

# **CHROMIUM(VI) HANDBOOK**



# CHROMIUM(VI) HANDBOOK

*Written by*  
**Independent Environmental  
Technical Evaluation Group (IETEG)**

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## *Preface*

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The purpose of this book is to evaluate the history and characteristics of chromium(VI) in the environment, in industry, and in society. The book was created by the Independent Environmental Technical Evaluation Group (IETEG), a volunteer research organization located in Northern California. It was created in 1997 to present objective scientific and engineering information about controversial environmental issues as a foundation for rational discussion and policy development. The IETEG's first project was *MTBE: Effects on Soil and Groundwater Resources* (CRC Press, 2000).

Chromium(VI) has been a controversial contaminant for a variety of reasons. This project was started in early 2001 to objectively evaluate the Cr(VI) issues. The IETEG's membership is multidisciplinary, including geologists, engineers, toxicologists, lawyers, regulators, and others working for environmental consulting and contracting companies, environmental equipment and product manufacturers, water companies, law firms, and academia. These environmental professionals are specialists in the assessment and remediation of soil, groundwater, and air, the complexities of environmental compliance, legal and regulatory issues, and the design of wastewater processing equipment. Given the level of misinformation on Cr(VI), this book was compiled to help facilitate a rational approach to the assessment and remediation of Cr(VI) contamination in the environment. The IETEG hopes that the book will contribute to maintaining the quality of our drinking water supplies contaminated by Cr(VI), the settlement and resolution of legal issues relating to Cr(VI), and the development of regulatory policies designed on scientifically based information.



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## *Overview of Chromium(VI) in the Environment: Background and History*

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**James A. Jacobs and Stephen M. Testa**

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## 1.1 Purpose

Chromium (Cr) is one of the world's most strategic and critical materials having a wide range of uses in the metals and chemical industries. Alloys containing Cr enhance metal resistance to impact, corrosion, and oxidation. In addition, Cr is used primarily in stainless steel and noniron alloy production for plating metals, development of pigments, leather processing, and production of catalysts, surface treatments, and in refractories. Cr occurs in various oxidation states, of which chromium(VI) [Cr(VI)] is a suspected carcinogen and a potential soil, surface water, and groundwater contaminant. Cr(VI) may also occur in the natural environment, but human-caused Cr(VI) contamination has recently been the focus of much scientific discussion, regulatory concern, and legal posturing.

Owing to the many industrial uses of Cr(VI) with an active industrial base, California and other urbanized states have sites with significant Cr(VI) contamination. Drinking water supply wells and water sources are affected by Cr(VI). Common to many Cr(VI) sites are the questions that continue to arise regarding the safety of the drinking water supply. As with most environmental challenges, questions of science compete with emotional and political responses and financial interests. There is still uncertainty regarding what daily dose of Cr(VI) is considered toxic and what ingestion concentration of Cr(VI) is acceptable.

To define the current state of technical knowledge of Cr(VI), the Groundwater Resources Association of California ([www.grac.org](http://www.grac.org)) presented a Cr(VI) symposium in Glendale, California on January 25, 2001. At this symposium, national experts discussed the science, regulatory policies, and legal issues associated with this controversial pollutant. Based on disagreement on even the most basic of scientific points, such as safe levels of Cr(VI) to consume, it became apparent that Cr(VI) is a topic of both great importance and widespread debate.

The Independent Environmental Technical Evaluation Group (IETEG), a volunteer research organization located in Point Richmond, California, was created in 1997 to objectively review scientific and engineering information concerning controversial environmental issues. The IETEG's first project was *MTBE: Effects on Soil and Groundwater Resources*, a CRC Press book published in 2000. The next (and current) project was started in early 2001 to objectively evaluate Cr(VI) issues. The IETEG group is multidisciplinary and includes geologists, engineers, toxicologists, lawyers, regulators, and others performing environmental consulting, contracting, environmental equipment, design and

manufacturing. Others work for, water purveyors, law firms, regulatory agencies and academia. Some of these environmental professionals are specialists in the assessment and cleanup of soil, groundwater, and air. The authors work on environmental compliance, legal and regulatory issues, or the design of water treatment equipment. Given the level of misinformation on Cr(VI), this book was prepared to help facilitate a rational approach to protect the quality of drinking water supplies that may contain Cr(VI).

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## 1.2 Introduction to the Chromium(VI) Problem

Each contaminant has a unique set of characteristics and issues that must be evaluated to proceed with more detailed remediation efforts or developing public policy. These factors include persistence in groundwater, taste and odor thresholds, health risk, transport and fate, current laboratory analytical methods and detection limits, groundwater remediation, and regulatory issues. For Cr(VI), each of these factors will be evaluated in more detail below and in this handbook's chapters.

### 1.2.1 Exposure Pathways

For some, a significant health concern is the possible adverse effects of human ingestion of Cr(VI) in drinking contaminated groundwater or surface water. This exposure risk is still being debated within the scientific community. Dermal contact through bathing or washing in Cr(VI)-contaminated water is another exposure pathway. A common form of Cr(VI) is a chromate, a compound containing the chromate ion,  $\text{CrO}_4^{2-}$ , such as potassium chromate  $\text{K}_2\text{CrO}_4$ .  $\text{CrO}_4^{2-}$  can enter the bloodstream through breaks in the skin.  $\text{CrO}_4^{2-}$  blood poisoning occurs when  $\text{CrO}_4^{2-}$  destroys red corpuscles. Inhalation is also an important human exposure pathway; however, it is less likely to be associated with exposure to Cr(VI)-contaminated soils and groundwater and more likely associated with industrial processes such as welding, cutting, heating of Cr alloys, and work-related practices which create Cr(VI) fumes and airborne dust. Even dental technologists are at risk of Cr(VI) inhalation disorders (pneumoconiosis) from breathing dust from chromium-cobalt-molybdenum (Cr-Co-Ino) based dental constructions (Selden et al., 1995). Local exhaust ventilation can significantly reduce the inhalation hazard. Inhaling mists while showering with Cr(VI) contaminated water is also a common exposure pathway.

For dermal exposure, chromated copper arsenate (CCA) pressure-treated lumber is ubiquitous in residential areas. This green-colored pressure-treated lumber is used for building residential decks, picnic tables, swing sets, and other play structures. Since January 1, 2004, the United States Environmental Protection Agency (USEPA) has banned the use of CCA-treated lumber for new residential use. The exception for residential use

will be permanent wood foundations. The USEPA is not banning the use of millions of CCA-treated wood products already in backyards and parks, however more affluent communities and school & districts have already removed CCA-treated play structures. CCA-treated wood is still be available for industrial and agricultural uses. With low pH rain or fruit juice (orange juice and lemon juice), the Cr can be leached off the wood surface. For those concerned about this possibility, coating that play set or picnic table with an appropriate penetrating oil every two years will minimize the potential for leaching and adverse dermal contact (Morrison, 2004).

### 1.2.2 Physical and Chemical Characteristics

Chromium is rarely found as a free metal in nature. A clean surface of Cr metal reacts strongly with the atmospheric oxygen (Kohl, 1967). However, the reaction stops quickly owing to the formation of a strong, dense, and nonporous Cr(III) oxide ( $\text{Cr}_2\text{O}_3$ ) surface layer, which is estimated to be one to three formula units thick. Chromium oxide passivates the metal from any further reaction with oxygen. This is why Cr does not corrode and why it retains its metallic sheen.

Chromium(III) oxide is among the ten most abundant compounds in the Earth's crust. Cr, a solid at room temperature, generally reacts with halogen gases (such as fluorine) at temperatures of  $400^\circ\text{C}$  and pressures of 200 atm to 300 atm. Cr also reacts with the other halogen gases such as chlorine, bromine, and iodine to form a variety of brightly colored compounds. Cr metal dissolves in dilute hydrochloric acid and sulfuric acid. Cr does not appear to react with nitric acid, most likely owing to passivation by surface chromium oxides. Many of the Cr compounds are toxic.

Chromium is one of the chief ingredients in mineral and metallic colors, being responsible for the color of some gem stones. Among the gem stones colored by Cr are emeralds, ruby, alexandrite, chrome garnet, and some sapphires.

Chromium's physical and chemical characteristics remained largely a laboratory curiosity for about hundred years from 1800 to 1900. Small amounts were used to harden steel alloys and its numerous compounds were used in many different industries. A rapid increase in Cr use occurred between 1915 and 1930, when Cr became a leading industrial metal, along with iron (Fe), copper (Cu), aluminum (Al), tin (Sn), lead (Pb), and nickel (Ni). The reason for the long delay between its discovery date and industrial use was its high resistance to heat and chemicals. Extracting Cr from its ores by early methods was costly and difficult. Cr's useful properties such as brittleness, toughness, and resistance to corrosion made it difficult to work with. Cr's brittleness is probably caused by oxide impurities.

With a variety of characteristics and uses, Cr(VI) has entered subsurface soil, surface water, and groundwater. Sampling in California and other states has shown that Cr(VI) can exist as  $\text{CrO}_4^{2-}$  and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) in groundwater. The oxidation number of Cr in groundwater is governed by

pH and Eh. Cr(VI) can exist naturally in groundwater that has been unaffected by local industrial activity. At least one hypothesis indicates that naturally occurring fluoride forms a soluble complex with Cr(III)-bearing minerals, after which the dissolved Cr(III) comes in contact with manganese(IV) dioxide ( $\text{MnO}_2$ )-containing aquifer material, causing oxidation to Cr(VI). Cr(VI) in groundwater can be reduced to Cr(III) at low pH and under reducing conditions.

Cr(VI) is rapidly reduced to usually insoluble Cr(III) when Fe(II) or manganese(II) [Mn(II)] occur in reduced groundwater. There have been several examples of this immobilization phenomenon, both in industrial situations in the U.S. and at a Cr chemicals plant in Poland. Recent work on isotopic ratios of Cr(VI) may prove useful in evaluating the source or distance traveled and whether Cr(VI) is natural or anthropogenic in origin.

Cr(III) is a stable oxidation state and slowly reacts to form complexes. Because of its low kinetic energy potential, Cr(III) is not a strong oxidizer and it appears that the stomach's acidity is enough to keep the Cr in the Cr(III) state. Cr(VI) is not as stable as Cr(III) because it is a strong oxidizing agent, is fast reacting, and likely forms complexes. As with many toxic substances, exposure to metals by inhalation poses the greatest risk. However, for Cr(VI) to be inhaled, a person must be exposed to Cr fumes or airborne dust in industrial processes such as cutting or welding Cr metals or to Cr(VI) in airborne dust or water droplets. Some scientists suggest that Cr(VI) can cause cancer even when inhaled as an aerosol by showering in Cr(VI)-contaminated water. Disagreements still exist over the safe limits of Cr(VI) ingested as drinking water. There remains a debate by experts about the absorption potential that Cr(VI) might have in the stomach's acid environment. There does not appear to be a perceptible odor or taste that Cr in any form imparts to drinking water.

### 1.2.3 Analytical Methods

The investigation of a groundwater resource impacted with Cr(VI) requires analysis of groundwater for both Cr(VI) and total Cr. Total Cr can be detected by atomic absorption (AA) spectroscopy and other instrumental methods. Cr(III) and Cr(VI) can be detected by ion chromatography. Cr(VI) can also be detected by titration with a standard mixture of  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{I}_2$  (American Public Health Association, 1989).

Analytical methods used include the USEPA method for drinking water, EPA 218.6. The equivalent method for wastewater (used for contaminated groundwater as well) is SW 7196A or SW 7199. Method SW 7199 is the more sensitive method, with a low detection limit of  $0.02 \mu\text{g/L}$  [or parts per billion (ppb)] of Cr(VI). This method uses ion chromatography to estimate Cr(VI). Total Cr is analyzed using inductively coupled plasma-mass spectroscopy (ICP-MS) using methods SW 6010 or SW 6020. While analyzing for Cr, it is important to account for interferences from sulfide ( $\text{S}^{2-}$ ), vanadium (V), Mo, and organic carbon to ensure the accuracy of analytical data (Winter, 2004).

### 1.2.4 Remediation Overview

For *in situ* remediation of soil and groundwater, a variety of geochemical fixation or anaerobic biological treatment methods have been designed which make use of Cr's ability to change the oxidation state of the oxidized, toxic, and highly mobile nature of Cr(VI) and convert it into the more stable, nontoxic, and immobile Cr(III). Cr(III) ultimately precipitates out as Cr(III) hydroxide [Cr(OH)<sub>3</sub>]. In these technologies, Cr is generally not removed from the environment, but becomes less toxic and immobile. Many treatment methods use sulfur-based reductants; anaerobic biodegradation enhancements use carbon-sources such as lactic acid, molasses, cheese whey, or corn syrup. Permeable reactive barriers use elemental iron [Fe(0)] technologies to create a reducing environment. These *in situ* technologies use period redox (or Eh) reactions with either biological or chemical processes to reduce Cr(VI) to Cr(III).

A variety of technologies (known as pump and treat) are used in the extraction and treatment of surface water or groundwater. Once on the surface, water containing Cr(VI) can be reduced by Fe(II) compounds followed by several procedures including alkaline precipitation, ion exchange with regenerant treatment, or disposal. Electrochemical reduction is another method used where Cr(VI) reduction is followed by alkaline precipitation in which Fe(II) forms electrochemically, instead of being added as a purchased chemical; acidic reduction of the Cr at pH < 3.0 with sulfur dioxide, sodium sulfite, sodium bisulfite, or sodium metabisulfite completes the conversion to Cr(III). If reduction with a sulfite compound is used, there is a greater potential for incomplete conversion of Cr(VI) to Cr(III). Consequently, these reactions must be monitored carefully to ensure complete conversion to Cr(III).

### 1.2.5 Regulatory Concentrations

Chromium is listed as number 16 in the Agency for Toxic Substances and Disease Registry, *Priority List of Hazardous Substances* (ATSDR, 199a). Cr(VI) has been found in at least 304 of the 1,591 current or former USEPA National Priority List Superfund Sites (ATSDR, 2000). Neither the federal or state governments limits Cr(VI) concentration in water, but both regulate total Cr. The USEPA Drinking Water Maximum Contaminant Level (MCL) for total Cr is 100 µg/L. California limits total Cr in drinking water to 50 µg/L. Total Cr for contaminated site generic soil screening levels is 390 mg/kg for ingestion, 270 mg/kg for inhalation, and 2.0 mg/kg for migration to groundwater (USEPA, 1996).

The California Office of Environmental Health Hazard Assessment (OEHHA) initially recommended a public health goal (PHG) of 2.5 µg/L for total Cr and 0.02 µg/L for Cr(VI). The OEHHA has since rescinded the PHG and the state is working to establish a Cr(VI) MCL (California Department of Health Services, 2002). For airborne Cr(VI), the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), regulates worker's exposure to Cr(VI) and other toxic compounds. OSHA exposure limits for Cr compounds vary with potential work activities.

### 1.2.6 Health

Although the elemental Cr and Cr(VI) can have adverse human health effects, normal mammalian metabolism requires minute amounts of Cr as an essential trace element. In addition to insulin, Cr is responsible for reducing blood glucose levels and is used to control certain cases of diabetes. Cr has also been used to reduce blood cholesterol by lowering the concentration of the unhealthy, low-density lipoproteins (LDL) in the blood. Cr is supplied in a variety of foods such as broccoli, Brewer's yeast, liver, cheese, whole grain breads, and cereals. Some claims have been made that Cr aids in muscle development. Chromium picolinate, a highly soluble form of Cr, is used in dietary supplements for body builders.

Cr(III) is an essential nutrient that helps the body use sugar protein, and fat. The minimum human daily Cr requirement for optimal health is unknown, but a daily ingestion of 50 µg/L to 200 µg/L is estimated to be safe and adequate according to the ASTDR (1989).

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## 1.3 Historical Perspective

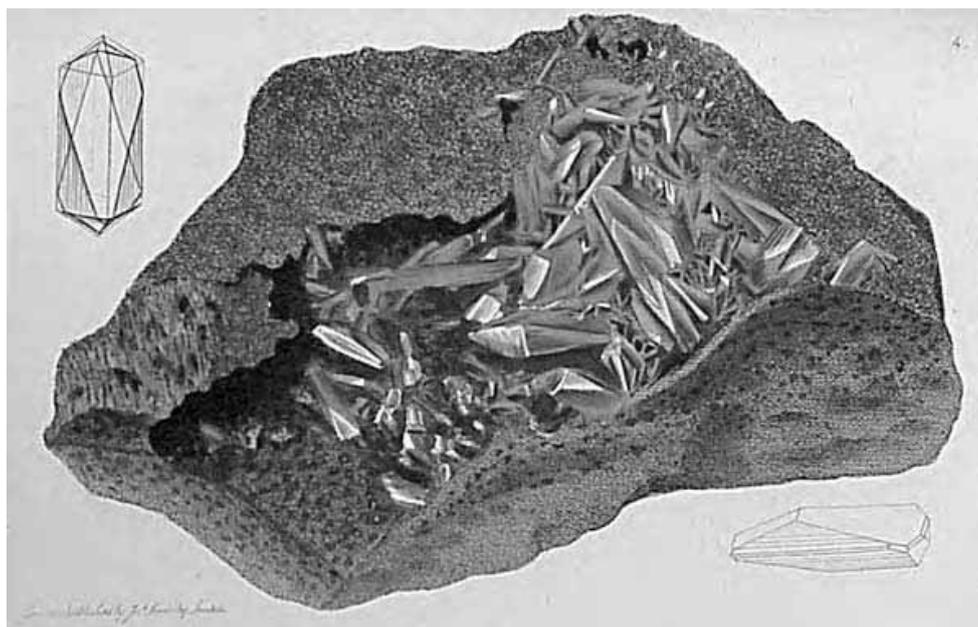
The history of Cr began over 200 years ago. Four Siberian Beresof gold mines had been worked for gold, copper, silver, and lead since 1752. In 1761, Johann Gottlob Lehmann obtained samples of an orange-red mineral that he termed "Siberian red lead," while visiting the Beresof mines located on the eastern slopes of the Ural Mountains. Upon his return to St. Petersburg in 1766, analysis showed that the samples contained lead "mineralized with a selenitic spar and Fe particles." This mineral turned out to be *crocoisite* or *crocoite*, a lead chromate ( $\text{PbCrO}_4$ ) (Figure 1.1). Lehmann described the mineral in a letter to the well known naturalist, Georges-Louis Leclerc comte de Buffon (1707 to 1788). Lehmann also observed that the mineral produced an emerald-green solution when dissolved in hydrochloric acid (HCl). Lehmann died the following year when a retort containing arsenic burst upon heating.

In 1770, Peter Simon Pallas also visited the Beresof mines and noted:

a very remarkable red lead mineral which has never been found in any other mine. When pulverized, it gives a handsome yellow guhr which could be used in miniature painting ... .

In spite of its rarity and difficulty in obtaining samples from the Beresof mines, the use of Siberian red lead as a paint pigment was mined both as a collector's item and for the painting industry as a paint pigment. A bright yellow made from crocoite rapidly became a fashionable color for carriages of the nobility in both France and England.

As a boy in Normandy, Louis-Nicholas Vauquelin (1763 to 1829) was fascinated with chemistry and mineral specimens. His father was a farm laborer who provided for his son's education. Progressing through school

**FIGURE 1.1**

Lead chromate mineral, Crocoite, from Beresou, Russia.

rapidly, at the age of 14 he became a dishwasher and assistant in an apothecary. He eventually went to Paris with a letter of introduction and worked for several apothecary shops. One pharmacy was owned by his cousin, Antoine-François comte de Fourcroy (1755 to 1809). Upon hearing of Vauquelin's interest in chemistry, Fourcroy hired his younger cousin as his assistant. Vauquelin continued to learn physics, chemistry, and philosophy while assisting Fourcroy with chemistry and teaching Fourcroy's students. With the onset of the French Revolution, Vauquelin left Paris in 1793, served as a pharmacist in a military hospital, and then returned to teach chemistry at the Central School of Public Works which later became the École Polytechnique. In 1797, Vauquelin, a professor of chemistry and assaying at the School of Mines in Paris, received samples of the crocoite ore.

Vauquelin noted the beauty and scarcity of this Cr ore (Figure 1.2). He noted its value equal to that of gold, and in an attempt to address several contradictory chemical analyses, he set out to determine the correct chemical composition of crocoite. Vauquelin boiled one part of pulverized crocoite with two parts of standard potash ( $K_2CO_3$ ), which resulted in a yellow-colored solution. The solution formed a red precipitate with a mercury salt and a yellow precipitate with lead. Adding HCl turned the solution green. In 1798, he was able to precipitate lead with HCl, dried the green solid, and then heated it for 0.5 h in a charcoal crucible with charcoal dust. The charcoal was used as a reducing agent. Upon cooling, he observed a mass of metallic needles with a mass of about half of that of the original. He thus discovered through subsequent analysis via heating  $Cr_2O_3$  with charcoal that crocoite was combined with an oxide of an unknown metal. Noting the many colors produced by the compounds, Fourcroy and Abbé