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Treatment Technologies for Chromium(VI)

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8.1 Treatment Concepts

The success of many different treatment technologies in remediating chromium(VI), Cr(VI), contamination has been demonstrated. However, most of these technologies require knowledge of site-specific conditions, flexibility in remediation design and creativity in optimization strategies, not adherence to a step-by-step recipe approach. Since the biogeochemical properties of Cr and the associated soil matrix can affect the removal efficiency of many treatment strategies, an understanding of these properties is essential for choosing an effective treatment method. Once the properties of Cr and the associated soil are understood and the behavior of Cr in the subsurface and treatment environments can be predicted, remedial alternatives for Cr(VI) can be addressed.

The approach employed in this chapter is to first summarize the different forms of Cr present in the environment as a function of environmental conditions. The form of the Cr determines toxicity, mobility, and treatment strategy applicability. Next, a summary of common chemical processes (reduction/oxidation, adsorption/desorption and precipitation/dissolution), biological processes (reduction/oxidation) and physical processes utilized in treatment technologies will be presented. Finally, treatment technologies will be organized into three different categories: toxicity reduction methods, removal treatments, and containment technologies.

8.1.1 Introduction: Chemistry of Chromium

The properties of Cr are highly dependent on the molecular structure of the Cr compound, particularly on the oxidation state (or oxidation number) of the Cr. Cr is an element that exists primarily in two different oxidation states, hexavalent and trivalent. These oxidation states are symbolized as Cr(VI) and Cr(III), respectively. Except for the rarely, naturally-found, elemental Cr with an oxidation number of zero, Cr(0), other oxidation states of Cr are unstable and therefore, are not found in the natural environment. The oxidation state of the Cr has a significant affect on the transport and fate of Cr and on the type and cost of treatment required to reduce Cr concentrations less than regulatory health-based standards.
Cr(VI) is far more mobile than Cr(III) and more difficult to remove from water. It is also the toxic form of Cr, approximately 10 to 100 times more toxic than Cr(III) by the acute oral route, presumably owing to the stronger oxidizing potential and membrane transport of Cr(VI) (Katz and Salem, 1992). The EPA classifies Cr(VI) as a known human carcinogen via inhalation, but classify Cr(III) as not known to cause cancer. The most common Cr(VI) forms are chromate (CrO$_4^{2-}$), and hydrogen chromate (HCrO$_4^-$) also called bichromate. The relative amount of these two species depends on pH. Dichromate (Cr$_2$O$_7^{2-}$) can also occur. Cr(VI) compounds are anions.

The equilibrium concentration of dissolved Cr(III) in natural waters is small compared to Cr(VI) concentration (Richard and Bourg, 1991). In water, Cr(III) is mostly in the free-ion form Cr$^{3+}$, although these ions associate with hydroxide OH$^-$ ions in a pH-dependent manner, forming Cr(OH)$^{2+}$, Cr(OH)$_2^+$, Cr(OH)$_3^+$, and Cr(OH)$_4^-$ (Rai et al., 1987). The solid precipitate Cr(OH)$_3$(s) will equilibrate with these dissolved species. Cr$^{3+}$ will also form complexes with organic and inorganic ligands such as SO$_4^{2-}$, NH$_4^+$, and CN$^-$. These are the major Cr species found in aqueous solutions. At pH<6 and Eh>0.6 V, HCrO$_4^-$ can also be dissolved in water.

In rocks and soil, Cr is a common trace mineral, found as amorphous Fe(III), Cr(III) hydroxides, eskolaite (Cr$_2$O$_3$(s)), and chromite (FeCr$_2$O$_4$(s)), all Cr(III) forms. There is a wide natural variation in Cr concentrations in soils and rocks. Shales, suspended river material, and soils with fine grain sizes have the highest concentrations, whereas granite, carbonates, and large-grained (sandy) sediments have the lowest concentrations (Richard and Bourg, 1991).

Typically, natural background Cr concentrations are dwarfed by anthropogenic contamination. Dissolved concentrations of total Cr in groundwater from natural processes are typically below 10 µg/l (Richard and Bourg, 1991). In contaminated areas, Cr(VI) concentrations are commonly 300 to 500 µg/l (CRWQCB, 2000; Maxwell, 1997) and have been reported to reach 14 g/l (Palmer and Wittbrodt, 1991). A yellow color is imparted to the water at about 1 mg/l Cr(VI) (Palmer and Wittbrodt, 1991). The federal regulatory standard for total Cr in drinking water is 100 µg/l; the World Health Organization (WHO) and State of California have adopted a standard of 50 µg/l.

The equilibrium distribution of the Cr between the two oxidation states is controlled by redox environment (either oxidizing, which most easily characterized by dissolved oxygen concentrations greater than 2 mg/l, or reducing, characterized by the absence of oxygen). For Eh/ph diagrams, see Figure 2.1 and Figure 2.2 (Motzer, Chapter 2). Oxidation kinetics depend on a variety of factors and make the actual ratio of Cr(VI)/Cr(III) more complicated. Kinetics are a function of biogeochemical conditions, including pH, redox and nutrient levels that govern microbial activity. Cr(VI) is converted to the less toxic and much less mobile form of Cr(III) by reduction reactions. The corresponding oxidation of Cr(III) to Cr(VI) also occurs, particularly in the presence of MnO$_2$ and bacteria (Richard and Bourg, 1991). However, the kinetics are slow.
Common reactions that occur in the subsurface are summarized in Figure 8.1. Each of these processes will be explained in more detail, as the preferential enhancement of one or more of these processes is often the basis for remediation strategies. The processes include oxidation/reduction reactions, adsorption/desorption, and precipitation/dissolution. These chemical processes can be biologically mediated—either directly through metabolic processes or indirectly as microorganisms change their geochemical environment.

### 8.1.2 Chemical Transformations

#### 8.1.2.1 Oxidation–Reduction

Some of the most common remediation strategies utilize oxidation–reduction reactions, converting Cr(VI) to Cr(III). An electron donor that commonly drives this reaction is Fe(II) which is either artificially supplied or is present from the natural weathering of iron oxides. Elemental Fe (Fe(0)), Mn(II), S\(^{2–}\), CH\(_4\) (methane), and reduced organics such as humic acids, fulvic acids, and amino acids can also be used as electron donors (Palmer and Wittbrodt, 1991).

If conditions do not favor Cr(VI) reduction, the opposite can occur. Cr(III) can be oxidized to Cr(VI). Mn(III, IV) hydroxides and oxides are the primary oxidizers present in the subsurface (Palmer and Wittbrodt, 1991). The mechanism of this surface reaction is still a topic of research. Palmer and Wittbrodt (1991) found that the oxidation rate of Cr(III) by MnO\(_2\) increased proportionately with the surface area to volume ratio and with decreasing pH. In the same study, they found that oxygen (O\(_2\)) did not play a major role in the oxidation process.

The reduction of Cr(VI) to Cr(III) may influence the redox and pH of the subsurface. The new conditions could favor the precipitation of Cr(III). Examples of reactions that generate alkalinity or acidity are shown in Equation 8.1 to Equation 8.3 (James et al., 1997).

\[
2\text{Fe} + 2\text{CrO}_4^{2–} + \text{H}_2\text{O} + 4\text{H}^+ \rightarrow 2\text{Fe(OH)}_3 + \text{Cr}_2\text{O}_3
\] (8.1)
Equation 8.1 illustrates the potential increase in pH associated with the formation of Cr(III) using Fe(0). Under moderate pH conditions, mixed Cr(III)-Fe(III) oxides and Cr(OH)$_3$(s) will form, increasing the redox reaction by Le Chatelier’s Principle as they precipitate. When Fe(II) is used as the electron donor, acidity is generated, as shown in Equation 8.2. Soil pH may decrease considerably, depending on the soil buffering capacity.

$$6\text{Fe}^{2+} + 2\text{CrO}_4^{2-} + 13\text{H}_2\text{O} \rightarrow 6\text{Fe(OH)}_3 + \text{Cr}_2\text{O}_3 + 8\text{H}^+ \quad (8.2)$$

Equation 8.3 shows a sample organic compound hydroquinone oxidized to quinone, with the generation of alkalinity. The newly formed Cr(III) can complex with organics, so Cr(III) does not build up and reoxidize to Cr(VI).

$$3\text{C}_6\text{H}_4\text{O}_2 + 2\text{CrO}_4^{2-} + 4\text{H}^+ \rightarrow 3\text{C}_6\text{H}_4\text{O}_2 + \text{Cr}_2\text{O}_3 + 5\text{H}_2\text{O} \quad (8.3)$$

One important question is the stability of the Cr(III) that forms during redox reactions. Forms of Cr(III) that are inert to reoxidation are desirable. Research has shown that 15% of freshly precipitated Cr(III) was reoxidized by manganese oxides (James et al., 1997). Aged precipitates were not as likely to undergo oxidation. The mobility of the Cr(III) is another relevant question. James et al. (1997) found that Cr(III) could be chelated by soluble organics and remobilized (James et al., 1997).

### 8.1.2.2 Sorption

Sorption processes for Cr can also be used in treatment strategies. However, Cr(III) is the primary form of Cr that is retained by sorption. The kinetics of Cr(III) sorption is rapid in clays, sands, and soil containing Fe and manganese oxides. For example, in one laboratory study, about 90% of Cr(III) added to clay minerals and iron oxides was adsorbed within 24 h (Richard and Bourg, 1991). Cr(III) behaves like a positively charged ion (such as Cr$^{3+}$) when adsorbing onto surfaces. As pH increases, surfaces are deprotonated, increasing the attraction between Cr(III) and the surface. Sorption is therefore enhanced as pH increases. If soil has a high organic content, sorption is also enhanced, as more sites are present for sorption to occur.

Although Cr(VI) is usually mobile in groundwater, under some conditions Cr(VI) can sorb, as indicated in Figure 8.2. However, Cr(VI) behaves like an anion (such as CrO$_4^{2-}$ and HCrO$_4^-$), so sorption of Cr(VI) decreases with increasing pH. At low pH values, surfaces will be neutral or positively charged, leading to charge attraction. In addition, the ratio of HCrO$_4^-$ to CrO$_4^{2-}$ is a function of pH. Richard and Bourg (1991) studied this relationship between pH and percent sorption of Cr(III) and Cr(VI) on Fe$_2$O$_3$ surfaces. However, sorption of Cr(VI) becomes less important as the concentration of competing anions sorbed to solid surfaces increases. In groundwater, therefore, adsorption of Cr(VI) is usually negligible (Richard and Bourg, 1991). Sorption processes are used indirectly to remediate Cr(VI); Cr(VI) is reduced.
to Cr(III), which can precipitate or adsorb to soil. The effectiveness of this strategy depends on the sorption characteristics of the soil, including the clay content, iron oxide, and aluminum oxide ($Al_2O_3$) content, and the amount of organic matter present. Iskandar (2001), and Evanko and Dzombak (2000) provide an overview on metals remediation of soil and groundwater.

### 8.1.2.3 Precipitation

Equilibration between solid and dissolved forms of Cr is a third physical–chemical interaction that is used in treatment processes. Precipitation of Cr(III) occurs as $Cr(OH)_3(s)$, $FeCr_2O_4(s)$, or $Fe_xCr_y(OH)_3(s)$ (Richard and Bourg, 1991). The solubility of Cr(III) governs its migration. Precipitation/dissolution is a function of pH, complexation by organic matter, and the presence of other ions. As pH increases, $OH^-$ concentration increases and more Cr precipitates. Organics can complex with dissolved Cr, making removal by precipitation or adsorption difficult. The precipitation of Cr(III)
is useful for increasing Cr(VI) to Cr(III) reaction rates, by Le Chatelier’s Principle.

Natural precipitation of Cr(VI) is not a major removal mechanism. CaCrO\(_4\) was observed to precipitate naturally during summer months at a hazardous waste site (Palmers et al., 1990). Based on laboratory studies, BaCrO\(_4\) and Cr/Al coprecipitates were suggested to occur at other sites (Palmer et al., 1990; Palmer and Wittbrodt, 1991). Plating tank sludge at the first site contained PbCrO\(_4\), PbCrO\(_4\)·H\(_2\)O, and K\(_2\)CrO\(_4\). However, the solids are highly soluble and are not a considerable removal mechanism for Cr(VI).

These three processes (redox reactions, sorption, and precipitation) form the basis of both chemical and biological treatment processes used to influence the balance between Cr(III) and Cr(VI).

8.1.3 Biological Transformations

Microorganisms often carry out enzymatic redox reactions as part of their metabolic processes. Cr(VI) can also be reduced nonmetabolically by reactions that occur on bacterial surfaces (Fein et al., 2001). This has been postulated by Fein et al. (2001) as the dominant pathway for reduction in natural geologic settings. A third mechanism for Cr reduction involves intra-cellular precipitation (Cervantes et al., 2001). However, most studies have focused on the first mechanism, where Cr is reduced metabolically in the presence of large amounts of electron donors. Chemical reducing compounds that require biological interactions include the use of molasses, lactic acid, and proprietary formulations such as the Hydrogen Release Compound (HRC), and cheese whey. These chemicals provide a carbon source in the environment, but require biological transformations to generate hydrogen in an anaerobic setting.

Bacteria can enzymatically reduce Cr(VI) by both aerobic and anaerobic pathways. However, other nonbiological Cr reduction pathways compete with the biological pathways. Under anaerobic conditions, biological reduction is slow so abiotic reduction by Fe(II) or hydrogen sulfide is expected to dominate. Microbial reduction only becomes kinetically important in aerobic environments (Fendorf et al., 2001). Oxygen concentrations in the system are the primary factor influencing reduction rate, followed by pH and geochemical conditions.

Microorganisms are always present in the environment. Their role in Cr reduction is still being defined through research. Topics of interest include the role of bacterial surfaces in Cr reduction, new tools for monitoring transformations such as infrared spectromicroscopy (FTIR Beamline) (Holman et al., 1999) and coupled biological remediation/chemical reduction processes.

Phytoremediation is the engineered use of plants in the environmental remediation process. Phytoremediation is also a cutting-edge topic in research. There are six basic subsets of phytoremediation: phytoaccumulation (also called phytoextraction or hyperaccumulation), phytodegradation (also called phytotransformation), phytovolatilization, phytostabilization, rhizodegradation (also called phytostimulation or plant-assisted bioremediation), and
rhizofiltration (also called contaminant uptake). Plants can take up Cr into their roots and aboveground tissues, storing it as Cr(III). When harvested, Cr is removed from the system. Plants can also stabilize Cr contamination in the soil, by one or several mechanisms, converting it to Cr(III).

### 8.1.4 Physical Remediation Processes

Chemical and biochemical processes render Cr(VI) unavailable by converting it to the less toxic and less mobile Cr(III) form. Physical processes separate Cr(VI) from the contaminated media (such as soil excavation and groundwater extraction) capture the extracted Cr (using ion exchange resins or granular activated carbon (GAC)), and/or isolate the contamination (using physical barriers around in-situ contaminants or liners in landfills).

Principles behind physical treatment concepts vary with the particular approach used. The basics and description of each technology are explained in Section 8.4 and Section 8.5.

### 8.2 Classification of Treatment Technologies

Taking a risk-based approach to the health problems associated with Cr(VI) inhalation/ingestion will provide a framework for classifying the numerous remediation strategies that have been developed and used to date.

#### 8.2.1 Reduction of Toxicity

The carcinogenic effects of Cr on a receptor species (a human or another ecological species) can be expressed as the product of exposure and the inherent toxicity of the compound. One method of alleviating health impacts of Cr is toxicity reduction. Cr that is ingested in a chemical form that is biologically unavailable will theoretically be harmless, as long as transformations do not occur within the body to render it toxic. As previously discussed, a major category of remediation technologies aims to decrease the toxicity of Cr(VI) by reducing Cr(VI) to Cr(III). This can occur naturally or by manipulating environmental conditions to stimulate selective biological activity (including bacteria, yeast, algae, and plants) or geochemical processes (Haq and Shakoori, 1998). Reduction can also occur when chemicals are added to directly reduce the Cr, such as ferrate or Fe filings.

All other remediation strategies target the second component of the health impact equation, intake rate. Intake rate, expressed in mg/(kg body mass)/day can be expressed mathematically in the following way:

\[
\text{Intake Rate} = \frac{\text{concentration} \times \text{exposure frequency} \times \text{exposure duration}}{\text{body mass} \times \text{lifetime}} \quad (8.4)
\]

where concentration is typically in mg/l, exposure frequency in L/day, exposure duration in day, body mass in kg body mass, and lifetime in day.
Body mass and lifetime cannot be changed to reduce exposure. Exposure duration or frequency may be decreased by institutional controls—for example, prohibiting ingestion of groundwater or site access in soil contaminated areas. Thus, in order to reduce intake rate, remediation must focus on decreasing concentration in soil or groundwater.

8.2.2 Destruction and Removal

To decrease total Cr concentrations, several approaches are used. Destruction technologies are not practical for Cr, since it is an element—the energy to change the atomic nucleus of Cr to a different element would be enormous. Simple removal technologies include conventional methods such as excavation and off-site disposal of soil or pump-and-treat of groundwater. However, soil may require further treatment before it is disposed off and groundwater extraction must be followed by ex-situ treatment. Other technologies involve separation of Cr from soil into a wastewater stream by soil washing, soil flushing or solvent extraction, concentration of Cr into a smaller waste volume or area using electrokinetics or phytoextraction, or the removal of Cr from groundwater by membrane technology (ultrafiltration, nanofiltration, reverse osmosis), ion exchange, or granular activated carbon.

8.2.3 Containment

Other technologies focus on preventing the spread of contamination into larger areas. These containment technologies include stabilization or solidification, biostabilization, phytostabilization, precipitation, encapsulation, and vitrification of soil. Slurry walls and other physical barriers are used for groundwater containment. Passive in-situ remediation can be achieved by permeable reactive barriers, and hydraulic containment can be attained through pump-and-treat (this process may be enhanced by addition of surfactants). Containment technologies focus on either isolating the contaminants (in the case of in-situ slurry walls) or immobilizing them. Passive remediation may occur as groundwater leaves the containment zone, as in the case of permeable reactive barriers. However, no attempt is made to decrease concentrations of Cr(VI) within the containment zone.

In summary, remediation technologies focus on either decreasing toxicity (reducing Cr(VI) to Cr(III)), removing Cr from soil/groundwater or confining the Cr to a certain area.

8.3 Toxicity Reduction Methods

Treatment systems based on the Cr(VI) reduction can be biological or abiotic, and is often a combination of these two.
8.3.1 Chemical Reduction

The term chemical reduction refers to abiotic in-situ or ex-situ reduction with an electron donor such as S, Fe(II) or Fe(0). The newly formed Cr(III) then precipitates out of solution. This approach achieves both a reduction in Cr toxicity and removal of the Cr from aqueous solution. Chemical reduction includes naturally occurring reduction by soil oxides and natural organic material.

Engineered chemical reduction technologies involve the addition or in-situ injection of an electron donor such as hydrogen sulfide (H$_2$S) (Thornton and Amonette, 1999), sodium dithionite (Na$_2$S$_2$O$_4$) (Fruchter et al., 2000), sodium metabisulfite (NaHSO$_3$), calcium metabisulfite (CaHSO$_3$), FeSO$_4$, calcium polysulfide (CaS$_5$) (Jacobs et al., 2001), Fe(II) (Seaman et al., 1999), Fe(0) (Ponder et al., 2000), or tin(II) chloride (SnCl$_2$). The pH is adjusted to optimize electrostatic surface interactions between Cr(VI) anionic species and the electron donor. Alternatively, for high Cr(VI) concentrations, such as those encountered in industrial waste streams, pH is increased so that Cr(III) will form S$^{2-}$ and/or OH$^{-}$ precipitates. Metal sulfides are far less soluble than metal hydroxides. Except for alkali-metal sulfides, metal sulfides are relatively insoluble over the pH range of most naturally occurring groundwater (pH 5 to 9).

Laboratory and pilot-studies with different electron donors have demonstrated that there is a high potential of successful removal during in-situ reduction. Actual results depend on the details; Powell et al. (1995) reported that different forms of Fe metal influence reduction kinetics. Impure, partially oxidized Fe was the most effective, with no reduction occurring when pure Fe(0) was used (Powell et al., 1995). This was explained by the hypothesis that Fe(0) does not have the materials needed to initiate the redox (corrosion) process to Fe(II). Surface area of the Fe is another factor that affects redox kinetics. Ponder et al. (2000) reported that reduction was 21 times greater for equal moles of Fe present when Fe nanoparticles (10 to 30 nm in diameter) were used instead of commercial Fe filings. H$_2$S has been demonstrated to reduce Cr, either by adding H$_2$S(g) to the soil in-situ, or by stimulating sulfate (SO$_4^{2-}$)-reducers in the subsurface.

Recently, field testing has shown that sodium dithionite (Na$_2$S$_2$O$_4$) successfully reduces chromate. During demonstration and treatability testing at the DOE Hanford Site, Washington, sodium dithionate was injected into an unconfined aquifer (USDOE, 2000). Chromate concentrations decreased from 900 µg/l to nondetect (<8 µg/l). Monitoring indicated that the treatment zone remained anoxic after 2 years and that chromate remained nondetect. Since no pumping and aboveground treatment is required, operation and maintenance costs are low. The DOE Hanford site cost analysis indicated that in-situ chemical reduction could save 60% relative to pump-and-treat system over 10 years of treatment (USDOE, 2000). Further testing with sodium dithionite at the Frontier Hard Chrome Superfund Site in Vancouver, Washington showed that chromate concentrations could be reduced from 4500 µg/l to nondetect (<20 µg/l) (Vermeul et al., 2002).
Ex-situ chemical reduction of Cr(VI) is well established, so extensive laboratory and pilot-scale testing is not necessary, prior to full-scale implementation. Extraction and ex-situ chemical reduction is frequently a component of selected treatment remedies at Superfund sites (USEPA 1989a and 1986b). However, chemical costs are high and the system must include filtration or sedimentation. In addition, these systems are not cost-effective for low concentrations of Cr(VI) in the wastewater.

In-situ chemical reduction is highly dependent on the existing site-specific physical and chemical conditions, including pH, permeability, lithology, water depth, concentrations of metals in water and soil, and alkalinity. Site data can be used to design and perform a series of simple bench-scale tests, followed by pilot scale tests in small areas of the site to verify treatability. After a successful in-situ pilot-scale test, a full-scale remediation may be performed.

For in-situ commercial applications, delivery is one of the key factors in successful remediation, since the treatment chemicals must fully contact and react with the Cr(VI). There are several methods of delivering chemicals into the subsurface. If screened correctly and located beneficially for the injection of treatment chemicals, existing wells or trenches can be useful for chemical delivery.

A more precise method of delivering liquid chemicals to the subsurface uses high-pressure injection technology, also called jetting. There are two main methods of jetting: one uses a direct push drilling technology method where chemicals are sprayed into the subsurface through specially designed steel injection rods, typically 25 to 50 mm in diameter. The rods are pushed into the subsurface using the probe rig. One method is to push the rods to the target depth and inject chemicals up to 41 atm (600 psi) as the rods are retracted from the borehole. The other method uses a 6.35 to 12.7 mm outer diameter lance system for the delivery of treatment chemicals (Jacobs, 2001). Hand-held jetting lances operate at tip pressures up to 340 atm (5000 psi) and allow accessibility in limited access areas such as underneath railways and buildings, around tanks, pipelines and subsurface utilities. Chemical compatibility of the injection equipment components and safety procedures become critical with the injection of strong chemicals.

In low permeability soil, permeability enhancement can be performed in the subsurface prior to chemical injection. Higher injection tip pressures on the lance or injection probe rods are used to induce hydrofracturing in low permeability sediments, allowing for additional movement of the treatment chemicals into the target zone.

### 8.3.2 Microbial Reduction

As described in Section 8.1, microorganisms can catalyze redox reactions by a combination of several mechanisms, including enzymatic extra-cellular reduction, nonmetabolic reduction by bacterial surfaces and intra-cellular reduction and precipitation. Microorganisms capable of reducing Cr(IV) to
Cr(III) include bacteria (*Psuedomonas, Microccus*, *Escherichia, Enterobacter, Bacillus, Aeromonas, Achromobacter, and Desulfomamaculum*) (McLean and Beveridge, 1999), algae (Cervantes et al., 1994), yeasts, and fungi.

External reduction reactions that are biologically mediated still require the presence of an external electron donor, such as Fe, Mn, or oxidized organic matter. The process is the same as chemical reduction, but is biologically mediated and is thus kinetically advantageous to nonbiological reactions, particularly under aerobic conditions. Alternatively, sulfur-reducing bacteria are stimulated to produce H₂S, which serves as the reductant. Recent work by Fein et al. (2001) has shown that bacterial surfaces can also catalyze Cr reduction.

Both eukaryotic and prokaryotic cells can actively transport Cr(VI) across their cell membrane. In yeasts, Cr(VI) may enter via the permease system, a nonspecific method of ion transport for anions such as phosphate (PO₄³⁻) and SO₄²⁻ (Cervantes et al., 2001). Cr is toxic to yeast because it inhibits SO₄²⁻ uptake. Differences in the retention of Cr(VI) by algae have been studied and reported. Green algae retain more Cr than red or brown algae (Cervantes...
et al., 1994). In general, cells do not take up Cr(III) because it is not water-soluble.

Laboratory studies have quantified the impact of various factors affecting the rate of microbial reduction, including dissolved oxygen and organic carbon concentrations, pH and mass loading rates of Cr. Although biological reduction can be either aerobic or anaerobic, reduction reactions are sensitive to oxygen concentrations. Under anaerobic conditions, both abiotic and biotic reduction mechanisms are competitive. Over time, pH may increase owing to the mineralization of organic matter to CO₂, which increases HCO₃⁻ concentration, or owing to an acid-consuming redox reaction. Optimal Cr(VI) loading rates have been determined by varying the influent concentration or dilution factor. Results are case-specific as environmental conditions determine which mechanisms will dominate in the system.

Bioremediation strategies used for Cr(VI) remediation include monitored natural attenuation (MNA), biostimulation, and bioaugmentation. MNA is
frequently evaluated at sites as a baseline remedial option and has been implemented at Superfund sites such as the Quality Plating Superfund Site, Missouri (USEPA, 1995). During biostimulation, also known as enhanced bioremediation, oxygen and/or nutrients are injected to stimulate indigenous microorganisms. This was chosen as part of the final treatment technology for a chrome electroplating facility in Kansas in 1999 (Ace Services Superfund Site) (USEPA, 1999). The plan involved recirculating water amended by a carbon source through the contaminated area to stimulate bacterial activity. In-situ bioremediation was intended to reduce source concentrations of Cr(VI) and thus reduce pump-and-treat timeframe for the site. Bioaugmentation refers to the injection and maintenance of cultured microorganisms into the subsurface. Bioaugmentation may not be necessary since a number of indigenous Cr(VI)-degrading cultures are present in the environment, and in some cases are superior Cr(VI)-reducers, as they have been acclimated to the site conditions (McLean and Beveridge, 1999).

8.3.3 Phytoremediation

Like biological and chemical reduction, phytoremediation is a multi-faceted approach towards Cr remediation. Plants contain the Cr by converting it to the less mobile Cr(III) (phytostabilization) and simultaneously reduce its toxicity. In addition, phytoremediation can be a removal technology, if Cr is sequestered in plant tissue and the plants are harvested (phytoextraction and rhizofiltration). For simplicity, all three mechanisms of phytoremediation are classified primarily as toxicity reduction methods and are discussed here. All three techniques are currently in the lab-scale or pilot-scale of development (USEPA, 1997).

Phytoaccumulation one of the most common forms of Cr(VI) phytoremediation, consists of the uptake of the Cr from the soil to the plant roots and ultimately into the above ground parts of the plants. Some plants can accumulate very large amounts of a specific metal, such as Cr. The plant, Leptospermum scoparium was found to contain soluble Cr in the leaf tissue as the trioxalatochromium(III) ion (Cr(Cr₂O₄)₃⁻). The function of the chromium-organic acid complex was to reduce the toxicity of the Cr.

Phytostabilization is perhaps the least advanced technology of the three currently in development. This method is sometimes viewed as a temporary measure until phytoextraction is further developed (USEPA, 1997). Plant and other biological secretions can stabilize Cr in the root zone. These can change pH or complex the Cr as Cr(III). In addition, plant roots minimize erosion and the migration of contaminated sediment. Phytostabilization is most useful for low concentration contamination or large polluted areas, when conventional chemical–physical methods are most expensive. Phytostabilization can be combined with best management practices such as phosphorus amendments, lime, or organic matter to enhance immobilization and avoid leaching.

Several varieties of grasses are commercially available for phytostabilization of copper (Cu), and acid or calcareous lead (Pb) and zinc (Zn), but none
Treatment Technologies for Chromium(VI) for Cr (USEPA, 1997). Trees and other high-biomass crops can be used for phytostabilization, since harvest is not performed. Phytostabilization using poplar trees is currently a topic of research (USEPA, 1997). Metal accumulating plants are undesirable for phytostabilization, owing to the risk of generating hazardous plant waste and/or passing Cr along in the food chain. Experimental data on phytostabilization in mining and industrial slag disposal sites has been reported by Hse in 1996 working on plantations of *Populus spp* (Hse, 1996).

More research has been conducted on phytoextraction and rhizofiltration of Cr. Cr reductases have not yet been identified in plants (Cervantes et al., 2001). Some research suggests that Cr is taken up as organic material/Cr complexes. Complexation with organics was identified as facilitating Cr availability to plants in lab-scale experiments (Cervantes et al., 2001). The sulfate transport system is apparently involved as it is for bacteria. In most experiments, Cr(VI) is preferentially taken up over Cr(III). Roots take up 10 to 100 times more Cr than shoots and other tissues.

Much research has been done on the toxic effects of Cr (VI) on plants. Cr(III) is relatively nontoxic. The reason that Cr(VI) is toxic is that it generates free *OH radicals as it is broken down to Cr(III). The energetic *OH radicals can mutate DNA and lead to other toxic effects. Cr(VI) causes plant growth reduction owing to root damage (Salunkhe et al., 1974).

Rhizofiltration refers to the uptake of Cr from wastewater by plant roots. Terrestrial plants with long fibrous roots and high surface areas are typically used because sorption onto the surface of roots provides an additional uptake mechanism. However, in some studies, only live roots were able to remove metals from solution (Dushenkov et al., 1995). Indian mustard seedlings grown in aerated water accumulated Cr(VI) by a factor of 100 to 250 times the concentration in water (Salt et al., 1997). Indian mustard has been used in other studies, including phytoextraction at an Ohio metal plating facility (Rock and Beckman, 1998) and lab-scale work differentiating between metal uptake efficiencies among various mustard species. *B. juncea* and *B. nigra* had the highest metal-accumulating ability and Cr had the highest extraction coefficient (followed by cadmium (Cd), nickel (Ni), Zn, and Cu) (Kumar et al., 1995). The wetland plant duckweed was also studied for phytoaccumulation of various metals (Zayed et al., 1998). Other lab studies have focused on alfalfa (*Medicago sativa*) (Gardea-Torresdey et al., 1998) and its ability to bind Cr from aqueous solution. Alfalfa shoots took up 7.7 mg Cr(III) per g of biomass and zero Cr(VI) from biomass.

Selected aquatic plants have the ability to tolerate Cr. Water hyacinth (*Eichhornia crassipes*) can accumulate Cr as Cr(III) in high concentrations (6 mg/g dry mass) was observed in the plant’s roots when it was growing in only 10 ppm Cr(VI) (Cervantes et al., 2001). *Herniaria hirusta* was also found to be a Cr accumulator (Cervantes et al., 2001). Sulfur-loving plants such as cauliflower, kale and cabbage showed huge concentrations of Cr accumulation (160 to 135 mg/kg in roots, 1.6 to 2.0 mg/kg in shoots) (Cervantes et al., 2001) with *Brassica spp*. accumulating the most. The sulfur
transport system may be responsible for the high uptake ability of these species.

Considerable work remains in the development of phytoremediation technologies. The mechanism(s) for uptake are not yet clear. Neither are the effects of organic matter and other soil amendments on uptake efficiency, possibly owing to the uncertainty associated with the mechanisms of uptake and/or precipitation.

8.4 Removal Technologies
8.4.1 Ex-Situ Technologies
Following excavation, soil contaminated with Cr can be transported offsite to landfill. Owing to high costs of transport and landfill space, it may also be treated on-site. Most ex-situ technologies are appropriate for removing Cr from liquid waste streams following groundwater extraction. Some have also been applied to highly concentrated wastes generated by Cr industries (tanneries, metal-plating shops and wood treatment facilities). Ex-situ treatment techniques that capture and remove total Cr from waste soils, sludges, sediments, and liquids are discussed in this section.

8.4.1.1 Ion Exchange
Ion exchange is a physical process in which an ion with a high affinity for the resin material of the ion exchange column replaces an ion with a lower affinity that was previously bound to the column resin. As water flows through, dissolved Cr(VI) ions bind to the resin and displace the previously bound ions (usually Cl\(^-\) or OH\(^-\) ions). The resins used for Cr sequestration are typically either a naturally occurring inorganic zeolite or a synthetic weak base or strong base anion exchanger resin. Once the resins have accumulated Cr on enough exchange sites that breakthrough surpasses a threshold value, they must be regenerated.

Ion exchange resins are capable of reducing Cr(VI) concentrations to less than the detection limit. Resins are typically most effective at low pH values, because Cr(VI) will be present as HCrO\(_4^-\) and Cr\(_2\)O\(_7^{2-}\), not as CrO\(_4^{2-}\). The ratio of ion exchange sites to Cr ions sequestered is then 1/1. When CrO\(_4^{2-}\) is present, two ion exchange sites are used to sequester each Cr ion. Competition by other anions (namely SO\(_4^{2-}\), nitrate (NO\(_3^-\)), and Cl\(^-\)) is not a problem in most applications, since Cr has a higher affinity for all polymeric anion exchangers. Increasing the ratio of competing ion concentration to Cr concentration may appreciably change the Cr selectivity (U.S. Filter Recovery Services, Inc., 2001). Breakthrough is gradual and is governed by equilibrium between the resin and the aqueous phase (U.S. Filter Recovery Services, Inc., 2001). Regeneration is typically accomplished using NaOH and alkaline
brine. Cr(VI) in the regeneration effluent is either disposed of in concentrated form or is recovered for reuse.

Bench-scale treatability tests are typically conducted at sites prior to the implementation of full-scale remedial activities. Variables include the type of resin that is most efficient for removal under the expected loading rate, the ion selectivity of Cr over sulfate and nitrate, the capacity of the system (time till breakthrough), and finally the possibility of organic fouling, which may also affect the duration of operation before regeneration. Bench-scale tests at the FMC-Fresno site in Fresno, CA (U.S. Filter Recovery Services, Inc., 2001), on six different commercially available ion-exchange media showed that ion exchange resins may not perform at the manufacturer’s stated loading capacity.

Ion exchange is commercially available for removing Cr from aqueous waste streams. The technology has been used at several Cr-contaminated Superfund Sites (USEPA, 2000c and 1986a). Ion exchange systems such as Ion Exchange Recovery of Cr (IERECHROM) have been developed to recover Cr(III) for future use, which is economically attractive for industrial facilities with concentrated Cr(III) waste streams (Petruzzelli et al., 1995).

8.4.1.2 Granular Activated Carbon

Granular Activated Carbon (GAC) is a well-established technology for removing organics from water supplies and has been demonstrated to remove heavy metals as well, including Cr. GAC has an extremely high internal surface area, on the order of 1000 m²/g. Cr(III) adsorbs only weakly to GAC and passes through the carbon. Cr(VI) is removed by two different mechanisms: electrostatic adsorption to GAC surfaces and reduction to Cr(III). Adsorption of Cr(VI) is a strong function of pH, owing to electrostatic surface interactions. Quantitative results vary with the type of GAC, because different types of GAC have different point of zero net charge (pznc) values (Corpapcioglu and Huang, 1987). The adsorption capacity of Calgon filtrasorb 400 GAC was shown to peak between pH 5 to 6 (Huang and Wu, 1977). Although CrO₄²⁻, HCrO₄⁻, and Cr₂O₇²⁻ are all adsorbed, HCrO₄⁻ is the most easily adsorbed species. Coconut-fibre pith-based GAC (pznc = 7.5) achieved optimal removal at pH 2 (Manju and Anirudhan, 1997). Grinding GAC particles did not change Cr(VI) adsorption owing to the relatively small change in GAC internal surface area (Huang and Wu, 1977).

However, GAC is not commonly considered/implemented at Cr-contaminated sites, owing to practical considerations. As explained in the Record of Decision for Coast Wood Preserving Superfund Site, Cr adsorption by GAC is a strong function of pH and would require chemical addition as a pretreatment to lower pH (USEPA, 1989a). During on-site GAC regeneration, adsorbed Cr would be released as Cr (IV), creating a second waste stream that would require treatment. On the other hand, Kysor Industrial Corp. Superfund Site used GAC as the primary remediation technology for Cr(VI) contamination. Spent GAC was transported to landfill instead of being regenerated (USEPA, 1989b).
Alternative sorbents have been proposed for removing Cr(VI), in order to save money and/or recycle waste material. Materials tested so far have ranged from used automobile tires to seaweed. Results have demonstrated that removal can be equivalent or superior to that of ion exchange resins (Bailey et al., 1999).

Researchers have tested living and dead biosorbents, including bacteria, yeasts, milled peat, microalgae, fungi and seaweed. Other natural materials tested include clays, peat moss, and plant litter. Low cost sorbents are not regenerated, but are disposed off as soon as significant breakthrough occurs. A summary of the adsorptive capacities of alternative sorbent materials is provided in Table 8.1, in terms of mg Cr(VI) sorbed per gram of sorbent (adapted from Bailey et al., 1999).

Values in Table 8.1 are not meant to represent maximum adsorptive capacity of the materials, but the range of adsorptive capacities possible under the experimental conditions. Since adsorption is an equilibrium process, the mass of Cr(VI) sorbed to the surface depends on both the concentration of Cr(VI) in the aqueous phase and the affinity of the sorbent for the Cr. This in turn depends on the types of chemical attractions between the sorbent and the Cr (such as ionic bonding, electrostatic attraction, and hydrogen bonding), which can vary with pH and the presence/absence of competing molecules. For example, GAC may have a maximum adsorptive capacity of 500 mg/g (Fendorf et al., 2001), yet only remove 65 mg/g at saturation (Henshaw Associates, Inc., 1998). Adsorption isotherm data are also available for a variety of alternative adsorbents.

Pretreatment for different natural and waste materials has also been tested, in attempts to improve adsorption performance. Chitosan, for example, is a deacetylated derivative of chitin. Free amino groups are exposed during deacetylation and serve as adsorption sites. To decrease the solubility of chitosan, loose crosslinking reactions can be performed. Different forms of chitosan (beads or powder) have also been created and tested for adsorption properties. Crosslinking has also been used for seaweed, to decrease swelling inside adsorption columns. Waste materials such as tires and sawdust were pyrolyzed prior to testing. Costs of materials increase with the amount of pretreatment that is necessary yet may result in greater cost savings in the end, owing to higher sorption capacity.

Semipermeable membrane filters are used in water treatment to filter soluble compound anions and cations from water, including HCrO$_4^-$ and CrO$_4^{2-}$. The flux of water through the membrane is proportional to the pressure that is applied. The flux of solute (Cr) can be related to the flux of water, the concentration of Cr and other empirically derived membrane parameters. Membrane filtration systems are categorized by pore size. From largest to smallest pore size, these include microfiltration, ultrafiltration...
Treatment Technologies for Chromium(VI)

TABLE 8.1
Summary of Reported Adsorption Capacities for Cr(VI)

<table>
<thead>
<tr>
<th>Class</th>
<th>Sorbent Material</th>
<th>Source</th>
<th>Adsorption Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>Chitosan</td>
<td>Masri et al., 1974</td>
<td>27.3</td>
</tr>
<tr>
<td>Clay</td>
<td>Wollastonite-fly ash mixture</td>
<td>Panday et al., 1984</td>
<td>0.271</td>
</tr>
<tr>
<td>Clay</td>
<td>Tailored bentonite</td>
<td>Cadena et al., 1990</td>
<td>5</td>
</tr>
<tr>
<td>Clay</td>
<td>Bentonite</td>
<td>Khan et al., 1995; Cadena et al., 1990</td>
<td>0.512, 55</td>
</tr>
<tr>
<td>Coconut-fiber</td>
<td>Coconut fiber pith</td>
<td>Manju and Anirudham, 1997</td>
<td>50</td>
</tr>
<tr>
<td>Dead biomass</td>
<td>Leaf mould</td>
<td>Sharma and Forster, 1994</td>
<td>43</td>
</tr>
<tr>
<td>Dead biomass</td>
<td>Green algae</td>
<td>Roy et al., 1993</td>
<td>162.23</td>
</tr>
<tr>
<td>Dead biomass</td>
<td>Rice hulls</td>
<td>Roy et al., 1993</td>
<td>164.31</td>
</tr>
<tr>
<td>Peat moss</td>
<td>Peat</td>
<td>Tummavuori and Aho, 1980</td>
<td>43.9</td>
</tr>
<tr>
<td>Peat moss</td>
<td>Irish sphagnum moss peat</td>
<td>Sharma and Forster, 1993 and 1995</td>
<td>119; 43.9</td>
</tr>
<tr>
<td>Tannin-rich</td>
<td>Walnut shell</td>
<td>Orhan and Büyükgüngör, 1993</td>
<td>1.33</td>
</tr>
<tr>
<td>Tannin-rich</td>
<td>Exhausted coffee</td>
<td>Orhan and Büyükgüngör, 1993</td>
<td>1.42</td>
</tr>
<tr>
<td>Tannin-rich</td>
<td>Nut shell</td>
<td>Orhan and Büyükgüngör, 1993</td>
<td>1.47</td>
</tr>
<tr>
<td>Tannin-rich</td>
<td>Waste tea</td>
<td>Orhan and Büyükgüngör, 1993</td>
<td>1.55</td>
</tr>
<tr>
<td>Tannin-rich</td>
<td>Turkish coffee</td>
<td>Orhan and Büyükgüngör, 1993</td>
<td>1.63</td>
</tr>
<tr>
<td>Tannin-rich</td>
<td>Sawdust</td>
<td>Bryant et al., 1992; Dikshit, 1989; Zarraa, 1995</td>
<td>10.1, 16.05, 4.44</td>
</tr>
<tr>
<td>Zeolite</td>
<td>EHDDMA-amended zeolite</td>
<td>Santiago et al., 1992</td>
<td>0.42</td>
</tr>
<tr>
<td>Zeolite</td>
<td>CETYL-amended zeolite</td>
<td>Santiago et al., 1992</td>
<td>0.65</td>
</tr>
<tr>
<td>Pyrolyzed tires</td>
<td>Pyrolyzed tires</td>
<td>Hamadi et al., 2001</td>
<td>25.62–29.93</td>
</tr>
<tr>
<td>Pyrolyzed sawdust</td>
<td>Pyrolyzed sawdust</td>
<td>Hamadi et al., 2001</td>
<td>20.09–24.65</td>
</tr>
</tbody>
</table>

Source: Adapted from Bailey et al. (1999).

(UF), nanofiltration (NF) and reverse osmosis (RO). Although RO membranes can achieve the highest effluent water purity, they must operate at higher pressure. For this reason, nanofiltration has attracted increasing attention.

Hafiane et al. (2000) tested a thin film charged surface (TFCS) nanofiltration membrane for Cr(VI) removal and found that results were promising (Hafiane et al., 2000). Owing to the negative surface charge of the membrane, Cr and other anions are repelled by the membrane surface. As ionic strength of the water increases; however, this effect is shielded, and Cr removal
decreases. As expected, Cr removal improves with increasing pH (membrane surfaces are deprotonated, increasing electrostatic repulsion, and Cr charge increases as \( \text{CrO}_4^{2-} \) forms). The rejection rate of Cr(VI) (equivalent to the removal rate) can be expressed as the following:

\[
\text{Rejection rate} = \frac{\sigma(1 - F)}{(1 - \sigma F)} \quad (8.5)
\]

where rejection rate is dimensionless (no unit), \( \sigma \) is the reflection coefficient and corresponds to the maximum rejection at an infinite volume flux, and \( F \) is defined by the following:

\[
F = \exp\left(1 - \frac{\sigma J_v}{P}\right) \quad \text{or} \quad e^{\left(1 - \frac{\sigma J_v}{P}\right)} \quad (8.6)
\]

Here \( J_v \) is the flux of water through the membrane, with units of volume per membrane area per time, and \( P \) is an empirical parameter, known as the solute permeability, also with units of volume per membrane area per time. Hafiane et al. (2000) determined the empirical \( \sigma \) and \( P \) parameters for different ionic strength and pH values, allowing Cr rejection efficiency to be predicted once ionic strength and pH are known.

Cr(VI) ions are too small to be removed by microfiltration or ultrafiltration membranes, unless pretreatment is performed to complex the Cr(VI) by larger molecules. Hexadecylpyridine chloride has been used in the past, followed by ultrafiltration through membrane with 17.5% of greater polymer content. Approximately 98% of the Cr(VI) was removed with this system (Bohdziewicz, 2000). Microfiltration has been used for removing Cr(III) precipitates from industrial wastewaters (Visvanathan et al., 1989).

8.4.1.5 Soil Washing and Separation Technologies

Soil washing is used to chemically or physically separate Cr-contaminated soil from other soils prior to disposal. Physical separation based on size or lithology can be performed using a variety of screens, rotary scrubbers, grizzlyshakers and settling tanks, technologies adapted from mineral processing. For example, if the Cr(VI) is primarily associated with the clay-rich fraction of a soil, sands and gravels can be separated from the clays physically. Contamination will then be concentrated in a smaller volume prior to subsequent treatment or disposal.

Chemical treatment typically involves the addition of an acid, oxidant, surfactant, or a chelating agent to the soil slurry to increase the amount of Cr in the aqueous phase. Alternatively, the soil can be sprayed with water or a leaching solvent applied under high pressures to chemically leach Cr out of the soil. Soil washing solvents include commercially available chelating agents, surfactants, and acids. Leachability of Cr(VI) increases with the pH of the washing solution. Owing to the need for subsequent wastewater treatment, soil washing is not commonly used for environmental remediation. Cr has been extracted from radioactive processing wastes to help decrease the
volume of high-concentration radioactive solids (Sylvester et al., 2001). Hot water washing of Cr slag (a mixture of ore processing residual and soil) has been used to recover Cr in the form of Cr(VI) for further industrial use (Ososkov and Bozzelli, 1994). After soil washing, the Cr(VI) wastewater can be further concentrated using ion-exchange resins. High removal rates (95 to 99%) of Cr(VI) from the waste ore have been reported (Ososkov and Bozzelli, 1994). Passive soil washing technologies, including heap-leaching methods have been applied for environmental remediation.

### 8.4.2 In-Situ Technologies

In-situ technologies are an attractive alternative to ex-situ remediation technologies, since excavation and/or pumping costs are eliminated. The in-situ removal technologies discussed in this section remove total Cr in the subsurface. Technologies include soil flushing, electrokinetics, and solvent extraction.

#### 8.4.2.1 In-Situ Soil Flushing

In-situ soil flushing is the extraction of Cr from the unsaturated zone using water or another solvent. It involves injection or infiltration of water through the unsaturated zone, which raises the water table into the contaminated area, and then extraction, followed by treatment and reinjection of the water. Soil flushing is analogous to soil washing, but the phase transfer of Cr occurs in the subsurface. Since Cr(VI) is soluble in water, it is easily removed with the water.

The depth of the water table and the initial and final target concentrations of Cr remaining in the subsurface determine the practicality of soil flushing. Surfactants have been used to enhance soil flushing. Two characteristics of a desirable surfactant are a high ratio of surfactant CrO$_4^{2-}$ extraction to water extraction of CrO$_4^{2-}$ and a high resistance of the surfactant to subsurface losses (sorption and precipitation). Nivas et al. (1996) tested different surfactants to enhance pump-and-treat operations, and found that extraction efficiency increased with surfactant concentration below the critical micelle concentration (CMC), and was fairly constant at doses above the CMC (Nivas et al., 1996). Adding a complexing agent, diphenyl carbazide (DPC), increased total Cr removal 9.3 to 12.0 times with respect to deionized water. The most effective surfactant tested was Dowfax 8390 (Nivas et al., 1996). This information was applied to ongoing pump-and-treat system at the U.S. Coast Guard Support Center, Elizabeth City, NC.

One Superfund Site using in-situ soil flushing is the United Chrome Products Superfund Site in Corvallis, Oregon. Cr concentrations in the soil are as high as 60,000 mg/kg and 19,000 mg/l in groundwater (USEPA, 2000b). The approach since 1985 has been to flush the subsurface with water so that the water-soluble Cr(VI) goes into the aqueous phase and is extracted. Infiltration basins and trenches are used to deliver water to the contaminated
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Soils. A groundwater extraction network is used to remove the chromium-contaminated water and recharge treated water.

Soil flushing has been the most successful in coarse soils of relatively high hydraulic conductivity. Cr(VI) concentrations in the water extracted by the well network decreased from 5000 to 50 mg/l over 2.5 years. Average concentrations in the groundwater plume decreased from 1923 to 207 mg/l after flushing with 15 million liter (1.5 pore volumes). Concentrations have not yet stabilized at asymptotic limits, indicating that additional Cr(VI) removal can be expected (USEPA, 2000b). Recently, soil with concentrations greater than 6000 mg/kg were excavated, in order to shorten the time for remediation.

8.4.2.2 Electrokinetics

Electrokinetic remediation applies low concentrations of voltage (50 to 150 V) across contaminated soil in order to mobilize Cr(VI) anions. The Cr(VI) contaminants will concentrate around the anode in aqueous phase. Less soluble Cr(III) may build up near the cathode. Electrokinetics is typically applied in-situ, with the electrodes placed directly in the ground to depths of 3 to 5 m. In most cases, groundwater is extracted at each electrode and treated above ground. During ex-situ electrokinetics, electrodes are installed on both sides of the contaminated soil or slurry.

Factors that improve electrokinetic performance include a low cation exchange capacity, high soil moisture but not saturated conditions, low salinity, low conductivity, and a high fraction of exchangeable or soluble Cr concentrations. Reddy et al. (2001) tested electrokinetic removal of Cr(VI), Cr(III), Ni (II) and Cd (II) in two different soil types: clay (kaolin) and glacial till. The exchangeable and soluble fraction of Cr(VI) migrated towards the anode in both cases, but Cr(III), Ni (II) and Cd (II) migration depended on the amount of exchangeable and soluble metal present. In glacial till, this soluble fraction of Cr(VI) was negligible. In kaolin, migration was observed.

Conductive pore fluids can be injected into the subsurface to enhance the electrokinetic process and make up for a lack of soil moisture in the unsaturated zone. Flushing the system with water can help counteract extreme changes in local pH as H_3O^+ and OH^- ions migrate in opposite directions. Extreme local pH can change the solubility and speciation of the contaminants.


In-situ electrokinetics was applied at the Naval Air Weapons Station, Point Mugu, CA in a field demonstration in 1998 (USEPA, 2000a). Both Cr and Cd were present and ranged from “nondetect” to 25,100 and 1810 mg/kg.
respectively. Soil was characterized as 85% sand, 7% gravel, 6% silt and 1% clay. Electrokinetic extraction was found to be much slower than originally expected, although current densities were lower than those used in bench-scale studies. After 22 weeks of operation, the pH front was just beginning to appear. Factors retarding performance were investigated for the rest of the study period. In general, the technology is still being developed and is not ready to be implemented at the full-scale until site-specific bench and pilot testing has been conducted.

8.5 Containment Technologies

Containment technologies are used to either physically stop the spreading of groundwater plumes or to chemically immobilize contaminants in a nonexchangeable, insoluble form. Most containment technologies are performed in-situ, with the exception of soil vitrification prior to landfill disposal. Groundwater containment technologies involve the construction of a physical, chemical, or hydraulic barrier that isolates the impacted zone, either directing impacted water through a treatment zone or stopping its migration. Soil contaminants are either physically isolated by a barrier or chemically treated to tightly bind and immobilize contaminants onto the soil.

8.5.1 Barrier Technologies

One advantage of physical barriers is the wide range of contaminants that can be contained and isolated, including Cr(VI). Physical barriers are constructed of low permeability materials such as grout, slurries, or sheet piling. Even in the best cases, however, a small amount of vertical or horizontal leakage is likely to occur. For this reason, chemical and hydraulic barriers have been developed as alternatives. Hydraulic control is maintained by an upgradient extraction system and must be accompanied by ex-situ treatment. Hydraulic control is commonly employed as an interim corrective action measure to stop plume migration while site characterization and remedial technology evaluation are being conducted. Chemical barriers can be passive or reactive. Both are designed to let water pass through the barrier zone while the contaminant is immobilized. Passive barriers need little or no maintenance to chemically immobilize contaminants, yet are not always an option for a site. Reactive barriers are maintained by chemical addition and/or contaminant extraction.

Barrier technologies work only if the groundwater gradient is consistent and unlikely to change over time. Costly mistakes can be made using containment technologies in locations where the groundwater table has large seasonal fluctuations or the groundwater gradient is shallow or inconsistent.
8.5.1.1 Low-Permeability Passive Physical Barriers

Physical barriers are passive technologies; after installation, monitoring is the only maintenance that is required. Barrier materials include bentonite, grout, sheet piling, and synthetic materials such as polyethylene. The most common barrier configuration is a continuous trench or wall. Horizontal barriers are also used to stop vertical migration; the most commonly used barrier is a surface cap.

Groundwater levels can mound upgradient of the barrier. In some cases, shallow trenches are used to collect and channel the ponding water. In places where groundwater mounding is extreme, groundwater can be pumped and treated.

A slurry cutoff trench/wall is constructed using backhoes or excavators by digging a narrow vertical trench, typically 0.6 to 1 m wide, and as deep as 11 to 15 m. The trench is then backfilled with a bentonite-water slurry, stabilizing the walls of the trench and preventing it from collapsing. The slurry penetrates into the nearby soils and seals the formation (USEPA, 1991). Common slurry mixtures include soil/bentonite (SB) and cement/bentonite (CB). Hydraulic conductivity values of well-constructed SB and CB walls are approximately $10^{-8}$ cm/s and $10^{-6}$ cm/s, respectively (USEPA, 1985).

One concern with slurry cut-off technology is the compatibility of the trench backfill material with the site geochemistry. Acids, bases, salt solutions, and some organic chemicals can desiccate slurry wells, possibly leading to cracking.

![Soil/bentonite slurry cutoff trench installation](Image)

**FIGURE 8.5**
Soil/bentonite slurry cutoff trench installation. (Source: USEPA, 1988.)
Compatibility testing may be required to investigate the stability of the wall under site-specific conditions. A second concern with slurry wall technology is the potential for leakage underneath the wall. For this reason, slurry walls are often combined with hydraulic control systems that maintain a positive vertical gradient.

Slurry cut-off trenches/walls can be installed downgradient of a source to prevent further migration of Cr, upgradient of a source area to divert clean groundwater around a source, or circumferentially around a source, in conjunction with capping, to isolate the contaminated soils and groundwater. Slurry walls and capping have been used to isolate contamination at the Gilson Road Superfund Site, NH (Weston, 1989). A downgradient slurry wall was installed at the Rocky Mountain Arsenal, Denver, CO (CSU, 1988).

Alternative materials used for trench/well construction include sheet piling and grout. Sheet pile walls are constructed by driving interlocking steel sheet sections into the ground with pile drivers (USEPA, 1991). Joints can be sealed with hydrated clay or tremie-grouted with clay or neat cement. Sheet piling is faster to install than slurry walls; however, it is difficult to install in rocky soils or in areas with shallow bedrock. It is only economical to install sheet piling to depths of approximately 6 to 9 m.

Grout curtains are formed by injecting liquid grout into soil rock under pressure to reduce the permeability of unconsolidated soil. Particulate grout, also called suspension grout, is a suspension of solid materials—cement, clay, bentonite, or some combination of these. Particulate grouts have large particle size and are only suitable for highly porous sediments and soils. Chemical grouts, on the other hand, consist of silica and alumina-based solutions that gel and harden or polymers that initiate polymerization reactions and harden. The viscosity of chemical grouts is initially low, so it can
be pumped into fine-grained soils. To prevent migration of groundwater from under the grout curtain, grouting must extend into low permeability clay or bedrock. Grout curtain materials must be compatible with site subsurface conditions and contaminants.

Grout injection points of the curtain can be arranged in three rows. Primary holes form a double line of touching columns. The third line of injections is designed to fill any gaps in the primary injection columns. Holes are typically spaced 1 to 1.5 m apart.

Recently, synthetic high-density polyethylene (HDPE) barriers have been installed for groundwater containment. Specialized trenching machines have been designed to trench and continuously install polyethylene barriers, minimizing the number of seams. HDPE membranes are formulated to resist...
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degradation by sunlight and most contaminants. Sheets are joined together with interlocking waterproof joints. Polyethylene barriers are used to depths of approximately 9 m. The main limitation is the potential for groundwater and contaminants to leak past the barrier.

A polyethylene barrier was used in conjunction with free-product (unchanged contaminant from source) recovery and hydraulic control to prevent migration of groundwater contaminants into the Little River in Star Lake, NY. The barrier extends along the riverbank for 400 m and is approximately 5 m deep (Horizontal Technologies, Inc., 1999).

8.5.1.2 Permeable Chemical Barriers
Permeable barriers do not impede the flow of groundwater, just the mobility of the contaminant. Barrier material is used to filter, reduce and precipitate Cr(VI), decreasing its toxicity and mobility. Passive systems can be used at sites where groundwater flow is slow and contamination is dilute. Types of permeable barriers discussed here include permeable treatment walls and remediation injection technologies.

Permeable treatment walls are made of a reactive medium such as Fe(0), Fe$_2$O$_3$, iron sulfide, CaS, or bone char phosphate, all reducing agents for Cr(VI). Alternatively, sorbents such as zeolites, granular activated carbon or
reactive polymers may be used. When designing a permeable in-situ treatment system, five main factors must be examined in detail. These include groundwater characteristics (velocity, flux through the barrier and vertical gradients), stratigraphy (depths and thickness of units, degree of fracturing

![Diagram of permeable subsurface treatment trench and zone of remediated groundwater](image-url)

**FIGURE 8.10**
Cross-section of a polyethylene barrier system. (Source: CSU, 1988.)

![Diagram of permeable treatment wall-caissons and chemical plume](image-url)

**FIGURE 8.11**
Permeable treatment wall-caissons or large-diameter borings filled with treatment material placed across the path of the Cr plume. (Source: CSU, 1988.)
and channeling), hydrochemistry (contaminant distribution and water chemistry) depositional environment (mineralogy, total organic carbon), and microbiology (GRA, 1999).

Several variables affect the overall reduction rate of Cr(VI) by an Fe barrier. The pH is naturally decreased as Cr(VI) is reduced by Fe(II). Low pH may inhibit Cr(III) precipitation. If the pH is increased by the addition of base, and the system is aerobic, Fe(II) will be preferentially oxidized by O₂, owing to faster oxidation kinetics at higher pH values. Therefore, detailed bench tests with pH controls and site-specific geochemical conditions is appropriate prior to installing a barrier system.

The most common emplacement technique is the conventional trench-and-fill method. In this method, sheet piles, or shoring may be required to keep the trench open while backfilling with treatment materials. Rapid, one-pass trenching machines can excavate and lay the treatment material using a conveyer belt on the trenching machine. No sheet piles or shoring is required in this method. Alternatively, a caisson (canister) can hold the reactive treatment material. Groundwater can flow horizontally through screened sections of the caisson(s), or vertically through the caisson (Warner et al., 1998).

When designing the treatment zone, the length of the flow path must correspond to the residence time required within the treatment media. Nonuniform groundwater flow may lead to channeling and higher groundwater velocity zones (Gallinatti and Warner, 1994), resulting in preferential flow paths and less than optimal residence times. The width of the treatment wall or gate must take into account the desired changeout period of the treatment media.

The funnel and gate barrier design is a hybrid technology of physical barriers that funnel contaminated groundwater through a series of permeable treatment zones (gates). Originally designed by the University of Waterloo, most treatment zones are less than 12 to 15 m deep. Deeper treatment systems to 21 to 30 m are possible with more specialized installation equipment. A funnel and gate barrier system was constructed in Sunnyvale, CA to treat solvents in 1994 (Yamane et al., 1995). Preliminary results of a Fe(0) barrier for Cr(VI) at the U.S. Coast Guard Support Center, Elizabeth City, NC indicate that the test barrier has reduced chromate in groundwater to below detection limits (Wilson, 1995).

8.5.2 Vitrification

In-situ vitrification (ISV) is accomplished by placed an array of electrodes into the soil and sending an electric current through the soil until it melts, sealing the metals in a glassy mixture. Resistance heating melts the soil. The melt grows outward since the molten soil usually provides additional conductance for the supplied current. An array of four electrodes can treat up to 907 metric tons of contaminated soil to depths of 6 m, at a typical treatment rate of 2.721 to 5.442 metric tons per hour. Larger areas are treated by fusing together multiple individual vitrification zones (Evanko and Dzombak, 1997). ISV is best for areas in which removal of contamination is not possible.
owing to depth or other physical constraints. Local energy costs are a major consideration for vitrification projects. If the soils are too dry, soil temperature and conductivity enhancements such as flaked graphite or ground glass particles must be placed around the electrodes to provide the initial flow path for the electric current.

The first full scale ISV application treated sediments contaminated with metals (Cr, As, Hg, Pb) as well as pesticides and dioxins at the Parsons Chemical/ETM Enterprises Superfund site in Grand Ledge, Michigan. The ISV program required eight separate melt events over a period of 10 to 20 days for each melt event. A hood was employed to capture volatiles. The treatment was successful, meeting TCLP limits for all the metals in the treated waste (Evanko and Dzombak, 1997). The only commercial ISV technology is offered by Geosafe Corporation. Owing to high costs of ISV, it remains a rarely used technology at Superfund and other hazardous waste sites. Another drawback of ISV is the remaining solidified block of glassy soil—making it not suitable for common tasks such as growing crops.

### 8.5.3 Solidification/Stabilization

Solidification refers to treatment that solidifies Cr into an immobile mixture with an additive, such as cement. Stabilization, also known as fixation, refers to the formation of an insoluble Cr compound. In addition, the permeability of the area containing the stabilized contamination is lowered, resulting in groundwater flow around the area rather than through it.

The main concern with stabilization and solidification technologies is long-term stability of Cr. Sometimes Cr(VI) can leach out of the system into groundwater over time or with a change in environmental conditions in the field (e.g., precipitation). Reducing Cr(VI) with S\textsuperscript{2}\textsuperscript{-} prior to solidification/stabilization reduces the chances of remobilization of Cr(VI). Allan and Kukacka (1995) found that stabilization with slag-modified cement grout did not leach as much Cr as lime or Portland cement grout. Leachability decreased as slag content increased.

Solidification/stabilization is an option at sites with shallow contamination (maximum depth 2 to 5 m). A final cost estimate for this technology should take into account the cost of pretreatment chemicals, solidification/stabilization reagents, equipment, labor, local energy rates, testing, and monitoring costs. Solidification and/or stabilization is well established, with over 200 Superfund sites choosing it as a component of soil remediation. Solidification/stabilization is considered to be the best available technology for Cr remediation in nonwastewater, along with reduction (Evanko and Dzombak, 1997).

### 8.6 Combining Multiple Approaches to RemEDIATE CR

Although it is convenient to group remediation technologies into categories, based on their principal mechanism of minimizing exposure to Cr(VI), most
remediation strategies combine multiple technologies and mechanisms. For example, toxicity reduction occurs when Cr(VI) is reduced to Cr(III). However, this will also result in containment, since Cr(III) will usually sorb or precipitate as a solid. Phytoremediation is a broad term that encompasses all three remediation strategies. Plants take up Cr, removing it permanently from the soil once they are harvested. Plants can also be used to stabilize contamination via reduction that occurs at the roots and subsequent precipitation or adsorption. Finally, this process converts Cr(VI) to Cr(III), reducing the Cr toxicity (Fein et al., 2001). Some remediation strategies employ a variety of different mechanisms owing to the complex nature of biological, geological and chemical processes and interactions. Scientists are just beginning to understand the mechanisms that contribute to remediation. For example, constructed wetlands are emerging as a way to reduce contaminants in a low-tech, natural setting. In a wetland, Cr(VI) will be reduced to Cr(III) and sorb to the soil, or be taken up by plants, algae, or bacteria. Cr may associate with organics or soil particles, and undergo colloidal transport.

More hybrid technologies are emerging, as advantages of each technology and the collaborative mechanisms under environmental conditions become apparent. For example, electrodynamics is being employed to enhance biological reduction in the Lasagna™ process. Reversing the polarity of the electrodes periodically leads to contaminant migration back and forth through the bioactive zone. New technologies that synthesize multiple treatment approaches will only continue to emerge in the future.

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