (*38*). This suggests that iron sulfide minerals present in some aquifer materials may effectively reduce Cr^{VI}. Work by Lancy (*39*) supports this suggestion; however, the method may not be effective in a large volume treatment process because the rate of reaction is relatively slow. In the presence of excess sulfite, the reduction of Cr^{VI} follows the reaction

$$6H^+ + 2HCrO_4^- + 3HSO_3^- \rightarrow 2Cr^{III} + 2SO_4^{2-} + S_2O_6^{2-} + 6H_2O$$

The $S_2O_6^{2-}$ can then reduce ferric iron if it is present. The reduction in the presence of excess Cr^{VI} follows

$$5H^+ + 2HCrO_4^- + 3HSO_3^- \rightarrow 2Cr^{III} + 3SO_4^{2-} + 5H_2O$$

(*30*). These reactions are believed to occur as one-step, three-equivalent reductions. The treatment process at the United Chrome Products site involves a reduction step using sodium bisulfite in the presence of sulfuric acid.

Another important soil constituent that contributes to the reduction of Cr^{VI} in the subsurface is soil organic carbon (SOC). The amount of reduction of dichromate by soil is often used as a measure of SOC (*40*). The overall reaction can be idealized as

$$2Cr_2O_7^{2-} + 3C^0 + 16H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$$

The reaction consumes hydrogen ions and therefore is

likely to be more rapid in acidic environments than in neutral or alkaline environments. Cr^{VI} is known to be reduced by functional groups such as carboxylic acids, alcohols, and phenols (*41*) commonly found in humic substances (*42*) or as contaminants in association with chromium. For example, oxalic acid can serve as a two-equivalent reducing agent for Cr^{VI} (*30*). The reduction of Cr^{VI} by isomeric cresols was found to be pseudo-first order in the pH range of 1 to 5 (*43*).

In many soils, a substantial fraction of the SOC is in the form of humic substances: humic acid (HA), fulvic acid (FA), and humin. Investigations reveal that FA and HA can reduce a variety of metal ions. Redox reactions involving HA and FA have been studied for a number of redox couples including Mo^{VI}/Mo^{IV}, V^{V}/V^{IV} (*44–46*), Fe^{III}/Fe^{II} (*47*), Hg^{II}/Hg^{0} (*48*), and I^{0}/I^{-1} (*49*). Reports of the standard reduction potential, E_0, for FA and HA indicate that FA is a better reducing agent than HA and that both have the potential for reducing Cr^{VI} (Fig. 2).

The presence of SOC has been demonstrated to reduce Cr^{VI} at pH above 7.0 (*50,51*). Bartlett and Kimble (*50*) found that reduction did not occur in an essentially organic-free soil unless an external source of organic matter was added, in this case cow manure. Even then, reduction did not occur until pH was lowered. They

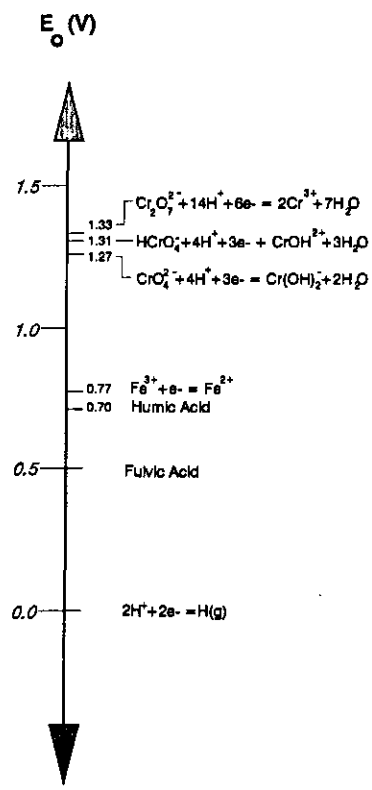

FIGURE 2. Standard electrode potentials for key reactions involving the reduction of chromium. Data from Wilson and Weber (*46*), Szilagyi (*47*), and Skogerboe and Wilson (*49*).

state that soil organic matter is more effective than cow manure at reducing Cr^{VI}. This observation may indicate that as organic matter becomes more "humified," it develops more reactive reducing sites. Bloomfield and Pruden (*51*) found that water-soluble soil organic matter was effective in reducing hexavalent chromium at pH less than 4 but not effective at pH greater than 5. Adsorbed forms of Cr^{VI} are, in some cases, more easily reduced than soluble forms in limed soils (*52*). The addition of fulvic acid to groundwater samples spiked with Cr^{VI} showed significant reduction, particularly in acidified samples (*53*). The rate of reduction was much less at 4°C than at 25°C.

The reduction of Cr^{VI} can also occur as a result of photoreduction reactions. Studies of photoreduction of Cr^{VI} on ZnO in neutral to alkaline solutions (*54*) have shown that large percentages of Cr^{VI} can be reduced (30 to 70%). The reaction likely occurs as the two half-cell reactions

$$CrO_4^{2-} + 8H^+ + 3e^-_{sc} \rightarrow Cr^{III} + 4H_2O$$

$$H_2O + 2h^+_{sc} \rightarrow \tfrac{1}{2}O_2 + 2H^+$$

where sc denotes that semiconductor and h^+_{sc} denotes a "hole" in the semiconductor where electrons have been displaced. The percentage of Cr^{VI} that is photoreduced is not greatly influenced by SO_4^{2-}, NO_3^-, or Cl^-, and other anions but is influenced by the cations in solution.

ZnO is not commonly found in streams and other surface waters, but these results indicate that photoreduction of other semiconductors such as iron oxides is possible. Amorphous ferric hydroxides and aqueous ferric iron present in streams may be photoreduced to ferrous ions (*55,56*). The ferrous iron would then be available for oxidation by either dissolved oxygen or Cr^{VI}. For pH less than 10, the rate of oxidation by Cr^{VI} is greater than the rate of oxidation by dissolved oxygen (*34*), therefore most of the ferrous iron could be used for the reduction of Cr^{VI}.

While there are many potential mechanisms for the reduction of Cr^{VI} to Cr^{III}, the potential mechanisms for the oxidation of Cr^{III} to Cr^{VI} appear to limited to oxidation by oxygen or by manganese oxides. However, recent studies have found that oxygen does not react appreciably with Cr^{III} (*57*). Bartlett and James (*58*) observed the correlation between the amount of Cr^{III} oxidized by soils and the amount of hydroquine-reduced manganese in the soils. They found that Cr^{III} was not oxidized in dry soils but it is oxidized in soils that are maintained in a moist condition. The drying of soils alters the surface of the manganese oxides by reducing the manganese and decreasing its ability to oxidize the Cr^{III}. The rate and amount of Cr^{III} oxidation by β-MnO_2 (pyrolusite) increases with increasing ratio of surface area to solution volume and with decreasing pH (*57*). In these same tests, it was observed that oxygen does not catalyze the reaction between β-MnO_2 and Cr^{III}. The stoichiometry of the oxidation of Cr^{III} by β-MnO_2 is

complex, and the exact reaction mechanism is not known. It is believed, however, that the desorption of $HCrO_4^-$ and the formation of a secondary manganese phase (MnOOH) may play important roles in the oxidation of the Cr^{III} (*57*).

Precipitation-Dissolution

Solid phases can play an important role in choosing an optimal remedial strategy. Both Cr^{III} and Cr^{VI} solid phases can be important. Recent experiments (*31*) indicate that between pH 6 and pH 12, Cr^{III} concentrations are limited by the formation of Cr^{III} hydroxide (Fig. 3). Rai et al. (*31*) found that the $Cr(OH)_3$ precipitated in their experiments was amorphous. However Swayambunathan et al. (*59*) found crystalline $Cr(OH)_3 \cdot 3H_2O$ precipitated from their chrome-alum and potassium hydroxide solutions. Eskolaite (Cr_2O_3) formed as their solution was heated to 100°C. In some cases, chromium hydroxide solid solutions may precipitate rather than pure $Cr(OH)_3$. In particular, if Fe^{III} is present within the aquifer, then an amorphous $Cr_xFe_{1-x}(OH)_3$ solid solution will form (*60,61*). This case is particularly important because of the potential reduction of hexavalent chromium by Fe^{II} followed by the precipitation of $Cr_{0.25}Fe_{0.75}(OH)_3$ (*34,60*). The solubility of the $Cr_xFe_{1-x}(OH)_3$ decreases with decreasing fraction of Cr^{III}.

Several hexavalent chromium phases can act as either sinks or sources for Cr^{VI}. Powder X-ray diffraction data of plating tank sludges disposed at the United Chrome Products site in Corvallis, Oregon, were found to contain $PbCrO_4$ (crocoite), $PbCrO_4 \cdot H_2O$ (iranite), and K_2CrO_4 (tarapacaite) as well as an unidentified mineral phase (*62*). The source of the lead is from the electrodes used in the plating process. The solubility of lead chromate is very low ($pK_{sp(crocoite)}$ = 13.68), and therefore it is not likely to serve as a source of Cr^{VI}. At high Cr^{VI} concentrations, these mineral phases may be more effective as a sink for lead rather than Cr^{VI}. K_2CrO_4 is highly soluble (>3.2 M Cr) (*28*) and can be a significant source of Cr^{VI}.

A yellow chromium salt was precipitating under evaporative conditions in a drainage ditch at the United Chrome Products site. The mineral was identified as $CaCrO_4$ (chromatite) by powder X-ray diffraction and chemical analysis (*62*). This mineral was observed to accumulate during the summer months but was not seen in the fall when there was greater precipitation and water levels within the drainage ditches were higher.

Rai et al. (*63*) have suggested that $BaCrO_4$ (hashemite) might be an important Cr^{VI} mineral phase that could form within soils at chromium-contaminated waste sites. These authors demonstrated that this mineral forms a continuous solid solution with $BaSO_4$ (barite). Solubility constants were given for several compositions with the general formula $Ba(Cr_rS_{1-r})O_4$. The ion activity products for laboratory soil/solution tests conducted by adding hexavalent chromium to soil mixtures appear to follow the solubility curves. Preliminary data for the United Chrome Products site (*62*) over a pH range of 3.8 to 7.5 indicate that the ion activity product (uncorrected for ionic strength effects) follows the $BaCrO_4$ solubility curve (Fig. 4), suggesting precipitation of that phase within the subsurface. The existence of such a mineral phase can significantly extend the time required to remediate an aquifer by pump and treat.

Mechanisms for the coprecipitation of Cr^{VI} with trivalent ions have been suggested. Bartlett and Kimble (*50*) found that the concentration of Cr^{VI} varied with

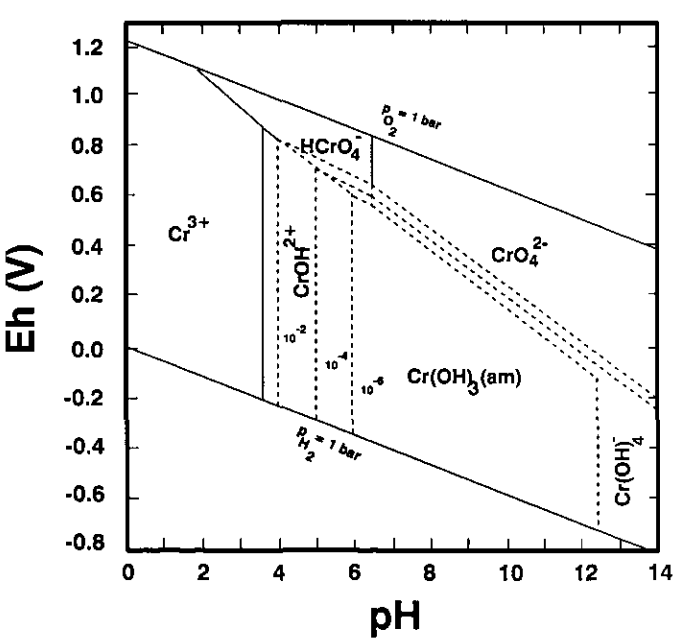

FIGURE 3. Eh-pH diagram for aqueous chromium species in equilibrium with amorphous $Cr(OH)_3$ in chromium-H_2O system. Based on data from Rai et al. (*31*), Wagman et al. (*99*), Hem (*100*), and Barner and Scheuerman (*101*).

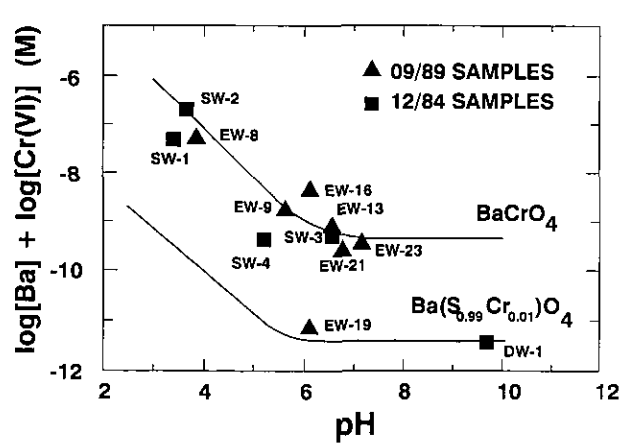

FIGURE 4. Solubility product of $BaCrO_4$ at the United Chrome Products site, Corvallis, Oregon. Data have not been corrected for ionic strength effects. Theoretical solubility curves from Rai et al. (*63*).

pH in an $AlCl_3$ solution and suggest that Cr^{VI} is coprecipitated with aluminum. However, they do not differentiate between adsorbed Cr^{VI} and precipitated Cr^{VI} in this particular experiment. James and Bartlett (*52*) suggest that Cr^{VI} may be coprecipitated with Cr^{III} hydroxide in the form $Cr(OH)_2HCrO_4$. These conclusions were based on the use of several extractants applied to both freshly precipitated and aged $Cr(OH)_3$. More Cr^{VI} was extracted from the aged $Cr(OH)_3$ than from the freshly precipitated material. However, Eary and Rai (*34*) found that the reduction of Cr^{VI} by ferrous iron proceeded stoichiometrically with the oxidation of three ferrous ions for every Cr^{VI} ion reduced, indicating coprecipitation of $Cr^{III}$and Cr^{VI} did not occur in their experiments.

Adsorption-Desorption

Other processes that can either remove or add Cr^{VI} from solution are adsorption and desorption reactions. For pH greater than 1, the predominant forms of Cr^{VI} in solution are the anionic forms $HCrO_4^-$, CrO_4^{2-}, or $Cr_2O_7^{2-}$. General observations of the adsorption of anions reveal that a greater fraction of anions tend to be adsorbed at lower pH than at higher pH. Also, Dzombak and Morel (*64*) note that anions generally tend to follow Langmuir-type isotherms:

$$S = S_{max}KC/(1 + KC) \tag{4}$$

where S (M/M) is the concentration on the soil, S_{max} (M/M) is the maximum concentration of potential adsorption sites on the soil, K (L^3/M) is the Langmuir adsorption constant, and C (M/L^3) is the concentration in the groundwater. Therefore, the general expectation is that Cr^{VI} will be more mobile under neutral to alkaline conditions than under acid conditions, and the adsorption isotherm will behave as a Langmuir-type isotherm.

These expectations are confirmed by various studies on the adsorption of Cr^{VI} on soils and ideal adsorbents. Griffen et al. (*65*) found Cr^{VI} adsorption onto kaolinite and montmorillonite increased with decreasing pH. A detailed study of Cr^{VI} adsorption onto kaolinite found a similar dependence on pH. Adsorption tests on amorphous iron hydroxide (*66–71*), geothite (*71*), α-Al_2O_3 (*66,68*), and α-TiO_3 (*68*) also show increased adsorption at lower pH. Griffin et al. (*65*) obtained Langmuir-type plots at pH 3, 4, 5, and 7 for both the montmorillonite and the kaolinite they studied. Stollenwerk and Grove (*16*) obtained linear Langmuir plots for the alluvial soils obtained from the Telluride, Colorado, area. However, their data for soils showed two linear segments, one for aqueous concentrations greater than 58 μM and another for aqueous concentrations less than 58 μM. They suggest that the two segments may represent two different mechanisms for adsorption: a specific chemical binding mechanism and a nonspecific electrostatic binding mechanism. Similar, two-series Langmuir plots were obtained for kaolinite by Zachara et al. (*72*) and for several soils (*73*).

A more general approach to adsorption phenomena is to use surface complexation models (*64*). Such models have been shown to be able to replicate experimental data on ideal adsorbents such as hydrous ferric oxides (*64,67,68*). A surface complexation model has been applied to the adsorption of chromate onto amorphous $Fe_2O_3 \cdot H_2O$ in the presence of several inorganic compounds (*67*). Other anions can influence the amount of Cr^{VI} adsorbed onto the soil, but cations have vary little effect. In particular, the common groundwater constituents $CO_{2(aq)}$, H_4SiO_4, and SO_4^- can significantly reduce Cr^{VI} adsorption. However, SO_4^- has little influence on the adsorption of Cr^{VI} on kaolinite and in one case apparently enhanced Cr^{VI} adsorption (*72*).

In addition to amorphous forms of iron, geologic materials often contain the crystalline iron oxide goethite (α-FeOOH) (*74*). Adsorption studies on synthetic geothites have shown that the method of preparation of the geothite can affect the site density on the geothite (*71*). Excellent fits of the adsorption data were obtained with the use of a triple-layer model over the pH range of 4 to 10.

While the study of adsorption onto ideal mineral phases can increase our understanding of adsorption processes, natural mineral phases often exist as parts of solid solutions and contain imperfections. For example, goethite in soils often contains aluminum substituting for Fe^{III} that can be a great as 33 mole% (*75*). The adsorption of Cr^{VI} onto the surface of such aluminum-substituted geothites is less than for pure geothite. However, the adsorption can be simulated by two-site surface complexation model that ignores adsorption onto the aluminum-O sites (*71*).

Zachara et al. (*73*) have provided some of the most detailed studies of the adsorption of chromate on soils. As expected, they found that the amount of adsorption generally increased with decreasing pH and that soils that contained higher concentrations of aluminum and ion oxides exhibited greater adsorption of Cr^{VI}. As with experiments utilizing synthetic iron precipitates, Cr^{VI} adsorption was depressed by the presence of SO_4^{2-} and dissolved inorganic carbon. Adsorption was greatly reduced after treatment with dithionite-citrates-bicarbonate (DCB), suggesting that adsorption was primarily on crystalline iron. Adsorption on the soils could be modeled using a triple-layer model and by using adsorption constants of model iron oxides. While these simulations could accurately model the pH adsorption edge above the pH where 50% of the adsorption occurs, it overestimated adsorption at lower pH. Moreover, the model is not unique. Adsorption on the oxidic and montmorillonitic soils used in their experiments could also be simulated by assuming Cr^{VI} adsorption onto kaolinite. However, this latter simulation requires a site density that is 10 times greater than that obtained from crystallographic methods (*73*).

Implications to Remedial Strategies

The physical and chemical processes described above can have direct implications to the design of the remedial system. Several common remediation strategies include the no action option, excavation and removal of the contaminated soil, pump-and-treat remediation, and soil solidification/ stabilization. Vitrification, chemical enhancements to pump-and-treat, and geochemical barriers are less frequently considered options that are likely to receive more attention in the near future. While this list is not exhaustive, it does provide a basis for evaluating potential application of these or other methods.

No Action

Remedial actions are expensive and should not be undertaken at sites where the combination of potential risk of exposure and potential impact to environment are marginal. If the contaminant is not likely to migrate from the site, then the no-action option may be viable. Cr^{VI} transport is affected by all of the chemical processes described above. However, adsorption only retards the rate of advection of the Cr^{VI}; it does not prevent the migration of the Cr^{VI} from the site. Therefore, adsorption reactions are not an important consideration in the no-action option except for how they affect other rate-dependent processes.

Oxidation-reduction and precipitation-dissolution reactions can be very important processes in the consideration of the no-action option. If ferrous iron, soil organic carbon, or some other reductant is present within the subsurface, then the more toxic Cr^{VI} can be transformed to the less toxic Cr^{III} form. For pH between 6 and 12, Cr^{III} precipitates as an amorphous hydroxide and the $Cr^{III}(aq)$ concentrations, controlled by the solubility product of $Cr(OH)_{3(amorph)}$ should be less than 10^{-6}M (Fig. 5) (*31*). If the reductant is ferrous iron, the solid solution series $Cr_xFe_{1-x}(OH)_3$ should precipitate and the $Cr^{III}_{(aq)}$ should remain below 10^{-6} M at pH as low as 4.5 (*60*).

There are several tests for determining if the reduction of Cr^{VI} is likely to occur within the subsurface (*76*). One of these tests is the total Cr^{VI} reducing capacity. Use of this test at the United Chrome Products site yields values of 10 (mg of Cr^{VI} reduced)/(g of soil). With a dry build density of 1.47 and the porosity of 0.47, the aquifer would have a total capacity for reducing 30,000 mg of Cr^{VI} per liter of water in contact with the soil matrix. Alternatively, if the groundwater contained 1000 mg/L Cr^{VI} and all of it was reduced as it passed through the soil, then 30 pore volumes could pass through the soil before the total reduction capacity would be exhausted. The total reduction capacity test is conducted in very acidic solutions and may not reflect the reduction capacity available at field pH.

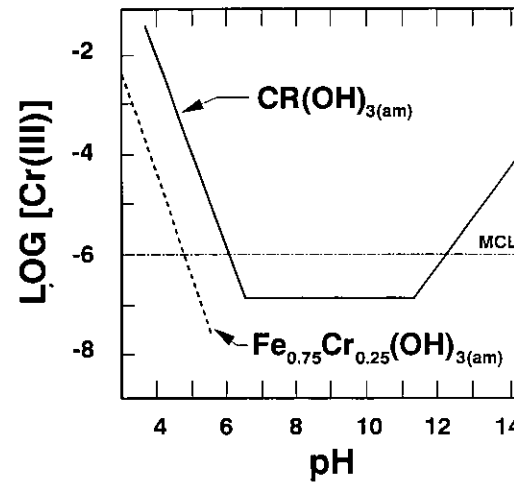

FIGURE 5. Cr^{III} concentrations in equilibrium with $Cr(OH)_3$ and $Fe_{0.75}Cr_{0.25}(OH)_3$. Based on data from Rai et al. (*31*) and Sass and Rai (*60*), respectively.

Excavation

In the past, contaminated soils have been excavated and removed from the site to a hazardous waste landfill. However, this option is now less desirable as *a*) regulatory agencies are beginning to view this as simply moving the problem from one locality to another, *b*) the cost of landfilling hazardous waste is increasing, and *c*) the potential risk of exposure may be increased by excavation process. In addition to removing contaminated soils form the site, excavation may also be used as part of an on-site treatment processes. Contaminated soils are excavated and then run through a treatment train that removes the contaminant, changes the redox state of the contaminant, or reduces the hydraulic properties of the soil.

A key disadvantage of soil excavation is that as the chromium-contaminated soils are removed, evaporation may concentrate the hexavalent chromium and precipitate it as soluble phases such as $CaCrO_4$. Precipitation of this phase has been observed under evaporative conditions at the United Chrome Products site (*62*). A review of animal carcinogenicity studies of chromium compounds (*77*) identified $CaCrO_4$ as a compound that causes tumor formation following inhalation. Another disadvantage to excavation is that contaminant plumes often have a vertical component of flow that carries the contaminants deeper into the aquifer while leaving the down-gradient surface soils uncontaminated (Fig. 6). Thus, large quantities of uncontaminated soils may have to be removed to get to the underlying contaminated materials.

Pump and Treat

Contaminated water can be pumped to the surface and either treated on site or at nearby treatment plant.

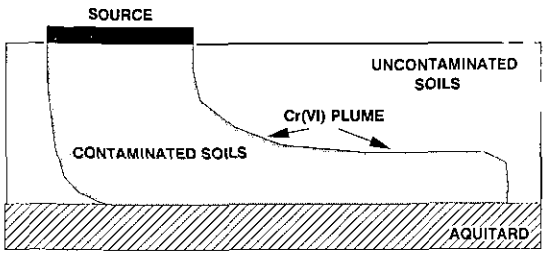

FIGURE 6. Chromium plume transported into lower portion of an aquifer as a result of vertical gradients. Soils above the plume are uncontaminated.

This "pump-and-treat" method is one of the most commonly used methods for aquifer remediation (*9*). It is used for two purposes: to remove contaminants from the subsurface for treatment and to maintain gradient control so as to prevent the contaminants from migrating farther from the site (*78*). A consequence of the latter option is, of course, that the contaminated water must be treated before discharge. While the concentrations of contaminants are initially high in the extraction well, with continued pumping they decrease to values that are significantly lower than the initial concentrations. One of the main concerns with using pump and treat as a method for removing contaminants from the subsurface is that these residual concentrations are above the maximum contaminant levels (MCLs) and will persist for long periods of time (Fig. 7). This behavior has been substantiated by recent report on ground water extraction systems at 19 hazardous waste sites in the U.S. and Canada (*78*). This tailing in the concentration-versus-time curve for the extraction wells is the result of several physical and chemical processes including *a*) the differential time it takes the contaminants to be advected from the boundary of the plume to the extraction well *b*) diffusive mass transport within spatially variable sediments, *c*) mass transfer from residual solid phases or residual and pooled nonaqueous phase liquids in the aquifer, and *d*) sorption/desorption processes (*79-81*).

Groundwater flows not only in response to an extraction well but also to the natural hydraulic gradient superimposed over the draw-down cone. As a result, not all of the water in the vicinity of an extraction well enters the well. Instead, there is a limited area, the capture zone, from which the extracted water is derived (Fig. 8). At the stagnation point, located down gradient from the well, the velocity toward the well equals the velocity induced by the natural gradient, the net velocity is zero, and there is little change in the concentrations of the contaminant during the pump-and-treat remediation.

The groundwater velocity of a parcel of water moving along a streamline from the edge of the plume to the extraction well (line *A* in Fig. 8) travels more quickly than a particle of water traveling along a streamline along the outside of the capture zone (line *B*). The differential time it takes the contaminated water to flow along individual streamlines from the edge of the contaminant plume to the extraction well is controlled by the thickness of the aquifer, the rate of groundwater extraction, the natural groundwater gradient, and the gradient induced by other injection/extraction wells. As the uncontaminated groundwater reaches the well, the concentration of the contaminant in the extraction water decreases (Fig. 9), and the concentration versus time curve exhibits tailing.

Geologic materials are by their very nature heterogeneous. Under a given hydraulic gradient, groundwater moves through the higher permeability layers, while the water in the lower permeability layers remains relatively immobile (*82,83*). Contaminants that have entered the subsurface and have remained there for decades have had time to migrate into these lower permeability layers by molecular diffusion. During pump-and-treat remediation, clean water is moved through the more permeable layers at a relatively high rate. The contaminants within these more permeable layers are removed relatively quickly as they are purged with this clean water. In contrast, removal of the contaminants from the lower permeability lenses is limited by the rate of diffusion into higher permeability layers.

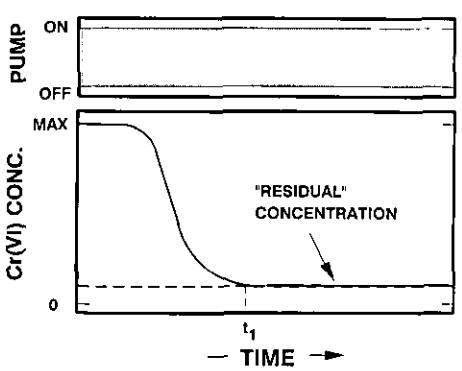

FIGURE 7. Concentration Cr^{VI} versus time in an extraction well under continuous pumping. After Keely et al. (*79*).

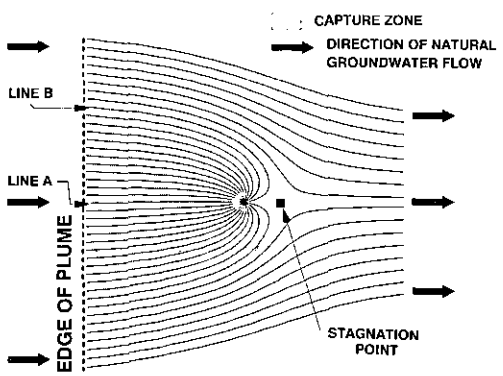

FIGURE 8. Streamlines in the vicinity of an extraction well outlining the capture zone, stagnation point, and differential flow path lengths.

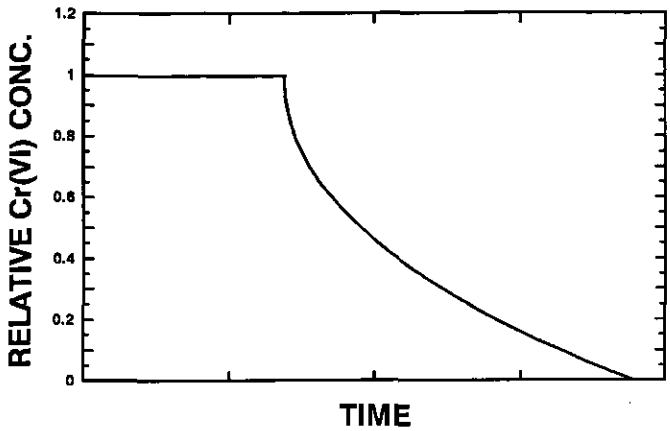

FIGURE 9. Cr^{VI} concentration versus time in a continuously pumping extraction well illustrating the effect of differential travel time along the streamlines.

This diffusive flux of contaminants from the lower permeability lenses maintains the concentrations of the contaminants in the higher permeability layer, and hence the extraction well, at some relatively low concentration that can be well above the established MCL. If pumping is discontinued, the velocities within the higher permeability layers decrease, and a parcel of water then has a greater residence time within the contaminated zone. With the longer residence time, the parcel of water acquires a greater mass of contaminant, causing the concentrations in the groundwater in the more permeable zones and hence the extraction water to increase (Fig. 10).

Contaminants can exist within the subsurface in relatively large reserves either as solid phase precipitates or as residual and pooled nonaqueous phase liquids. For chromium-contaminated sites, a likely reserve is $BaCrO_4$. The source of the barium may be the contamination itself or it may be from the natural soil. The solubility of $BaCrO_4$ is such that large amounts of it may be precipitated within the aquifer when Cr^{VI} concentrations are high. After the initially high levels of Cr^{VI} have been removed by pump and treat, the concentrations in solution may be controlled by $BaCrO_4$ that can still supply Cr^{VI} concentrations in the part-per-million range until the solid-phase reserve is depleted (Fig. 11). Palmer et al. (*62*) have suggested that contaminated groundwater Cr^{VI} concentrations at the United Chrome Products site are in equilibrium with $BaCrO_4$ (Fig. 4). Column leaching tests of contaminated soils show a significant leveling of the Cr^{VI} concentrations (Fig. 12), indicating that a solid phase may be controlling the concentration in the extraction water. Ammonium acetate and acid extractable barium are as high as 120 and 450 mg/kg. If the amount of $BaCrO_4$ present in the soil is equal to the amount of exchangeable barium on a molar basis, and the waters equilibrate with the solid phase, then 109 pore volumes are required to remove the $BaCrO_4$. However, the removal process is not this simple because of the other competing reactions such as adsorption that affect the concentrations of both the Cr^{VI} and the Ba^{2+}.

Another important reserve of Cr^{VI} within the subsurface is the chromium adsorbed onto the soil matrix. As described above, Cr^{VI} exists in solution as the anions $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$. Adsorption experiments on ideal adsorbents indicate that at a constant pH anions often follow Langmuir adsorption isotherms (*64*). Langmuir isotherms have been shown for the adsorption of Cr^{VI} onto individual oxide surfaces (*65,72*) as well as onto soils (*16,73*). One-dimensional transport under these conditions can be described by the nonlinear transport equation:

$$D\partial^2 C/\partial x^2 - v_w \partial C/\partial x = \partial C/\partial t + (\rho_b/\theta_s)\partial S/\partial t \quad (5)$$

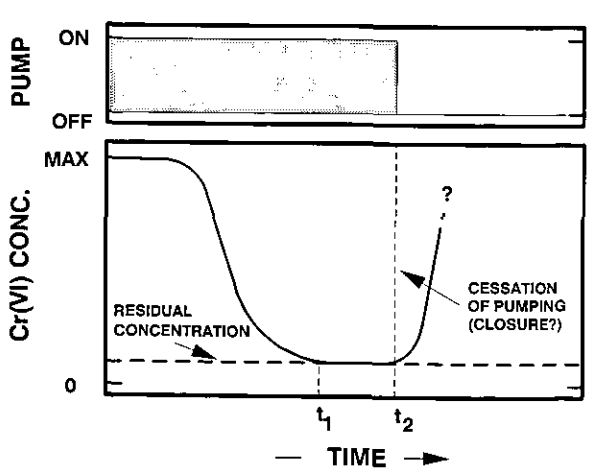

FIGURE 10. Cr^{VI} concentration versus time in an extraction well illustrating an increase in concentration after cessation of pumping. After Keely et al. (*79*).

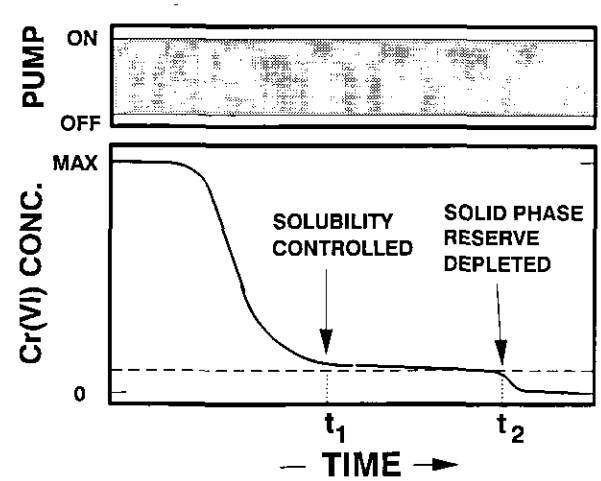

FIGURE 11. Cr^{VI} concentration versus time in an extraction well when there is a solid phase controlling the concentration of the chromium at time later than t_1.

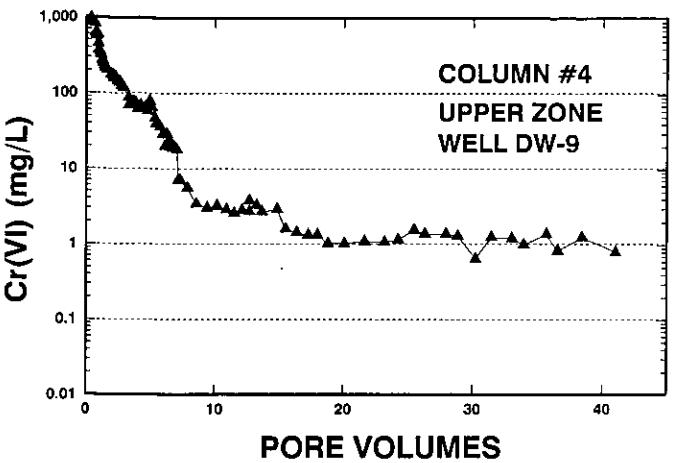

FIGURE 12. Cr^{VI} concentration versus pore volume for a contaminated soil from the United Chrome Products site, Corvallis, Oregon.

where S is the concentration of the adsorbed Cr^{VI} on the soil. If the S is related to C through Eq. (4) then Eq. (5) can be written as

$$D\partial^2 C / \partial x^2 - v_u \partial C / \partial x = \partial C / \partial t \left(1 + \rho_b S_{\max} K / \left[\theta_s (1 + KC)^2 \right] \right) \quad (6)$$

To illustrate the effects of adsorption on the remediation of aquifers, Eq. (6) was used to calculate the concentrations of Cr^{VI} in the groundwater and on the soil as a function of time (Fig. 13). The soil was assumed to be saturated and have a porosity of 0.47 while the groundwater velocity was assumed to be 3 m/yr. The adsorption parameters K (0.19 L/mg) and S_{max} (135 μg/g) were those used by Grove and Stollenwerk (*84*). The initial concentrations in the aquifer were 100 mg/L. The equation was solved using a one-dimensional Eulerian-Lagrangian method (*85*) using linear finite elements. This method was chosen so that large Peclet ($v_u \Delta x / D$) and Courant ($v_u \Delta t / \Delta x$) numbers could be used in the simulation. For comparison, the results are plotted along with the groundwater concentrations for the case where there is no adsorption. The concentration of the Cr^{VI} is plotted on a log scale rather than the more commonly used linear scale to emphasize the need to reduce the concentrations by orders of magnitude. The results indicate that at the higher concentrations there is little retardation of the Cr^{VI}. Decreases in concentrations follow that of the nonreactive tracer over the first log cycle. However, it becomes more difficult to remove the Cr^{VI} as the concentrations decrease over the succeeding log cycles. It also takes longer to attain the same relative reduction in Cr^{VI} concentration on the soils as in the groundwater.

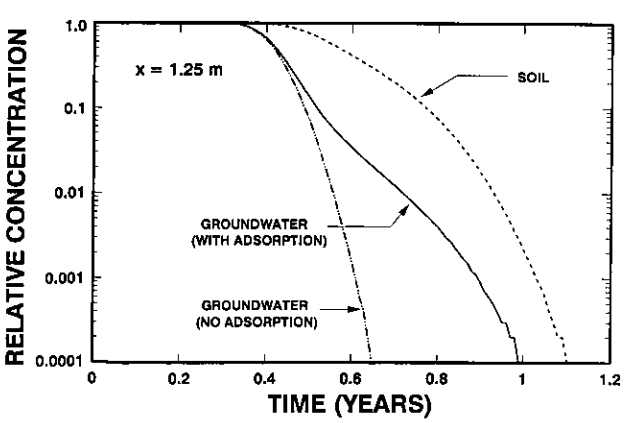

FIGURE 13. Cr^{VI} concentration versus time showing the effects of adsorption. Adsorption is assumed to follow a Langmuir-type isotherm, and adsorption parameters are those used by Grove and Stollenwerk (*84*).

Decades of operation may be required for pump-and-treat remediation to decrease Cr^{VI} concentrations below the MCL, nonetheless, it is still a very valuable remediation tool. Pump and treat is very effective at removing highly contaminated waters in relatively short periods of time, substantially reducing health risks and environmental damage. Once these highly contaminated waters are removed, technologies that are more effective at low chromium concentrations can be used. Pump and treat can also be used for gradient control to prevent migration of chromium from the site while other cleanup technologies are being implemented. Pump and treat is therefore likely to find continued use in the remediation of chromium-contaminated sites.

Soil Solidification/Stabilization

A soil stabilization process has two key objectives: *a*) to put the chromium into a chemical form that is relatively insoluble so the rate of release is very low and *b*) to reduce the permeability of the material so that groundwater tends to flow around the treated area rather than through it (*86*). Several soil solidification and stabilization technologies for wastes have been investigated by EPA (*87*). These methods include cement solidification, silicate-based processes, sorbent materials, thermoplastic techniques, surface encapsulation, organic polymer processes, and vitrification (*86*). While these technologies can be used on soils, they have required excavation of the contaminated soil. Leaching tests on cement mixtures containing $CrCl_3$, CrO_3, or Cr_2O_3 showed that cement was very good for immobilizing Cr^{III} as a result of the formation of $Cr(OH)_3$. However, Cr^{VI} readily leached from the cement at relatively high concentrations (*88*). The release of the Cr^{VI} is similar to the release of Ca^{2+} and may be related to the formation of $CaCrO_4$ within the cement mixture. Therefore, reductants should be added during the mixing process to reduce the Cr^{VI} to Cr^{III} before materials are added to solidify the contaminated soils. However, the material should be tested to determine the effects that excess reductants have on the properties of the cement. Re-

cently, an *in situ* soil mixing methodology that enables *in situ* soil solidification and stabilization of contaminated soils has been applied to hazardous waste cleanup (*89,90*). Stabilization tests on soils from the United Chrome Products site resulted in a 96.5% decrease in the toxic contaminant leach procedure (TCLP), but the soils still yielded 1.3 mg/L Cr^{VI} (*91*). Lead and strontium concentrations in the extracts increased in the stabilized soil.

In situ vitrification (ISV) is another method for soil solidification. ISV requires heating soil to 1600°C to 2000°C with a series of electrodes. At these temperatures the soil melts and upon cooling forms a glass that can entrap metal ions such as chromium. ISV has the greatest potential for isolating contaminants from the environment; however, the cost of such technology is likely to be too great for many common applications. In particular, if water is present, the energy consumption is too great. Soils with a hydraulic conductivity greater than 10^{-4} cm/s may require barrier walls and dewatering (*92*). Vitrification was one of the most expensive alternatives considered at United Chrome Products (R. Pratt, CH2M-Hill, personal communication).

Chemical Enhancement to Pump and Treat

The extended periods of time required by pump-and-treat operations make it worthwhile to consider technologies to enhance the removal of chromium from the subsurface. One of these technologies is the injection of chemical constituents or "reactive agents" that can react with the chromium and enhance its removal from the subsurface. Such "chemical enhancements" to pump-and-treat remediation have been reviewed by Palmer and Fish (*93*). They identified four major areas of concern with regard to the use of chemical enhancement to pump-and-treat operations: *a*) delivery of the reactive agent to where it is needed within the aquifer, *b*) the interaction between the reactive agent and the contaminant, *c*) the removal of the contaminant and the reactive agent from the subsurface, and *d*) the treatment of the extracted water and disposal of the resulting sludges. All of these areas depend on the type of physical and chemical processes discussed above.

Palmer and Fish (*93*) suggest that different types of reactive agents can be chosen. A reactive agent may compete with the chromium for adsorption sites, complex the chromium, change its redox state, or any combination of these processes. It is very important to understand the specific processes that control the tailing in the concentration versus time curve of the extract well. If the tailing is controlled by physical processes such as differential travel times along streamlines or heterogeneity, then there is no advantage to employing chemical enhancement, and the cost of employing the technology is wasted. If the tailing is controlled mainly by a solid phase precipitate such as $BaCrO_4$, then the addition of a chemical extractant that competes for the adsorption sites does not shorten the remediation time and may even exacerbate the problem causing additional precipitates to form in response to an increase in the ion activity product as the adsorbed chromium is brought into solution.

Regulatory agencies may require that chemical extractants be removed from the subsurface. If target levels are low, the remediation problem may shift from the removal of the chromium to the removal of the reactive agent. There is no advantage to using chemical enhancements for the removal of chromium if it takes as long a period of time to remove the reactive agent from the subsurface as it does to remove the chromium.

The economics of the chemical enhancement of pump-and-treat remediation need to be considered. Chemical enhancement of pump and treat may shorten the overall time required for remediation of a chromium-contaminated site, which is advantageous given the high operation and maintenance cost for pump-and-treat facilities. However, several factors can increase the cost of chemical enhancement. Complexing agents are usually not very selective. They can readily complex iron and aluminum as well as chromium. As a result, treatment of the extracted waters can yield larger volumes of sludge with a lower percentage of chromium. The net result may be substantial increases in the cost of disposal of the sludges. Also, the increased load of chromium in the short term may required larger treatment facilities and hence increased capital costs. It may be cheaper to build smaller facilities that must operate over a 10-year period than a larger facility that only operates for 1 or 2 years. In addition, many potentially responsible parties may prefer to pay more money over longer periods of time than to pay larger initial capital costs.

Geochemical Barriers

Rather than trying to actively extract groundwater from the subsurface or excavate soil for treatment, groundwater could be remediated more passively through the use of geochemical barriers. The basic concept of a geochemical barrier is to allow the groundwater to pass through an engineered structure containing a material that reacts with the chromium to enhance its removal from solution.

Artiole and Fuller (*94*) suggested that crushed limestone could be used a barrier material. They found that limestone was more effective in removing Cr^{III} than Cr^{VI} and that the material only delayed the migration of the Chromium. From a process point of view we can expect that limestone is effective in removing inorganic Cr^{III} from acid waters because the neutralization of the water results in the precipitation of $Cr(OH)_3$. Under acid conditions, however, significant amounts of Cr^{VI} should be adsorbed onto the aquifer matrix, and its rate of transport will be relatively low. However, should this Cr^{VI} ever reach the barrier, beyond which pH is more alkaline, there is less adsorption of the Cr^{VI} and its rate of migration should increase.

Grove and Ellis (*95*) suggest for Cr^{VI} spills that acidification and addition of reducing agents such as leaf litter may be effective in reducing the Cr^{VI} to Cr^{III}. Once the reduction is complete then lime can be added to precipitate $Cr(OH)_3$. If such material is used, then an undesirable increase in the dissolved organic carbon (DOC) is likely. Some of this DOC may complex Cr^{III} and transport it beyond the barrier.

Materials that promote the reduction of Cr^{VI} and the precipitation of Cr^{III} are going to the most effective barriers. Barrier materials that adsorb chromium will not be effective. Adsorption reactions can delay the rate of transport of the chromium through the barrier, however, the chromium will eventually break through the barrier and will be transported from the site. Common inexpensive materials that are likely to promote the reduction of Cr^{VI} include organic matter, pyrite, biotite, and hematite. Organic matter may generate high levels of DOC that may also complex the Cr^{III}. Pyrite will generate high acidity iron and heavy metals unless the barrier is neutralized with crushed limestone. Even then, the pyrite may generate high but tolerable levels of sulfate. The use of any material that contains ferrous iron as the reductant may be limited by the precipitation of $Fe_xCr_{1-x}(OH)_3$. This precipitate may cover reactive sites and clog pore space, ultimately leading to failure of the barrier. Therefore, barriers are most likely to find their application at sites with concentrations of chromium that are not far above the MCL and where the total mass of chromium passing through the barrier over its entire lifetime is small relative to the available surface area within the barrier.

Summary and Conclusions

There are many chemical and physical processes that affect the rate of migration and the chemical state of chromium at contaminated sites, including groundwater flow, diffusion-controlled mass transfer across heterogeneous boundaries, complexation, oxidation/reduction, dissolution/precipitation, and adsorption/desorption. These processes affect which remedial action is most effective for the cleanup of chromium-contaminated sites. However, differentiation of the mechanisms is not an easy task. The commonly used methods of sequential extraction can help by placing limits on the amount of chromium that may be adsorbed or precipitated; however, their use does not provide an unequivocal interpretation of the distribution of chromium in soils. Innovative methods for interpreting chemical processes in soils need to be developed and applied to the remediation of waste sites.

Mathematical models can be useful tools for evaluating different remediation designs if they have a firm basis in the physical and chemical mechanisms affecting the migration and transformation of chromium. However, these processes are complex and parameters such as the heterogeneity of the aquifer may be difficult to measure. The local equilibrium assumption (*96*) is unlikely to hold in short soil column tests that are often used for testing models or in soils where the flow path is short and the rate of reaction is fast relative to the rate of groundwater flow. Therefore, models that incorporate the kinetics of reactions may be necessary.

Some mathematical models have already been developed. Grove and Stollenwerk (*84*) were able to simulate Cr^{VI} migration in columns by assuming that the adsorption/desorption was controlled by film-diffusion processes. However, important processes such as reduction and dissolution-precipitation were not considered. Selim et al. (*97*) used a kinetic adsorption model with several other equilibrium and kinetic "retention/release" reactions including precipitation-dissolution. Unfortunately, they found that they were not able to simulate the transport of Cr^{VI} using independently determined rate constants for these reactions. The use of empirical rate laws rather than process-dependent rate laws may partially explain the poor comparisons of the experimental data to the simulations.

The problem of estimating the rate of migration of chromium and the time for remediation of contaminated sites is further complicated if mixtures of contaminants are present. For example, a study of the interaction of organic ligands with chromium in soils and tannery wastes found that under one set of conditions citrate facilitated the oxidation of Cr^{III} to Cr^{VI}, while in another set of conditions it reduced Cr^{VI} and complexed the resultant Cr^{III} (*98*). Thus, co-contaminants may facilitate or exacerbate the remediation process.

Advances are being made toward improving our understanding of the processes controlling the transport and fate of chromium. However, adsorption in heterogeneous soils is still not well understood. The rate and amount of reduction of Cr^{VI} in soils is difficult to predict. There is also a great need for better methods of remediation that apply what is known about chromium migration and transformation. Recent advancements in numerical techniques such as the Eulerian-Lagrangian methods (*85*) provide hope for the development of appropriate multidimensional, multicomponent transport models. Such models will be useful in evaluation of proposed remedial strategies. As our scientific and engineering knowledge advances, so will our ability to find practical solutions to the remediation of chromium-contaminated sites.

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