HEXAVALENT CHROMIUM

Beyond Erin Brockovich

OWEA POLA
5/22/14

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Chromium is an element that has the symbol Cr and atomic number 24.

It is the first element in Group 6 of the periodic table.
It is a steely-gray, lustrous, hard, and brittle metal that takes on a high polish, resists tarnishing, and has a high melting point. Name is derived from the Greek word χρώμα, chrōma, meaning color because of its many colored compounds.
Chromium exhibits a wide range of possible oxidation states.

- The +3 state is most stable energetically.
- The +3 and +6 states are most commonly observed in chromium compounds.
- The +1, +4, and +5 states are rare.
In the environment, water treatment processes, and water distribution systems, chromium occurs mostly as:
- Trivalent chromium (chromium-3, Cr(III), Cr+3)
- *Hexavalent chromium* (chromium-6, Cr(VI), Cr+6).
Trivalent chromium has been considered an essential human nutrient.

- Recent studies, however, have shown no ill-effects from low Cr(III) in the diet.
- No known biological mechanistic function for Cr(III) in cells.
- So, in small doses, trivalent chromium is not considered toxic to humans.
Hexavalent chromium is used in making stainless steel, textile dyes, wood preservation, and as anti-corrosion and conversion coatings and a variety of niche uses.
Hexavalent chromium compounds are used in a variety of industries.

- Chromate pigments in dyes, paints, inks, and plastics
- Chromates added as anticorrosive agents to paints, primers, and other surface coatings
- Chromic acid electroplated onto metal parts to provide a decorative or protective coating.
Hexavalent chromium can be formed when performing "hot work" such as welding on stainless steel or melting chromium metal. Here, the chromium is not originally hexavalent, but the high temperatures result in oxidation that converts the chromium to the hexavalent state.
Hexavalent chromium in drinking water was first brought to the public’s attention in 1993 when Erin Brockovich highlighted contamination in groundwater near Hinkley, CA by the Pacific Gas and Electric Company.
**ENVIRONMENTAL CONCERNS**

- **Hexavalent chromium** has been demonstrated to be a human carcinogen when inhaled (USEPA, 1998).
  - Decades of epidemiological studies have shown that occupational exposure of workers in various industries (electroplating, chrome pigment, mining, leather tanning, and chrome alloy production) to airborne hexavalent chromium posed increased risks of lung cancer.
The health effects of hexavalent chromium through ingestion—the dominant exposure route for drinking water—are currently under review at the federal level by the USEPA.

*Erin Brockovich is not pleased with this!*
The Agency noted in March 2010 that it had initiated a reassessment of the health risks associated with chromium exposure and that the Agency did not believe it was appropriate to revise the national primary drinking water regulation while that effort was in process.
FROM THE USEPA

In September 2010, USEPA issued “TOXICOLOGICAL REVIEW OF HEXAVALENT CHROMIUM with the stipulation “This document is a reassessment of the non-cancer and cancer health effects associated with the oral route of exposure only.””

From the USEPA website “Basic Information about Chromium in Drinking Water”

It still has not been finalized and currently no move has been made by the USEPA to create a Cr+6 MCL.

WHILE IN CALIFORNIA...
The California Department of Public Health (CDPH) today submitted to the Office of Administrative Law (OAL) its final proposed regulation establishing the first ever drinking water Maximum Contaminant Level (MCL) for hexavalent chromium (Cr VI).

“The drinking water standard for hexavalent chromium of 10 parts per billion will protect public health while taking into consideration economic and technical feasibility as required by law,” said Dr. Ron Chapman, CDPH director and state health officer.
If the regulation is approved as expected, implementation of the new drinking water standard for hexavalent chromium will begin July 1, 2014.

Today’s filing also complies with timelines imposed by the Alameda Superior Court in *Natural Resources Defense Council, Inc. v. California Department of Public Health*. 
**HEALTH CONCERNS**

- **CANCER!**

**Proposed Mode of Action (MOA) 1**

1. Ingestion of Cr(VI) in drinking water
2. Reductive Capacity of GI Tract
3. Elimination of Cr(III)

At low concentrations, the GI system should be an effective barrier to Cr(VI) being absorbed.

*QUESTION: How low is low...*
Proposed MOA 2

Ingestion of Cr(VI) in drinking water

Reductive capacity of GI tract exceeded

Cr(VI) enters the cell via active sulfate transporters

Reduced to Cr(III) - binds to DNA

Mutates, Proliferates, forms tumors
CR+6 IN THE NEWS

- Erin Brockovich Helps File Tumor Lawsuit
  April, 2009

Report_ Hexavalent Chromium Used As Fertilizer.mp4
ENVIRONMENTAL OCCURRENCE AND HUMAN EXPOSURE

- Air - Chromium is present in the atmosphere in particulate form, usually as very small particles (approximately 1 μm in diameter).
  - Can enter ambient air from anthropogenic point sources such as smelters, windblown soil, or road dust.
  - Chromium levels in the air in the U.S. are typically <0.01 μg/m³ in rural areas, and in the range of 0.01 to 0.03 μg/m³ in urban areas (ATSDR*, 2000).

*Agency for Toxic Substances and Disease Registry*
Soil

- Chromium occurs naturally in crustal rocks, but an important source of chromium in soil is probably disposal of commercial products.
- Chromium is present in rock (basalts and serpentine) and soil primarily in the form of the insoluble oxide, $\text{Cr}_2\text{O}_3$. Chromium is generally not mobile in soil (ATSDR, 2000).
Water - Chromium enters environmental waters from anthropogenic sources (listed industries) as well as leaching from soil.

- Rivers in the U.S. have been found to have from <1 to 30 μg/L of chromium.
- U.S. lakes usually have < 5 μg/L of chromium.
- When high levels are present, they can usually be related to sources of pollution.
- A survey of drinking water sources in the U.S. conducted for 1974 to 1975 found chromium levels ranging from 0.4 to 8.0 μg/L, with a mean of 1.8 μg/L (ATSDR, 2000).
NPDES
- How many have it on their permit?
- Limits?
- Why do we need to test for it?
  - Pretreatment
  - Health of the plant
  - Public health - capture & treat
Part I, A. - INTERIM EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

1. During the period beginning on the effective date and lasting until April 30, 2014, the permittee is authorized to discharge in accordance with the following limitations and monitoring requirements from the following outfall 3PF00001001. See Part II, OTHER REQUIREMENTS, for locations of effluent sampling.

Table - Final Outfall - 001 - Interim

<table>
<thead>
<tr>
<th>Effluent Characteristic</th>
<th>Discharge Limitations</th>
<th>Loading* kg/day</th>
<th>Measuring Frequency</th>
<th>Sampling Type</th>
<th>Monitoring Months</th>
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<tbody>
<tr>
<td></td>
<td>Concentration Specified Units</td>
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<td></td>
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<tr>
<td></td>
<td>Maximum Minimum Weekly Monthly Daily Weekly Monthly</td>
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<tr>
<td>Water Temperature - C</td>
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<td>- - - - - - - - -</td>
<td>1/Day</td>
<td>Maximum Indicating Thermometer</td>
<td>All</td>
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<tr>
<td>Dissolved Oxygen - mg/l</td>
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<td>- - - - - - - - -</td>
<td>1/Day</td>
<td>Continuous</td>
<td>All</td>
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<tr>
<td>Total Suspended Solids - mg/l</td>
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<td>17600 11734</td>
<td>5/Week 24hr Composite</td>
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<tr>
<td>Oil and Grease, Hexane Extract</td>
<td>- -</td>
<td>1/2 Weeks -</td>
<td>Grab</td>
<td>All</td>
<td></td>
</tr>
<tr>
<td>Nitrite Plus Nitrate, Total - mg/l</td>
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<td>1/2 Weeks -</td>
<td>24hr Composite</td>
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<tr>
<td>Phosphorus, Total (P) - mg/l</td>
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<td>880 587</td>
<td>2/Wk 24hr Composite</td>
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<td>Cyanide, Free - mg/l</td>
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<td>Nickel, Total Recoverable - ug/l</td>
<td>- - - - - - - - -</td>
<td>- - - - - - - - -</td>
<td>1/Month</td>
<td>24hr Composite</td>
<td>All</td>
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<tr>
<td>Zinc, Total Recoverable - ug/l</td>
<td>- - - - - - - - -</td>
<td>- - - - - - - - -</td>
<td>1/Month</td>
<td>24hr Composite</td>
<td>All</td>
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<tr>
<td>Cadmium, Total Recoverable - ug/l</td>
<td>- - - - - - - - -</td>
<td>- - - - - - - - -</td>
<td>1/Month</td>
<td>24hr Composite</td>
<td>All</td>
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<tr>
<td>Lead, Total Recoverable - ug/l</td>
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<td>- - - - - - - - -</td>
<td>1/Month</td>
<td>24hr Composite</td>
<td>All</td>
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<tr>
<td>Chromium, Total Recoverable - ug/l</td>
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<td>- - - - - - - - -</td>
<td>1/Month</td>
<td>24hr Composite</td>
<td>All</td>
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<tr>
<td>Copper, Total Recoverable - ug/l</td>
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<td>- - - - - - - - -</td>
<td>1/Month</td>
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<td>All</td>
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<td>Chromium, Dissolved Hexavalent - ug/l</td>
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<td>- - - - - - - - -</td>
<td>1/Month</td>
<td>Grab</td>
<td>All</td>
</tr>
<tr>
<td>Fecal Coliform - #/100 ml</td>
<td>- - - - - - - - -</td>
<td>- - - - - - - - -</td>
<td>1/Day</td>
<td>Grab</td>
<td>Summer</td>
</tr>
<tr>
<td>E. coli - #/100 ml</td>
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<td>- - - - - - - - -</td>
<td>1/Day</td>
<td>Grab</td>
<td>Summer</td>
</tr>
<tr>
<td>Flow Rate - MGD</td>
<td>- - - - - - - - -</td>
<td>- - - - - - - - -</td>
<td>1/Day</td>
<td>Continuous</td>
<td>All</td>
</tr>
</tbody>
</table>
Table IB—List of Approved Inorganic Test Procedures - 18. Chromium VI dissolved, mg/L, 0.45-um filtration followed by any of the following:

- AA chelation-extraction - EPA 3111 C-1999
- Ion Chromatography - EPA 218.6, Rev. 3.3 (1994), SM 3500-Cr C-2009, ASTM D5257-03.
- Colorimetric (Diphenyl-carbazide) SM 3500-Cr B-2009, ASTM D1687-02(07)(A)

[Link to ECFR website]
40 CFR Part 136 continued

Table II—Hold time

- Container: P, FP, G
- Preservation: Cool, ≤6 °C, pH = 9.3-9.7
- Maximum Holding Time: 28 days

**WHAT!?!**

- To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. Interesting that 218.6 states to analyze within 14 days...
- Lachat Method 10-124-13-1-A states maximum hold time of 24 hours.
TEST METHODS

- **SM 3111 C**
  - The method consists of chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction into methyl isobutyl ketone (MIBK), followed by aspiration into an air-acetylene flame.
  - Will allow for detection in the high ppb range.
Ion Chromatography SM 3500-Cr C-2009
- Sample is filtered, pH adjusted to 9 to 9.5 (preserves hexavalent chromium oxidation state).
- Sample injected into eluent stream of ammonium sulfate and ammonium hydroxide.
- Cr(III) separated from the Cr(VI) by the column.
- After separation, hexavalent chromium reacts with an azide dye to produce a chromogen that is measured at 530 or 540 nm.
- Low ppb (0.5) detection.
TEST METHODS

- Ion Chromatography SM 3500-Cr C-2009
Ion Chromatography EPA 218.7 - Determination of Cr(VI) as Chromate Ion

- Samples are preserved to a pH of > 8.
- $\text{CrO}_4^{2-}$ is separated on an anion exchange column and is derivatized with 1,5-diphenylcarbazide in a post-column reactor then detected spectrophotometrically at a wavelength of 530 nm.
- The concentration of Cr(VI) as $\text{CrO}_4^{2-}$ is calculated using the integrated peak area and the external standard technique.
- 0.02 ppb PQL, lower MDL
Colorimetric (Diphenyl-carbazide) SM 3500-Cr B-2009

- Measures only hexavalent chromium. Determined colorimetrically by reaction with diphenylcarbazide in acid solution.
- A red-violet colored complex of unknown composition is produced and colorimetrically determined at 540 nm.
TEST METHODS

- Colorimetric (Diphenyl-carbazide) SM 3500-Cr B-2009 continued
  - Curve is 5.00 - 500 ppb
  - MDL = 0.6 ppb
  - Samples are filtered through a 0.45-um filter prior to analysis.
  - QC (ICV, ICB, DLC, CCV, CCB, LCB, LCS, MS/MSD)
  - Background correct if necessary (run with no color reagent)
TEST METHODS
Micro-remediation (a.k.a Bio-reduction)

Chemical reduction
  - Zero valent Fe
  - Sulfur compounds

Chemical precipitation

Chemical sorption

All can be done in situ
  - aquifers
The future impact of hexavalent chromium on the environment is uncertain. Depending on the outcome of the health effects review, USEPA may decide to promulgate an MCL specifically for hexavalent chromium, and the level at which the MCL is set will determine the magnitude of its effect. In California, where an MCL is certain, the remaining question is where that MCL will be set.
While much is known about Cr+6 in the environment, more needs to be determined:

1. Uncertainty remains about the health effects of hexavalent chromium in drinking water.
2. New analytical techniques (EPA 218.7) continue to be promulgated and others, including HPLC-ICP-MS or IC-ICP-MS should be investigated.
3. Treatment methods for removing chromium may need to be refined to meet a low MCL, and cost estimates updated to reflect any treatment modifications on the water side. **WW side watch out!!**
Thanks for your time and attention.

Contact Information

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