Background: Chromium (Cr) is a white, hard and lustrous metal, familiar in many consumer products such as the 1950 DeSoto shown above. Many corrosive agents render the metal passive and hence chemically inert. This accounts for its extensive use as an electro-plated protective coating.

Chromium is similar to sulfur in that it has oxidation states ranging from -II to +VI. The familiar chromium metal is, of course, Cr(0) but the stable forms in soils and natural waters are Cr(III) and Cr(VI). These are often called trivalent and hexavalent chromium. These two forms have very different aqueous chemistry, as will be discussed below.

Chromite is the only commercially important ore mineral of chromium. Its composition is FeO\text{Cr}_2\text{O}_3 with a chromic oxide (Cr_2O_3) content of about 68%. South Africa is the largest chromite producer in the world. Production has nearly doubled in the last 15 years reflecting the increasing demand for chromium in a wide variety of industrial applications.

The earliest industrial use of chromium was in the manufacture of paint pigment around 1800 in France, Germany, and England, although its use in pigments probably goes back to prehistoric times. By the middle 1800s chromium was also used extensively for coloring textiles and tanning leather. Tannery wastes from old industrial sites are an important environmental pollutant in certain areas where leather was processed in the past such as New England. Vast quantities are chromium are used in the production of stainless-steel and chrome plated metals.
Heat resistant ("refractory") brick used in furnaces is made of chromite, reflecting the very high boiling point of chromium. Due to its high boiling point, chromium vapor condenses rapidly as oxide on the surface of tiny airborne articles. Airborne chromium on particles are thus likely to penetrate deeply into the respiratory tract. Airborne chromium levels around chrome factories may exceed 1 mg/m³ as compared to a natural background level approximately one million times lower.

The principal chromium discharges into surface waters are from metal finishing processes such as electroplating and pickling (acid washing). These discharges merit special attention because they typically contain the relatively toxic hexavalent form of Cr. Such emissions are highly regulated in most industrially advanced countries but establishing the levels of discharge permitted in a given situation often requires extensive modeling and risk analysis. Less important sources of hexavalent Cr include the discharge of cooling waters treated with chromate as a corrosion inhibitor, although this practice has been largely phased out. Cooling towers from power generation plants formerly were a source of airborne hexavalent chromium. Soil can be contaminated by the land disposal of slag (containing 2-6% Cr) as by-products of chromium steel production or by phosphate fertilizers, some of which contain high levels of Cr (100-10,000 mg/kg).

**Chromium Chemistry:** As mentioned above, the different redox states of Cr have dramatically different chemical properties. In addition, Cr(VI) is toxic whereas Cr(III) is relatively inert and, in minute doses, a nutritional element.

**Cr(VI) Chemistry:** In dilute to moderately strong solutions the main species of Cr(VI) are chromic acid (H₂CrO₄), bichromate (HCrO₄⁻) and chromate (CrO₄²⁻). Note the similarity to sulfate speciation. The acid-base relationships are:

\[
\begin{align*}
H_2CrO_4 & = HCrO_4^- + H^+ & \text{pK}_a & = 0.7 \\
HCrO_4^- & = CrO_4^{2-} + H^+ & \text{pK}_a & = 6.5
\end{align*}
\]

Hence in waters in the natural pH range nearly all hexavalent Cr is bichromate or chromate, both anions. At low pH and at very high total Cr(VI) a dimer of chromate (the dichromate ion) forms:

\[
2 HCrO_4^- = Cr_2O_7^{2-} + H_2O
\]

In industrial use, hexavalent Cr is often supplied as a dichromate salt such as K₂Cr₂O₇. In highly concentrated solutions (e.g., an electroplating bath) Cr₂O₇²⁻ is an important species, but we focus here on more dilute conditions where monomeric species predominate. Hence, we will write the redox reactions below in terms of HCrO₄⁻ as the active species in the pH range of interest.

When performing calculations, Cr(VI) is often entered as the species CrO₄²⁻. Notice however that chromate is a weak base (comparable in strength to bicarbonate) and that HCrO₄⁻ is the dominant species below pH 6.5. Thus, each mole of CrO₄²⁻ added to solution adds one equivalent of alkalinity. If a bichromate (HCrO₄⁻) salt is added, the chromate alkalinity is already neutralized and is not added. Of course, in an acid solution, remember that both H₂CrO₄ and HCrO₄⁻ add to the *mineral acidity* of the water.
Less obvious is the proton stoichiometry of dichromate. When a dichromate salt is diluted, each dichromate ion combines with a water molecule to form two bichromate ions, in the reverse of the reaction shown above. Therefore, each mole of dichromate added is equivalent to adding two moles of HCrO$_4^-$.

The effects on alkalinity or mineral acidity are then the same as if you just added two moles of HCrO$_4^-$. Like sulfate, Cr(VI) species are typically quite soluble over a wide pH range, which allows them to be easily transported, both in natural waters and into organisms exposed to the ions. The similarity to sulfate means that cell membranes will actively transport Cr(VI) into the cell, mistaking it for sulfate. Within the cell, Cr(VI) is rapidly reduced to Cr(III) but intracellular Cr(III) can bind to DNA and RNA and lead to cell mutation and carcinogenesis. Although Cr(VI) is not as toxic as many other heavy metals, it is of special concern because of its potential for causing cancer and birth defects (teratogenesis).

Cr(VI) species can adsorb onto metal oxide surfaces in soils and natural waters which may retard its movement to the environment. As with most anions, Cr(VI) species are most strongly adsorbed at neutral to acid pH. The strength of Cr(VI) adsorption typically ranges from week to moderate.

Cr(III) Chemistry: Whereas Cr(VI) behaves much like anionic sulfate, Cr(III) acts like a more typical transition metal and occurs in various forms of the Cr$^{3+}$ cation. The chemistry of Cr$^{3+}$ is analogous to that of Fe$^{3+}$ in that it is a strong Lewis acid that tends to hydrolyze water and form hydroxide complexes and solids such as:

- $\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+$
- $\text{Cr}^{3+} + 2\text{H}_2\text{O} = \text{Cr(OH)}_2^{+} + 2\text{H}^+$
- $\text{Cr}^{3+} + 3\text{H}_2\text{O} = \text{Cr(OH)}_3(\text{s}) + 3\text{H}^+$

Like Fe(III), Cr(III) tends to be highly insoluble at pH > 4 and the precipitated Cr(OH)$_3(\text{s})$ is especially resistant to re-dissolution. Soluble Cr(III) species strongly adsorb to metal oxide surfaces at neutral to basic pH. The low solubility and mobility of Cr(III) is a major factor in its very low toxicity.

To sum it up, think of Cr as having two very distinct and different “personalities” in nature. Cr(VI) behaves like the nonmetallic anion sulfate and Cr(III) is much like the transition-metal cation Fe(III).

Redox Chemistry of Cr: Cr can shift between its stable oxidation states. The electrochemical reduction of Cr(VI) to Cr$^3+$ is important in the chrome plating process:

- $\frac{7}{6} \text{H}^+ + \frac{1}{6} \text{HCrO}_4^- + e^- = \frac{1}{6} \text{Cr}^3+ + \frac{2}{3} \text{H}_2\text{O}$

The consumption of a proton by this reaction means the reaction is more favorable at low pH, so Cr plating solutions are typically acidified with sulfuric acid. Although this reaction is essential to a plating operation, it has no direct environmental significance because the half-cell potential is so extremely reducing ($E_{i1}^o = -317$ mV) that the reaction occurs only in an electrolytic cell with powerful applied voltage.
In contrast, the reduction of Cr(VI) to Cr(III) is easily achieved with chemical solutions and therefore is important in both natural waters and in waste treatment.

\[
\frac{7}{3} \text{H}^+ + \frac{1}{3} \text{HCrO}_4^- + e^- = \frac{1}{3} \text{Cr}^{3+} + \frac{4}{3} \text{H}_2\text{O} ; \quad \text{pe}^o = +20.2
\]

Because the proton is a reactant, this reaction is favored at low pH. Note also that we have therefore written bichromate (HCrO$_4^-$; dominant at pH < 6) as the reactive species, so be careful how you set up the equilibrium equation. Although low pH favors reduction, at higher pH the Cr$^{3+}$ can be removed from solution as the hydroxide precipitate which also tends to encourage the forward (reduction) reaction. Thus Cr(VI) can be reduced over a fairly wide range of pH. In an engineered waste treatment facility, is often most efficient to reduce Cr(VI) at a relatively low pH and then raise the pH to quickly and completely precipitate Cr(OH)$_3$. Because Cr(OH)$_3$ is so insoluble is possible to achieve very low concentrations of total Cr in the final discharge.

The Cr reduction reaction shown above requires electrons supplied by another reagent undergoing oxidation. In the reactions below we pair up the two “half cell” reactions and then sum them to show the overall reaction. In treatment of Cr(VI) waste, reduced sulfur species can provide a convenient source of electrons. Sodium bisulfite (NaHSO$_3$) is often used:

\[
\frac{1}{2} \text{HSO}_3^- + \frac{1}{2} \text{H}_2\text{O} = e^- + \frac{1}{2} \text{SO}_4^{2-} + \frac{3}{2} \text{H}^+ ; \quad \text{pe}^o = -5.35
\]

\[
\frac{7}{3} \text{H}^+ + \frac{1}{3} \text{HCrO}_4^- + e^- = \frac{1}{3} \text{Cr}^{3+} + \frac{4}{3} \text{H}_2\text{O} ; \quad \text{pe}^o = +20.2
\]

\[
\frac{1}{2} \text{HSO}_3^- + \frac{1}{3} \text{HCrO}_4^- + \frac{5}{6} \text{H}^+ = \frac{1}{2} \text{SO}_4^{2-} + \frac{1}{3} \text{Cr}^{3+} + \frac{5}{6} \text{H}_2\text{O} ; \quad \text{pe}^o = +14.85
\]

Bisulfite is a weak acid (pK$_a$ = 7.0) so it has the advantage of providing the acidity that helps promote the reaction. Also, the sulfate product is soluble and harmless. Thiocyanate salts can also be used in a similar reaction:

\[
\frac{1}{8} \text{S}_2\text{O}_3^{2-} + \frac{5}{8} \text{H}_2\text{O} = e^- + \frac{1}{4} \text{SO}_4^{2-} + \frac{3}{4} \text{H}^+ ; \quad \text{pe}^o = -4.85 \text{ (as written)}
\]

However, bisulfite is generally cheaper than thiocyanate. Hydrogen sulfide (H$_2$S) could also be used but the gas is very toxic and sulfide salts are unstable and difficult to handle.

An inexpensive and convenient reductant is Fe(II), from a source such as ferrous pickle liquor:

\[
\text{Fe}^{2+} = e^- + \text{Fe}^{3+} ; \quad \text{pe}^o = -13.0
\]

\[
\frac{7}{3} \text{H}^+ + \frac{1}{3} \text{HCrO}_4^- + e^- = \frac{1}{3} \text{Cr}^{3+} + \frac{4}{3} \text{H}_2\text{O} ; \quad \text{pe}^o = +20.5
\]

\[
\frac{7}{3} \text{H}^+ + \frac{1}{3} \text{HCrO}_4^- + \text{Fe}^{2+} = \frac{1}{3} \text{Cr}^{3+} + \frac{4}{3} \text{Fe}^{3+} + \frac{4}{3} \text{H}_2\text{O} ; \quad \text{pe}^o = +7.5
\]

The principal drawback to this method is that when the pH of the solution is raised to hydrolyze and precipitate the Cr(III), the Fe(III) follows suit and yields Fe(OH)$_3$ sludge at a ratio of three units of Fe for every unit of Cr removed. This adds substantially to the disposal cost of the sludge. Also, each mole of Fe$^{3+}$ consumes 3 moles of OH$, considerably increasing the amount of base needed to raise the pH and adding to the chemical costs. However, in some applications, such as when other toxic metals are present, the Fe sludge is beneficial because it is an excellent adsorbate that will sweep many other ions out of solution. In addition, Fe(OH)$_3$ sludge may promote better settling and easier handling of the Cr(OH)$_3$ solids.
These types of reduction reactions also can easily occur when Cr(VI) in a natural water encounters a suitable reducing agent such as sulfide or reduced Fe(II). Cr(VI) is therefore expected to disappear quickly in anaerobic environment such as a reduced sediment or an oxygen-free groundwater. Such natural attenuation of Cr(VI) is an important detoxification process that may drastically diminish the dangers of Cr(VI) contamination.

**Adsorption of Cr Species to Hydr(oxide) Surfaces:** Species of both Cr(III) and Cr(VI) can adsorb to metal (hydr)oxide surfaces. As with all ionic adsorption, the formulation of the reactions depends of the model used. Below we give samples reactions and reaction log $K$ values for hydrous ferric oxide (HFO or amorphous Fe(OH)$_x$) using the diffuse layer adsorption model (DLM) and the binding constants recommended by Dzombak and Morel (1990). The notation / S (as in / SOHE) indicates the binding (surface complexation) site on the surface.

Cr(III):

\[
/ \text{SOHE} + \text{Cr}^{3+} + \text{H}_2\text{O} \rightarrow / \text{SOCrOH}^+ + \text{H}^+
\]

$\log K_{\text{ads}} = 2.06$

Cr(VI):

\[
/ \text{SOHE} + \text{CrO}_4^{2-} + \text{H}^+ \rightarrow / \text{SCrO}_4^- + \text{H}_2\text{O}
\]

$\log K_{\text{ads}} = 10.85$

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**Fig. 1.** Chromate (Cr(VI)) adsorption data and DLM prediction. Solid line is best fit of these experimental data; dashed line is fit given by mean $\log K_{\text{ads}}$ value given above. Note strong adsorption at neutral pH and below.

**Fig. 2.** Cr(III) adsorption data and DLM prediction. Solid line is best fit of these experimental data; dashed line is fit given by mean $\log K_{\text{ads}}$ value given above. Note strong adsorption at all pH values greater than about 4. Both figures adapted from Dzombak and Morel (1990).