14
The Future, Emerging Mitigation and Remediation Technologies

CONTENTS
14.1 Emerging Mitigation and Remediation Technologies...........................565
  14.1.1 Process Description ..................................................................567
  14.1.2 Key Design Criteria ..............................................................568
  14.1.3 Photoreduction of Cr(VI).......................................................569
  14.1.4 Pollution Prevention Trends .................................................570
Bibliography ......................................................................................572
14.2 Conclusions ..................................................................................573

14.1 Emerging Mitigation and Remediation Technologies
Stephen M. Testa, James F. Begley, and James Jacobs

Some of the emerging technologies for the mitigation and remediation of Cr(VI) include microbial strategies for in-situ and on-site bioremediation strategies, and use in permeable reactive barriers. Discovery of microorganisms capable of reducing Cr(VI) to Cr(III) have significant potential in development of in-situ or on-site bioremediation strategies. In 1977, the first reported bacterial strains, Pseudomonas, were isolated from chromate-contaminated sewage sludge (Romanenko and Korenkov, 1977). Since 1977, several other chromate reducing strains have been reported including other strains of Pseudomonas, as well as strains of Achromobacter, Aeromonas, Bacillus, Desulfomamaculum, Enterobacter, Escherichia, and Micrococcus species (Gvozdyak et al., 1986; Horitsu et al., 1987; Bopp et al., 1983; Wang et al., 1989; and Fude et al., 1994).

An indigenous bacterium capable of reducing and immobilizing Cr to an insoluble Cr(III) precipitate on its surface, thus removing Cr(VI) from solution,
Chromium(VI) Handbook

has been isolated at a wood preserving site located in Acton, Ontario (McLean and Phipps, 1999). The operation utilized a copper-arsenate-chromate solution to preserve the wood, which resulted in soil and groundwater contamination. A yet unidentified gram-negative strain, tolerant to high concentrations of Cr(VI) [up to about 500 milligrams per liter (mg/l)], and possibly Cu and As (up to about 40 mg/l), has been noted. McLean and Phipps (1999) state that the high tolerance ensures that unpredicted release of adsorbed metals will not inhibit the reduction reaction. Laboratory studies showed the bacterium exhibited a broad range of reduction efficiency under minimal nutrient conditions at temperatures between 4 and 37 °C, pH 4 to pH 9, and under aerobic and anaerobic conditions. The exact mechanism by which the indigenous microorganism reduces aqueous Cr(VI) to Cr(III) remains uncertain since a combination of biochemical and surface mediated reactions have been implicated in the process.

In the consideration of permeable reactive barriers in the deep subsurface, metabolic capabilities of dissimilatory metal-reducing bacteria (DMRB) have shown merit (Gerlach et al., 1999). These capabilities have the potential to create zones of reduced indigenous metals (i.e., Fe(II)) in the path of a groundwater contaminant plume, thus forming redox-reactive barriers. Essentially, starved cells of *Shewanella alga* BrY were resuscitated with artificially associated Fe(II), which in turn almost instantaneously reduced Cr(VI) to Cr(III), the Cr(III) precipitating onto the sand media. In batch and column studies, the microbiially-generated surface-associated Fe(II), produced from indigenous Fe(III), has been shown to reduce Cr(VI) to Cr(III), resulting in the precipitation of Cr(III) on existing surfaces, forming stable end products, and eliminating Cr(VI) from the water phase.

In organic-carbon-poor subsurface environments, sucrose-amended, yeast extract-amended, and lactate-amended systems were observed to be effective for the microbial reduction of Cr(VI) (Hong and Sewell, 1999). Depending on the supply of the electron donor (i.e., lactate), a reduction sequence of nitrate, Cr(VI), and sulfate was observed. Acetate and benzoate amended systems were found not to be as effective as electron donors, allowing for only 34.5 and 13.7% removal of Cr(VI), versus 100% removal utilizing sucrose, lactate, and yeast extract-amended systems.

Use of the bacterium *Pseudomonas Putida* ATCC17484 was deemed successful for the biodegradation of naphthalene with the presence of Cr(VI) (Ghoshal et al., 2001). The presence of Cr(VI) however inhibited bacterial growth and reduced the biodegradation rate of the naphthalene. Complete reduction of Cr(VI) was achieved at concentrations up to 6.3 mg/l. In another study, a bench-scale treatability study was performed to evaluate the feasibility of in-situ bioremediation of perchlorate (ClO₄⁻) and Cr(VI) (Perlmutter, 2001). Two media (sand and gravel), and four electron donors (acetate, molasses, composted manure, and concentrated fruit juice) were considered. Acetate and molasses were found to be acceptable electron donors. It was determined that acetate may be required to initiate the treatment system, but molasses would be used as the long-term electron donor. It was further
noted that the Cr(VI) concentrations used in this study (up to 8.0 mg/l) did not inhibit ClO$_4^-$ reduction (originally set at 1500 mg/l) and was routinely reduced to below its analytical detection limit during the study.

Another emerging technology is an enhanced anaerobic treatment of Cr(VI) contaminated groundwater using biostimulation of indigenous soil bacteria by adding an alkane gas. An alkane gas, such as propane is used as a growth substrate to promote conditions leading to the reduction the Cr(VI). With this approach, the added substrate serves as both the electron donor and primary growth substrate for the bacteria. Cr(VI) is potentially the final electron acceptor in the process.

Cr(VI) is known to be reduced both aerobically and anaerobically in different bacterial systems (Suthersan, 2002). While consuming propane, the microbes use up the oxygen and create the geochemical conditions necessary for the reduction of Cr(VI).

Microbial transformation of Cr(VI) varies with the oxidation state. In groundwater, the predominant form of Cr is the oxidized form, Cr(VI), present as chromate (CrO$_4^{2-}$) and dichromate (Cr$_2$O$_7^{2-}$) ions (Suthersan, 2002). Cr(VI) is the oxidized, toxic, and mobile version and Cr(III) is less toxic and less mobile. Cr(III) precipitates as a Cr(III) hydroxide [Cr(OH)$_3$] at groundwater pH of 4.5 to pH 10.5, within the range of most naturally occurring groundwaters. A variety of aerobic and anaerobic microbes enzymatically reduce Cr(VI) to Cr(III), but the details of the process are not well understood (Suthersan, 2002). There are several hypotheses to explain these reduction reactions, including the following:

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
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<tbody>
<tr>
<td>Detoxification</td>
<td>Move Cr away from the cells</td>
</tr>
<tr>
<td>Cometabolism</td>
<td>Fortuitous enzymatic reactions</td>
</tr>
<tr>
<td>Respiration</td>
<td>Use of Cr(VI) as a respirator electron acceptor</td>
</tr>
<tr>
<td>Indirect reduction</td>
<td>Microbes reduce Cr(VI) by producing sulfide, Fe(II), and reduced organic compounds</td>
</tr>
<tr>
<td>Chemical reduction</td>
<td>The Cr(VI) is reduced as the aerobic environment is changed using chemicals that react with oxygen. As the oxygen is used up the environment changes into a reducing environment, without the aid of microbes. In the reduced environment, the Cr(VI) is converted into Cr(III), and ultimately precipitates out as chrome hydroxide.</td>
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**14.1.1 Process Description**

Treatment by direct infusion of an alkane gas through a gas infusion emitter into a monitoring well is a straightforward process to treat Cr(VI). The iSOC unit introduces sparge-free gases into the saturated zone. No mounding of groundwater occurs with this in-situ method. The iSOC gas emitter tool consists of a microporous, hollow-fiber membrane enclosed in a stainless-steel casing that is lowered into a 50.8 mm diameter well. The source of the
Chromium(VI) Handbook

568

propane is a portable gas cylinder. The gas cylinder contains a two-stage, low-flow gas regulator and is attached to a control box and flow meter with 6.35 mm diameter polyethylene tubing. The iSOC tool is also connected to the control box and flow meter with 6.35 mm diameter tubing. This gas infusion system runs on the pressure in the gas cylinder; there are no moving parts in the system and no power is required.

The iSOC gas infusion tool is placed in the 50.8 mm diameter treatment well, provides an inherently large surface area that allows for alkane gas delivery by direct contact with groundwater and ultra efficient mass transfer by direct infusion. Propane a somewhat soluble gas in water, can dissolve to 66 ppm with a minimum of 1.5 m of water in the well, and up to 175 ppm with 15 m of water column in a well. The treatment area established by direct infusion can be designed as a grid to treat Cr(VI) source areas and/or as a treatment curtain or fence of treatment wells to cut off Cr(VI) plume migration by creating reducing conditions. The radius of influence for 50.8 mm diameter wells being supplied with propane is approximately 3 to 5 m.

14.1.2 Key Design Criteria

To achieve supersaturated conditions, propane is infused at a standard rate of 15 cm³/min, promoting the growth of soil bacteria. A concentration of

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**FIGURE 14.1.1**
Gas infusion technology process diagram.

Au: Pls all cite Figures in text
66 mg/l of propane can be achieved in groundwater with a water column of 1.5 m in a well above the iSOC unit. Spacing of iSOC injection wells are typically 6 to 9 m to apart, depending on lithologies.

Performance monitoring wells should be placed within the center of the groundwater plume and at cross-gradient locations to assess the area of influence. In addition, based on consistent groundwater flow direction data, the downgradient sampling points should be evaluated because changes within the plume occur over several months. Monitoring parameters should include at a minimum, oxidation-reduction potential, dissolved oxygen, dissolved propane, pH, and the target contaminant concentrations. Changes in plume characteristics, as well as reduction in Cr(VI) concentration occur slowly in anaerobic systems over a period of several months to several years. Obtaining equilibrium with propane in an aquifer is likely to take 3 to 6 months or more.

14.1.3 Photoreduction of Cr(VI)

Medical researchers have found that Cr(VI) in the form of potassium dichromate can be photoreduced to Cr(III) in aqueous solutions containing
glycerol. The photoreduction of Cr(VI) occurred after irradiation with either UVA (320–400 nm) or a wide spectrum light source. A lower spectrum UVB (290–320 nm) light source did not work at photoreducing the Cr(VI). The photoreduction of Cr(VI) was noted to be pH-dependent and did not occur in dilute solutions of sodium hydroxide. In the acidified solutions, the photoreduction of Cr(VI) occurred at elevated rates and at lower concentrations of glycerol. This reaction is apparently dependent on the unsubstituted alcohol groups of glycerol since alpha-phosphoglycerol or beta-phosphoglycerol did not support the photoreduction of Cr(VI) (Yurkow et al., 2000).

### 14.1.4 Pollution Prevention Trends

A systematic approach to pollution prevention can go far in identifying and reducing adverse environmental effects. Pollution prevention from a manufacturing perspective can include material substitution, process improvement, product change or redesign, or a combination or these strategies. Material substitution is essentially the use of different materials that are deemed less toxic or nontoxic. Replacement of Cr with non-Cr bearing raw
materials or replacement of equipment that does not require Cr is a clear examples of material substitution. Paint waste can be eliminated as a hazardous waste stream via the removal of lead and Cr from most paint formulations. Paint sludge is now recycled into building materials such as quarry tile, asphalt, mastic, and binder.

Process improvement allows for the reduction or elimination of the need to utilize Cr. This can be accomplished by increasing the operating efficiency of certain equipment or process, development of stringent maintenance programs, and formulation of training programs to reduce the risk of waste generation.

With the prevalent use of Cr(VI) in plating operations, improvement in the type of bath used presents a good example of how a slight modification in equipment can significantly reduce the amount of Cr required and waste generated. A technique of porous pot bathing has been used to extend the bath life, thereby reducing the discharge of pollutants, and reducing the amount of Cr needed for the plating operation. During the plating process, concentrations of iron and other cationic impurities build up in a Cr(VI) bath to the extent that the plating becomes unacceptable. If the bath is contained in a porous pot where a semipermeable membrane separates cathode from anode and power is applied, the iron and other contaminant metal ions pass through the membrane. These ions accumulate in the cathode chamber from which they are periodically removed for subsequent disposal. Chromate ion remains in the anode compartment as part of the solution and can be returned to the plating tank for reuse.

Approximately 80% of the available power supplied to a Cr(VI) bath generates hydrogen gas during decorative and functional plating applications. The gas produces a mist of fine water particles with entrained Cr(VI), thereby creating a potential inhalation hazard to workers and increased costs for waste-water treatment to reduce Cr(VI) to Cr(III). However, with certain plating operations, notably decorative plating, the use of Cr(III) has proven successful in eliminating the need for misting and subsequent wastewaster treatment. Furthermore, the use of Cr(III) allows for improved adherence, throw and coverage, and higher rack densities, with lower volumes of sludge produced during the process. Plating coatings are typically limited to less than 0.00254 mm since thicker coatings are prone to cracking and spalling; thus, the use of Cr(III) is usually unsuitable for hard chrome coatings which can be 0.508 mm or more in thickness.

Product change or redesign in some cases may eliminate Cr from the manufacturing process altogether (www.epa.state.oh.us/opp/mfrm.txt). For example, colorants, adhesives, and dispersions used for the plastics industry, typically using lead chromate pigments, may be replaced with organic compounds. In another example, an aluminum extruding facility in Ohio was able to remove Cr(VI) by (a) changing from an alkaline cleaner to a dispersion cleaner that was Cr-free, (b) substituting an iron phosphate conversion coating in the pretreatment process for the previous Cr(VI) process, (c) removal of Cr(VI) from the paint line by changing to a powder coating, and (d) removal
of Cr(VI) from the anodizing line by implementing a totally non-Cr conversion coating process.

**Bibliography**


14.2 Conclusions

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Chromium (Cr) occurs naturally in the environment in three oxidation states, +3, +6, and rarely, 0. These oxidation states are named chromium(III) (Cr(III)), chromium(VI) (Cr(VI)), and elemental chromium/chromium(0) (Cr(0)), respectively. Owing to its unique properties, Cr is a strategic element in industry. Moreover, it is important to handle Cr safely regardless of its oxidation state and especially so for (VI).

Although some properties of Cr were known 200 years ago, it is only during the last 50 years that the toxic nature of Cr(VI) became known and that the Cr(VI) form of Cr was measured in the environment. Because Cr(VI) is very soluble in water under most environmental conditions (whereas Cr(III) is not usually soluble in water), it can be transported in groundwater thousands of meters from its source. And, since the mid 1970s, numerous industrial facilities and landfills have contaminated the groundwater with Cr(VI) at concentrations greater than the U.S. Environmental Protection Agency (USEPA) and California drinking water standards of 0.1 mg/l (0.1 ppm) and 0.05 mg/l (0.05 ppm), respectively.

Cr(VI) will continue to be used by industry. Fortunately, the processing of waste water has improved so that insignificant or no release of Cr(VI) should occur. Worker exposure to elemental Cr and Cr(VI) from operations that produce airborne particles or fumes such as welding, grinding, cutting, machining, and heating must be minimized.

There are many ongoing studies regarding the exposure of Cr to humans and its toxicity. Experimental evidence suggests that Cr(VI) is mostly toxic when inhaled and that it is reduced to essentially nontoxic Cr(III) when ingested. Cr(III) at low concentration is a necessary human nutrient.

There are effective remedial methods for cleaning up Cr-contaminated soil and groundwater to minimize exposure to Cr. These mainly use processes that reduce Cr(VI) to Cr(III) (usually to the insoluble Cr(OH)₃), thus achieving a reduction in toxicity and Cr mobility. In order to determine the effectiveness of remediation and to more accurately estimate the health risk from any remaining contamination, better chemical analysis methods for the speciation of Cr in the environment or industrial settings (i.e., to measure the concentration of Cr(III), Cr(VI), and Cr(0)) are needed.