CHAPTER : 1

GENERAL INFORMATION ON METAL CHROMIUM AS A TOXICANT
Chromium (Cr) is a metallic element which is listed by the Environmental Protection Agency as one of 129 priority pollutants. Chromium is considered one of the 14 most noxious heavy metals. Chromium is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites.

The element chromium was first isolated in 1797 by Vauguelin from the mineral crocoisite (PbCrO4). He coined the element as “Chromium” from greek terminology (Chroma = Colour), since its compounds are coloured. Although chromium is widely dispersed in natural deposits, it is never found in the combined state. Chromite, FeOCr₂O₃ is the important ore of chromium.

Structure:

The dichromate salt of Potassium has the following structure:

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CrO2
  O
CrO2
  OK
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The salt has the formula K₂Cr₂O₇.
1.1 **Metal chromium as a toxicant**

Little is known about the relationship between concentration of chromium in a given ecosystem and the biological effects on the component organisms. The same elemental concentration of chromium has a wide variety of mobilities and reactivities depending on the physical and chemical state of the ion. Therefore, the observed effects of chromium exposure vary widely. In addition, species sensitivity to chromium differs greatly, even among closely related species (Steven *et al.*, 1976). The toxicity of chromium ions is highly dependent on oxidation state. Only the trivalent and hexavalent chromiums are biologically significant. Trivalent chromium is the only form of chromium found in biological material. Trivalent chromium does not readily cross cell membranes, and it forms stable complexes with serum proteins. As a result, it has a low overall toxicity potential and is relatively inactive in vivo. In contrast, hexavalent chromium is readily taken up living cells and is highly active in diverse biological systems. Although the known harmful effects of chromium in animals are attributed to exposure to the hexavalent form, it is the trivalent form that is ultimately damaging as it is formed from the reduction of hexavalent chromium and complexes with intracellular macromolecules.
1.2 Different forms of chromium:

Chromium can exist in oxidation states ranging from -2 to +6, but is most frequently found in the environment in the trivalent (Cr+3) and hexavalent (Cr+6) oxidation states. The +3 and +6 forms are the most important because the +2, +4 and +5 forms are unstable and are rapidly converted to +3, which in turn is oxidized to +6.

Trivalent chromium is the most common form in rocks of the earth’s crust, but both trivalent and hexavalent chromium occur as dissolved chromium.

The hexavalent state is the second most stable state. However, hexavalent chromium forms anthropogenic sources. Most of the chromium (+6) found in nature is a result of domestic and industrial emissions. Various forms available (1) Chromium metal as lumps, granules, or powder, (2) high or low carbon ferro-chromium, (3) single crystals, high purity crystals, or powder run 99.97% pure (Sax,N.I. and R.J. Lewis, Sr., eds., Hawley’s condensed chemical dictionary, 11th ed. New York : Van Nostrand Reinhold Co., 1987.280).

1.3 Occurrence

Chromium does not occur free in nature, in bound form it makes up 0.1 – 0.3 parts per million of the earth’s crust. Elemental
chromium is very stable, but is not usually found pure in nature. Chromium can exist in oxidation states ranging from -2 to +6, but is most frequently found in the environment in the trivalent (Cr +3) and hexavalent (Cr +6) oxidation states. Most compounds are prepared from chromite ore (that is aggregate of minerals from which chromium compounds can be extracted).

Chromium compounds are stable in the trivalent state and occur in nature in this state in the form of ores such as ferrochromite (FrCr₂O₄). The hexavalent state is the second most stable state. However, hexavalent chromium rarely occurs naturally, but is produced from anthropogenic sources. Most of the chromium (+6) found in nature is a result of domestic and industrial emissions. Interaction of +6 chromic oxide, dichromate or chromate compounds with organic compounds can result in reduction to the comparatively less toxic trivalent form. Hexavalent chromium occurs naturally in the rare mineral Crocoite.

The principle are of chromium is chromite or chrome iron stone which is ferric chromite (FeCr₂O₄) or ferrous chromite (FeO. Cr₂O₃). It is found in South Africa, Russia, U.S.A., Turkey and India (in the states of Andhra Pradesh, Bihar and Karnataka).
Chromium also occurs as lead chromate, barium chromate, sodium chromate, potassium chromate, sodium or potassium dichromate, chromium acetate, chromium citrate, chromic chloride, chromic acid mist, zinc chromate, calcium chromate and strontium chromate.

1.4 General properties of chromium

Chromium is a crystalline, steel-gray, lustrous, body-centered cubic structure, blue-white hard metal. It is odourless, and actually relatively insoluble, and dependent upon form in water. The Atomic weight of chromium is 51.996, and atomic number 24. Its density/specific gravity is 7.14, melting point 1900°C and boiling point 2642 °C. The oxidation states are chiefly - +2, +3 and +6. The divalent (+2) chromous ion is relatively unstable and rapidly oxidized to trivalent (+3) chromic form. Hexavalent chromium compounds (chromates) are oxidizing agents. The chromous salts are powerful reducing agents. The basic character of chromium decreases while acidic character increases with increasing oxidation state (See Table 1.1).
### Table No. 1.1 SOME GENERAL PROPERTIES OF CHROMIUM

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>24 (Dutt &amp; Dutt, 1979)</td>
</tr>
<tr>
<td>Density/specific gravity</td>
<td>7.14 (The Merk Index, 10th ed. 1983)</td>
</tr>
<tr>
<td>Atomic volume, ml</td>
<td>7.28 (Dutt &amp; Dutt, 1979)</td>
</tr>
<tr>
<td>Melting Point, °C</td>
<td>1900°C (The Merk Index 10th ed. 1983)</td>
</tr>
<tr>
<td>Boiling Point, °C</td>
<td>2642°C (The Merk Index, 10th ed. 1983)</td>
</tr>
<tr>
<td>Atomic radius, A</td>
<td>1.27 (Dutt &amp; Dutt – 1979)</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>1 MM HG @ 1616°C (Sax, N.I., 1984)</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>APPROX 81.7 KCAL/G-ATOM (The Merck Index, 10th ed. 1983)</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>1590 ± 50 mN/m in Vacuum at 1950°C (sessile drop method), 1700 ± 50 mN/m in air at melting point. (Dynam drop wt. method); 1520 mN/m in air or Helium at 1800°C (sessile drop method. Ref-[Weast, R.C. 1987-1988].</td>
</tr>
<tr>
<td>Ionic radius M^2+ A</td>
<td>0.84 (Dutt &amp; Dutt, 1979)</td>
</tr>
<tr>
<td></td>
<td>M^3+ A</td>
</tr>
<tr>
<td></td>
<td>0.64 (Dutt &amp; Dutt 1979)</td>
</tr>
<tr>
<td>Inosiation Potential, ev. E,volt,M/</td>
<td>6.76 (Dutt &amp; Dutt 1979)</td>
</tr>
<tr>
<td></td>
<td>M^2+</td>
</tr>
<tr>
<td></td>
<td>0.91 (Dutt &amp; Dutt.1979)</td>
</tr>
<tr>
<td></td>
<td>M^3+</td>
</tr>
<tr>
<td></td>
<td>0.74 (Dutt &amp; Dutt 1979)</td>
</tr>
</tbody>
</table>
1.5 Uses of Chromium

(A) Industrial Use

Chromium is principally utilized in metallurgical, refractory and chemical industries. An important consumer of chromium for many years has been the tanning industry. It is also used in pigment production and application, graphic industry, cleaning and duplicating, textiles, mining, electroplating, metal finishing industries, pharmaceuticals etc. Ferro chromium and chromium metal are the important classes used in alloy industry. The alloy nicrhome (Ni 60, Fe 25, Cr 15) has a high resistance and used for resistance heaters. Chromium vanadium steel is extremely hard and is used in locomotive wheels and axle shafts. Chromium steel is extremely hard and tough and is used in making armour plates, cutting tools, etc. Stainless steel with 12 – 14% of chromium is extensively used in cutlery. Stainless steel is a compound of 18% chromium, 6% nickel with or without the addition of titanium, silicon or niobium besides steel. It is used for making watches and springs.
(B) Biological uses

Trace quantities of certain forms of chromium are considered helpful or necessary. Chromium supplement pills are even sold in some health food stores. Chromium in biological materials is usually in the +3 form, and is the form that functions as an essential element in mammals by maintaining efficient glucose, lipid and protein metabolism.

Chromium appears to play an important role in the maintenance of vascular integrity. A deficiency of this metal in animals results in elevated serum cholesterol levels and increases atherosclerotic aortic plagues. Autopsies of humans have revealed virtually no chromium in the aortas of individuals dying of atherosclerotic heart disease, in comparison with normal individuals dying of other causes.

In humans and animals, chromium (III) is an essential nutrient that plays a role in glucose, fat and protein metabolism by potentiating the action of insulin.

The biologically active form of chromium, called glucose tolerance factor (GTF), is a complex of chromium, nicotinic acid and possibly amino acids (glycogen, cysteine and glutamic acid).
Protein-Calorie, mal nutrition and the syndrome of Kwashiorkor and Marasmus improve when children are fed one dose of 250 µg Cr.

A chromium supplement such as Brewer’s yeast extract can have beneficial effects in some cases, particularly with the elderly, malnourished children and diabetics.

Besides, chromium is also used in the manufacture of fertilizers as phosphates.

1.6 Hazards of Chromium

Many chromium compounds with a valence of 6 are called chromates, dichromates or chromic acid, most have a yellow colour, and all are toxic. Hexavalent chromium compounds tend to be oxidizers (many strong oxidizers) and are associated with cancer risk and kidney damage.

Hexavalent chromium is more toxic than the +3 form because its oxidizing potential is high and it easily penetrates biological membranes. Chromium +6 is unstable and can be reduced to chromium +3 by many oxidizing agents. Metallic and acidic +6 chromates and dichromates tend to be strong oxidizing agents. Strong oxidizing agents can cause damage to DNA and many other tissues structure.
Certain hexavalent chromium (Cr 6+) compounds when administered via inhalation at high doses have the potential to induce lung tumors in humans and experimental animals.

Exposures incurred in the production of dichromate, in the use of chromates in chemical, steel and alloy industries, in refractory work and in the chromium plating industries are potentially hazardous. In electroplating industry, the health hazard is caused by chromium containing mist. Chromium exposure in welders may constitute a health hazard since chromium is an important constituent in stainless and acid-stable steel and chromates are extensively used in anticorrosive paints (Langard and Norseth, 1979).

Experiments on localized effect in animals, though few, reveal that chromium is potentially hazardous. The chromates are reported to induce chromic ulcers to skin and “Bronchiolization” of alveoli i.e. lining of alveolar walls by cells resembling bronchial epithelium in different animals (Langard and Norseth, 1979).

In humans, hexavalent chromium due to its corrosive action induce chromic ulcers. In the case of tannery workers, the dermal ulcers may be due to chromic compounds like chromic acid, dichromate compounds or other hexavalent chromium compounds. Chromium in hexavalent form also causes acute irritative dermatitis.
Chromium compounds also cause allergic ‘eczematous dermatitis’ in a variety of occupations such as housewives, wood workers, cement and lime stone workers, painters, polishers, furriers and others. The main causative agent in cement eczema is chromium in traces as chromate compounds in cement. Another important chromium hazard is the ulceration and perforation of the nasal septum observed in chromate workers (Langard and Norseth, 1979)

Chromium is a carcinogen poses very serious health hazards to mankind. Reports of “Adeno-Carcinoma” in a worker who had been involved in chromate pigment production for 20 years is also evidenced. American studies indicate an increased incidence of highly excessive lung cancer rates among chromate producers and chromepigment makers. Hexavalent chromium is proved to be the prime carcinogen in all the cases. Chromates are shown to have a mutagenicity in bacterial models. Inhalation of chromate dust or chromic acid fume induces typical bronchial asthma in humans. High incidence of bronchial asthma is also reported in workers of Ferrochromium Industry (Langard and Noreseth, 1979).

Chromium potentially possesses toxicological, carcinogenic and mutagenic properties and is extremely hazardous to aquatic bioata. Hence, the removal of chromium by Albizia lebbeck pods as suggested
by Neelam Verma and Rajbir Rehal (1996) or by other treatment producers from the industrial effluents is very essential before it is released in any form into the aquatic environment.