Chromium

Chromium as a water contaminant

Emphasis on natural chromite deposits and remediation

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Abstract

Chromium is of major concern to many as it is a well known water contaminant. Hexavalent Chromium is the most toxic form, and is produced in many anthropogenic sources. Trivalent Chromium is the most stable state of chromium, and is not known to be toxic. Research into the natural sources of Chromium, mainly ophiolite deposits that contain chromite, will result in a better understanding of chromium as a water contaminant on a natural level.

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Chapter 1

Introduction

1.1 Chromium background

For centuries Chromium has been used for many different things, but it wasn't until the early 1900's that it was used in metal alloys. Before this, Chromium was used as a coloring in paints in the late 1700s and throughout the early 1800s, and found its way into different industries that used the chromium dye. In the early 1900's the first electric arc furnace was built that could smelt chromite into the master alloy, ferrochromium. This led to the use of chromium in the metal industry, and led the way to stainless steel, which was a major breakthrough. Chromium is very important in metallurgy, as it endows alloys with a whole series of properties, shown in table 1.1.

Chromium began to be used in many other areas, including magnetic tapes, leather tanning, cement, paper and pulp mills, CCA wood treatments, and metal plating and finishing industries.

1	Resistance to corrosion
2	Resistance to wear
3	Resistance to temperature
4	Resistance to decay
5	Strength
6	Hardness
7	Permanence
8	Hygiene
9	Color

Figure 1.1: Properties given to alloys with addition of Chromium

1.1.1 Chromium Facts

Two forms of chromium can occur in water sources: trivalent Chromium (Cr^{+3}) and hexavalent Chromium (Cr^{+6}). Trivalent Chromium is an essential nutrient at trace concentrations, but hexavalent Chromium is toxic. The ratio of the two forms can vary quite a bit in natural waters, but the maximum contaminant level is set based on hexavalent Chromium. Chromium has an MCL set for 0.1 ppm. [8]

Everyone is exposed to Chromium at some levels through water, air, soils and food. The Toxic Chemical Release Inventory (EPA) listed 929 industrial facilities that produced, processed, or otherwise used chromium in 1988. In compliance with the Community Right-to-Know Program, the facilities reported releases of chromium to the environmental which were estimated to total 9.9 million lbs. The atmospheric chromium concentration in the United States is typically less than 0.01 g/m3 in rural areas and 0.01-0.03 g/m3 in urban areas. In the United States it was calculated that 64% of the atmospheric chromium emissions, which originate from coal, contain 1.5-54 ppm chromium. It is been reported that tap water contains 0.4-0.8 g chromium/l. The chromium concentration in rivers and lakes is usually between 1 and 10 g/l. The earth's crust and rocks contain about 100 ppm chromium; soils contain, on the average, about 400 ppm. Typical chromium levels in most fresh foods are low. Chromium has been detected in vegetables, fruits, grains, and cereals at concentrations between 20 and 50 g/kg. CPSC investigated the potential hazard to consumers from chromium-containing inks, printed products, and non-printed consumer products. Although chromium was present in some inks used in printed products, the levels found in the final products did not warrant further investigation. [7]

Chapter 2

Chromium and Ophiolites

There are many anthropogenic sources of Chromium, and a lot of time has been put into researching the effects of these different contaminants. The effects of trivalent and hexavalent chromium is of great concern due to the health benefits of the former and detriments of the latter. It is more likely more important to understand the natural order of chromium, where chromium comes from, and how it acts in the wild.

2.1 Natural Chromite Deposits

Chromium occurs in natural deposits as Chromite typically in Ophiolite sequences. Chromite ($FeCr_2O_4$ S.G. = 4.5-5.1) is metallic brownish-black to iron-black, frequently pitchy; contains substantial amounts of Mg substituting for Fe^{2+} and there is extensive solid solution to magnesiochromite ($MgCr_2O_4$); Zn, Al, Mn and Fe^{3+} may also be present. [3] Chromite occurs in mafic and ultramafic igneous rocks, typically pyroxenites, dunites and peridotites. It sometimes is also found as a detridal mineral, or in placer deposits due to its high specific gravity.

2.1.1 Explanation of an Ophiolite

An Ophiolite is a piece of the oceanic plate that has been thrust onto the edge of a continental plate. Ophiolites are found in the Ophiolite sequence, which is made up of a classic sequence of rocks. The base of this sequence is typically made up of carbonates and a melange, where the oceanic plate was pushed onto the continental plate. The next layers are Peridotite, Layered Gabbro, Massive Gabbro, Dikes and Volcanic rocks, including Pillow Basalt.

Summary of Layers:

7	Pelagic Sequence	Overlying sedimentary strata.
6	Pillow Basalt	The result of the magma eruption at the top.
5	Sheeted Dikes	"Feeder tubes" that carry magma up to the top.
4	Massive Gabbro	Settles out at bottom of magma chamber.
3	Layered Gabbro	Settles out at bottom of magma chamber - layered.
2	Peridotite	Forms below magma chamber. – chromite here
1	Carbonates	bottom of sequence, top of continental plate.

Peridotite –
The Peridotite is made up harzburgite (mostly olivine and enstatite) and has many dikes of gabbro and dunite. Peridotites are basically depleted mantle formed underneath the magma chamber beneath the mid-oceanic ridge. The peridotite is typically deformed, and is overlain by dunite. Dunite is made up primarily of olivine and is an intrusive igneous rock. Chromite deposits appear within this area of the Ophiolite, as the chromite settles out within the magma chamber.

Gabbro –
On top of the peridotite you have layered gabbro, which is an intrusive igneous rock made primarily of plagioclase and clinopyroxene (augite) which also turns into massive gabbro, without the layering. Gabbros are formed from the crystallization of the magma chamber through repeated injections of magma.

Volcanic rocks –
This grades into dikes and pillow basalt, which was what erupted on the ocean floor. These volcanic rocks are formed from magma erupting from the magma chamber through the mid-oceanic ridge and forming dikes and pillow basalts.

This entire suite of rocks is formed at the mid-oceanic ridge. The resulting ophiolite sequences that we can see now are the result of the oceanic plates being thrust onto the continental plate. Ophiolites occur around the world, especially in California and throughout the western United States, the Stillwater complex in Montana, The northeast of the united states, Canada, Cyprus, Turkey, the Himalayas, and other areas. There are many ophiolite complexes that are at the surface, and a lot of these are mined for their abundance of metals, especially Chromite, as this is basically the only source of chrome that is worth mining.

2.1.2 Chromite mineralization

Chromite appears to mineralize in two main ways. The first as Podiform chromite bodies inside dunite pockets within harzburgite, and the second is

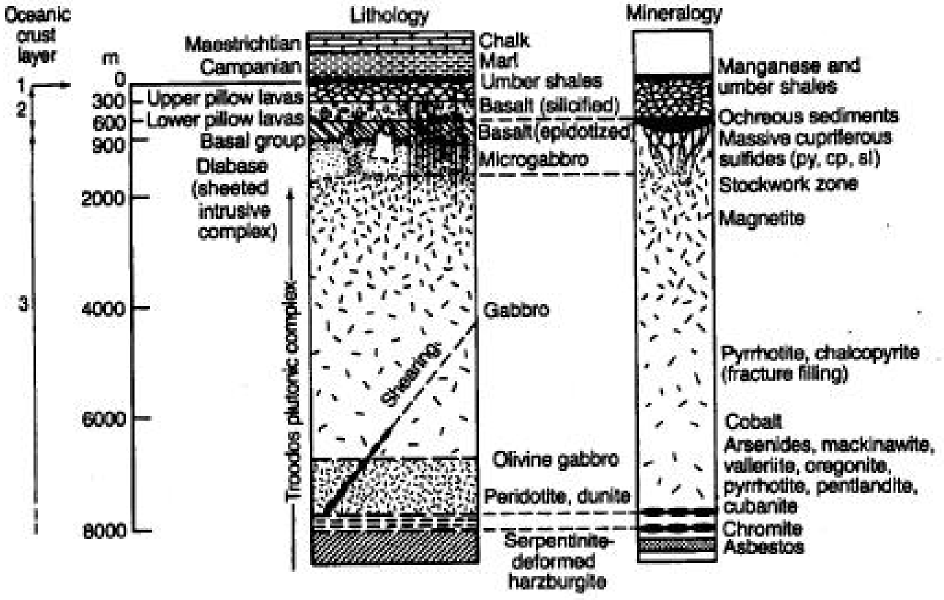

Figure 2.1: Typical Ophiolite complex [9]

stratiform chromite deposits in non-deformed cumulate zones within gabbro-peridotite sequences. As seen in Figure 2.1 the main chromite band within an ophiolite deposit is at the bottom. This is due to the fractional crystallization of chromite from the magma chamber. It is still not entirely accepted that this is the only way the chromite is formed, but it seems to be a very good possibility.

2.1.3 Chromite as a natural contaminant

Almost all of the worlds chromite deposits are formed within ophiolites by way of fractional crystallization and settling out within the magma chamber. The mining of chromium ore causes many problems due to the increase in surface area of chromite deposits as well as the waste products of mining. The main concern of liberating chromium is that hexavalent chromium will be unleashed on the environment in concentrated amounts.

An interesting fact is that both natural and anthropogenic sources of chromium have the same amount of trivalent and hexavalent species.[10] The main reason that anthropogenic sources get such grandiose press is that the processes we put chromite through liberates a vast amount of hexavalent chromium, which can easily become airborne and is very soluble in water. Once in the air, hexavalent chromium can fall out in precipitation, and become enriched in soils and plants, and end up within the food chain.

There is evidence that hexavalent Chromium is reduced to trivalent Chromium within acidic environments and when in contact with organic matter. The amount that can be reduced is typically not that high, and hence the horrible effects of chromium on humans when exposed to large quantities of hexavalent chromium.

2.1.4 Health effects of Chromium

Trivalent Chromium is thought of as a needed trace nutrient for humans, but hexavalent Chromium is highly carcinogenic. The health effects of hexavalent Chromium range from short term skin irritation, ulceration, long term damage to liver, kidney circulation and nerve tissues; to the more drastic cancers.

It seems that the jury is still partially out on some of the health effects of chromium, as it was shown to cause cancer in rats if it was in their water supply, but it is believed that some of the previous experiments were flawed, and that it does not cause cancer in humans.[11] Either way, the concern around chromium in water supplies is most likely warranted, as hexavalent Chromium is carcinogenic, mutagenic and highly toxic to living organisms as it occurs in soluble chromates that readily cross cell membranes. It is this crossing of cell membranes that causes damage to DNA replication, as the reactive hexavalent Chromium steals electrons from within the cell, reducing first to pentavalent chromium, then to trivalent Chromium.[13] The large amount of evidence suggests that the Environmental Protection Agency should keep a Maximum Contaminant Level on Chromium, and should regulate the output of chromium in these industrial plants and around natural deposits. Even if it is found out that Chromium of any sort has no effect on humans, the old adage of "everything in moderation" will almost always shine true; as it could be found out that hexavalent chromium isn't what is causing damage, but the combination of a high amount of hexavalent chromium along with other metals that reacts to cause ill effects in humans.

2.1.5 Detection and Remediation of Chromium

Chromium is detected through a few different methods, but the best method is through Ion Chromatography. Ion Chromatography is more than 1,000 times more sensitive than any other method to determine the amount of chromium is in a given sample. This method has a detection limit as low as 0.01 ug/L in dilute bicarbonate solutions, and can be used to measure ambient air risk to 1ng/m^3.[12]

If Chromium limits within a given water sample are found above the EPA MCL's, then the chromium will have to be filtered out of the water. Some of the treatments of water to remove Chromium are Coagulation/Filtration, Ion Exchange, Reverse Osmosis and Lime softening.[8]

Recent studies by Hoi-Ying Holman and associates at the Lawrence Berkeley national Laboratory found that basalt core samples from beneath a radioactive waste management complex at DOE's Idaho National Engineering and Environmental Laboratory were showing a reduction in hexavalent chromium due to populations of living organisms reducing the toxic materials to trivalent chromium. [13] Within Figures 2.2-1 and 2.2-2 it is shown how there is a correlation between high protein signatures that are consistent with microbes and an increase in reduced chromium (Trivalent Chromium). With this natural reaction already in the rocks, it may be a foreseeable way for remediation of hexavalent chromium spills in the future, and it may already also be happening in nature, near the basaltic ophiolites portions that host chromite deposits.

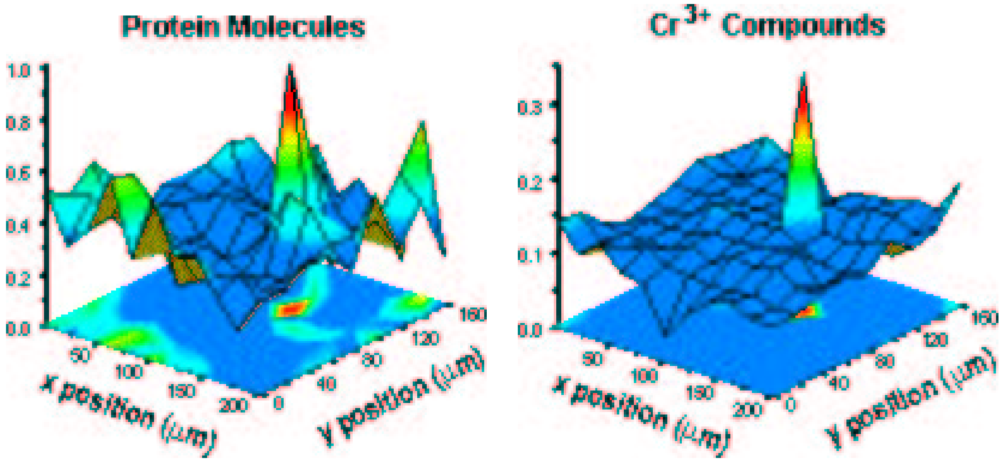

Figure 2.2-1

Figure 2.2-2

Figure 2.2: Spatially resolved infrared spectroscopy of a basalt surface shows a strong correlation between concentrations of biological molecules characteristic of microbes (2.2-1) and peak concentrations of reduced chromium (2.2-2). [13]

The most effective bacteria strain was found to be 'Arthrobacter oxydans' which typically concentrates in areas rich in magnetite. It had been ruled out that the magnetite itself was doing the reduction through a series of tests conducted by Hoi-Ying Holman, and was shown to be the main bacteria strain that reduces chromium. The presence of Toluene (C_7H_8)

was shown to increase the reduction reaction, which is also present in a lot of waste sites. The transformation of hexavalent Chromium to trivalent Chromium is done by microorganisms that aerobically reduce hexavalent to trivalent by relying on metal oxides to catalyze the reduction reaction. This new outlook on natural remediation shows that some of the potential sites that may seemingly be worse off due to heavy metal and fuel leaks, may actually be a better home for reducing bacteria that help clean up the area.

Chapter 3

Summary

The continued study between natural deposits of chromite and anthropogenic sources of chromium should be conducted in order to come to some conclusions about the effects of chromium in our environment. Mainly the link between hexavalent Chromium and negative health impacts on humans, as well as higher cancer rates around the outputs of different waste sites. Considering the large areas of chromite deposits and the relative similar isotopic relationship between anthropogenic chromium and natural chromium, higher cancer (or negative health) rates should be seen throughout areas of high concentrations of natural hexavalent chromium - as apposed to areas without natural chromite deposits. If no such evidence exists, then the relationship between hexavalent chromium within drinking water supplies around anthropogenic sources and cancer rates may actually be due to some other reaction or anthropogenic contaminant that might have been overlooked in past tests.

As with many large environmental tasks, it seems that there is a need for more environmental testing and comparisons. It seems as though there is a good opportunity to find out if we are polluting our environment more than the environment itself, as well as finding out if the environment has a way of dealing with our pollution in a natural way, and learning from it.

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