Unsafe Chromium and Its Environmental Impact Assessment

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Abstract: - Most of the chromite mines are located in Orissa. It increases the economic status of our country, but adversely reduces the ecological cover. Chromium and its compounds are exclusively used in chromium based industries such as leather tanning, textiles, metallurgical industries, mechanical and mining engineering industries, chemical and metal finishing industries, ferrochrome, pigments, electroplating and photography. These generate considerable quantity of toxic chromium pollutants which contaminate 6000-18000 mg/kg (ppm) of total chromium (including hexavalent chromium) in air, water and soil environment. This chromium pollution produces adverse health effects on the workers and those people who are exposed in the vicinity. They suffer from chromium based diseases such as chromium poisoning, ulcer, allergic dermatitis, lung cancer, lever necrosis, brain damage, premature death, lever and kidney problems. Several countries have initiated regulatory measures to control chromium pollution, but Indian companies have not initiated so far. It is essential to evolve control and preventive measures which are to be taken at the planning stages in these industries as prevention is better than cure, very little or nothing can be done if the toxic chromium reaches the air, water and soil environment. In these industries, workers must be provided with personal protection equipments, adequate safety guards and devices. It is to be ensured that Worker’s Compensation Law and Occupational Disease Law must be enacted in these industries. Experience has shown that approximately 80% of all industrial disasters are preventable (2006). In this paper how chromium exposure can lead to the toxic effects on health of the people and necessary proactive steps to eliminate chromium pollution through case studies have been provided.

Key-Words: - alternate, assessment, technologies, chromium, eco-friendly, impact, hexavalent, product, unsafe

1 Introduction
Chromites mining has vastly improved the economic status of several people in Orissa. But it has severely affected the ecology and reduced the forest cover. Moreover, Chromium poisoning has had toxic effects in workers employed in chromium-based industries. Chromium and its compounds are exclusively used in many industries such as Leather tanning, textiles, ferrochrome, pigments, electric plating, and photography to name a few. Chromite is the only known economically important mineral of chromium and almost all chromium-based industries originate from chromites. Leather tanning is the contributor to chromium pollution. Over 90% of the chromites deposits in India are located in Orissa. Chromium based industries generate considerable quantity of pollutants containing toxic hexavalent chromium [1]. Case studies pertain to chromium pollution in leather tanneries are given.

2 Problem Formulation
2.1 Case studies - Chromium Pollution Load from Tanneries in India
The tannery process has consisted upon the following unit operations namely curing, washing, soaking, liming-unhairing, deliming - bating, washing after deliming-washing, bating, deliming-washing, bating-pickling and chrome tanning. All the processes have produced wastes which contained organic compounds to a smaller or greater extent except chrome tanning process waste. This process has contained chromium waste. The concentration of Cr^{6+} was varied between 2000-5000 mg/l in waste
water coming from chrome tanning process. The concentration of Cr\(^{6+}\) in chrome tanned leather was 1000-4000 mg/kg, (ppm) and that of total chromium between 8000-11000 ppm and 13000-30000 ppm respectively[7]. The dust-producing, grinding CCLC leather washers and rollers used in ginnery have contained this level of chromium concentration, which was hazardous to human health. The following table 1 gives the details of average pollution loads in tannery wastewater discharged and dust-producing grinding CCLC leather in ginnery (dry).

**Table 1 , Comparative Analysis of Pollution Load from Tannery**

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Description</th>
<th>Conventional Chrome Tanning</th>
<th>Improved Chrome Tanning</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pelt weight</td>
<td>700 kg</td>
<td>700 kg</td>
</tr>
<tr>
<td>2.</td>
<td>Quantity of chromium applied</td>
<td>14.98 kg</td>
<td>14.98 kg</td>
</tr>
<tr>
<td>3.</td>
<td>Chromium content in spent liquor</td>
<td>4,714 mg/l</td>
<td>5,244 mg/l</td>
</tr>
<tr>
<td>4.</td>
<td>Quantity of total Cr discharged in waste chrome liquor</td>
<td>5.77 kg</td>
<td>3.68 kg</td>
</tr>
<tr>
<td>5.</td>
<td>Hexavalent Cr in the water coming from chrome tanning process</td>
<td>3100 mg/l</td>
<td>3800 mg/l</td>
</tr>
<tr>
<td>6.</td>
<td>Chromium uptake by the hides</td>
<td>61%</td>
<td>75.43%</td>
</tr>
<tr>
<td>7.</td>
<td>Quantity of chromium in wet blue</td>
<td>9.21 kg</td>
<td>11.3 kg</td>
</tr>
<tr>
<td>8.</td>
<td>Total chromium content in the leather</td>
<td>13157 ppm</td>
<td>16142 ppm</td>
</tr>
<tr>
<td>9.</td>
<td>Hexavalent chromium in rollers</td>
<td>2000-5000 ppm</td>
<td>3000-7000 ppm</td>
</tr>
<tr>
<td></td>
<td>First sampling tannery waste water Cr(^{3+})</td>
<td>8289 mg/l</td>
<td>8650 mg/l</td>
</tr>
<tr>
<td></td>
<td>II sampling tannery Cr(^{6+})</td>
<td>2590 mg/l</td>
<td>2410 mg/l</td>
</tr>
</tbody>
</table>

2.2 Pollution load of tannery waste water

Table 2 shows average pollution load discharged per ton for processing raw hides and skins to the finished leather. The data given in total chromium.
Table 2, Average Pollution Load Discharged Per Ton Of Hides/Skins Processed For Raw To Finished Leather (As Total Chromium)

| Soaking operation | Nil |
| Beam house operation | Nil |
| Tan yard operation | 5 kg of total chromium/ton of hide/skin |
| Post tanning and wet processing | 1.5 kg of total chromium/ton of hide |
| **Total pollution load** | **6.5 kg of total chromium/ton of leather** |
| 0.0065 kg/kg = 6.5 g/kg |
| ∴ 1 litre = 6500 ppm in the tannery water |
| ∴ 1 litre = 0.001 m³ |
| ∴ One litre of tannery waste water = One kg of tannery waste water |

As per environmental protection rules, 1986, the effluent for disposal by cotton textile industries / tanneries should not exceed 2 mg/l as total chromium.

Table 3, Chromium Pollution Load Analysis

<table>
<thead>
<tr>
<th>Sl.No. Description</th>
<th>Indian Leather Survey</th>
<th>Present Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Total Cr in chrome leather</td>
<td>13157-16142 ppm</td>
<td>45333.3 ppm</td>
</tr>
<tr>
<td>2. Total Cr in waste water</td>
<td>5250-8240</td>
<td>23111.1</td>
</tr>
<tr>
<td>3. Quantity of chromium applied/kg pelt</td>
<td>21.4 kg/1000 kg</td>
<td>68 kg/1000 kg</td>
</tr>
<tr>
<td>4. In terms of total Cr</td>
<td>21400</td>
<td>68000-68444</td>
</tr>
<tr>
<td>5. Total chromium in composite waste</td>
<td>8000-11000</td>
<td>14000-20000</td>
</tr>
<tr>
<td>6. Cr⁶⁺ in ppm or mg/l in waste water coming from chrome tanning process (hexavalent chromium impurity content)</td>
<td>2000-5000</td>
<td>3500-5000</td>
</tr>
<tr>
<td>7. Chromium content in roller gin rollers</td>
<td>13200-30000</td>
<td>20000-40000</td>
</tr>
<tr>
<td>Cr⁶⁺ impurity content in roller</td>
<td>6000-8000</td>
<td>10000-12000</td>
</tr>
</tbody>
</table>

2.3 Results And Discussion On Chromium Pollution

Chromium compounds like dichromate, sodium chromate and sulphate have 30% to 60% basicity were used in the tanning industries. The impure chromates have hexavalent form of chromium salts mixed with chromium sulfate of 50% basicity were used for making semi-finished leather. This has been used for making ginning rollers by the locally made indigenous manufacturers in Kanpur, Ahmedabad, Chrompet and Chennai[4]. The chromium percent contained in leather was approximately 3 to 4 by weight basis. About 66% of the total chromium compounds applied were absorbed in leather during the tanning process and rest was discharged to effluent. The reaction of chromium compounds in tanning solution with hide collagen have been studied...
extensively. It was firmly established that cross-linking was accomplished by bonding of various chrome species with free carboxyl groups in the collagen side chains. It is mentioned that BCS having 33% basicity contains Cr$^{3+}$ form as 9% of total chromium. A brief outline on chromium and leather chemistry is given below:

1. Chromium salts were used in tanning materials either in Cr$^{3+}$ and Cr$^{6+}$ salts or mixed condition.
2. The experiment results have showed that out of chromium used in tanneries, the leather has been absorbed 66% and effluent as 33%. The analysis has showed that dry leather contained 3% to 4% as total chromium or 30,783 ppm that was 30,783 mg of total chromium / kg of CCLC.
3. The analysis has expressed that traces of Cr$^{6+}$ were found even in analar grade Cr$^{3+}$ compounds and complications have raised due to the reducibility nature of these traces of Cr$^{6+}$ that affected the organic tissues in the body. These regenerating effects occurred rapidly and were dependent upon the doze.
4. Water consumption in tanning operation was 74 m$^3$ per ton of raw material.
5. Composition of total waste from polish chrome tanneries as total chromium was 11 to 3,226 mg/l.
6. Average composition of total waste from ten Russian tanneries was 0-300 mg/l.
7. Characteristics of effluents from tan yard operations of tanneries processing hides by chrome tanning during tanning operation was 2,500-5,000 mg/l as total chromium and during re-chroming operation was 700-1,600 mg/l as total chromium. Chrome tanning was done in wooden drums with a processing capacity of 1-1.25 ton of pickled pelts per batch. In the conventional chrome tanning process, the leather on an average has absorbed 60% of the chromium compounds namely sodium chromate, dichromate or basic chromium sulphate applied and the balance was discharged to the effluent. According to 2000-2001 estimate about 65,000 tons of sodium chromate, dichromate and BCS was used for chrome tanning of leather in India. Out of this quantity, about 26,000 tons of chromium was discharged into effluent stream. The proportional ratio of chromium compounds were 55% as Cr$^{3+}$ and 45 % as Cr$^{6+}$. The impurity content of hexavalent chromium in the leather was 45%. Total pollution load as total chromium was 6.5 kg in tannery wastewater discharged for one ton of hides/skins processed from raw to finished leather that was 6,500 ppm. The chromium uptake to leather was 8,500 ppm. Cr$^{6+}$ impurity content of this compound was 45% on the chromium leather[8].

Chromium content as Cr$_2$O$_3$ in the spent liquor was 4,714-5,244 mg/l (ppm) (with hexavalent chromium as impurity content of 3100-3800 mg/l (ppm). Neosyn BG 96 and Neosyn EB were the specialty chemicals used for chrome tanning to enable greater uptake, exhaustion of chrome and self-basifying characteristics. Gloden chrome, star chrome and TANASCO, Chrome Syntan were the locally made indigenous chemicals used by the local tanners in India[6].

3 Problem Solution
3.1 Environmental Impact Assessment of Chromium Pollution

Workers in chromium-based industries have been found to suffer from toxic effects arising from exposure to chromium. Such toxic effects may range from ulcers, allergic dermatitis and lung cancer to renal insufficiency to liver necrosis. Pollution from these chromium-based industries is mainly in the form of dust, slag and process water. A huge amount of dust in released into the atmosphere by mining, metallurgical and chemical industries.

The water from chromite mines and process water are invariably contaminated with hexavalent chromium. Mine water is released into the adjoining water sources (drinking and domestic) without treatment. Process water is treated by only a few industries. The slag is usually dumped underground. This contains chromium compounds in different valence state. Hexavalent chromium is formed due to still unknown chemical reactions and this percolates to the subsoil and terrestrial water sources during the rainy season. Sometimes the slag is manually broken and washed to retrieve the product and in this process some contaminated water and shine are generated(1998).

Spent solid and liquid waste from leather tanning, electroplating, bichromate and chromium chemical manufacture are very hazardous. Solid wastes from bichromates are known to permanently affect the drinking water sources in their vicinity due to percolation[3].
Hexavalent chromium, Cr(VI), does not bind to soil and is not affected unless there is some organic matter. The unaffected hexavalent chromium enters the subsoil aquifers. In Ludhiana, with a large number of electricity units, the hexavalent level in underground water was found to be more than 12 mg/l water of the Yamuna river in New Delhi contains high level of chromium. Kanpur in Uttarpradesh is a highly industrial city. Due to uncontrolled discharge and dumping of wastes, the chromium content in the ground water is higher than 31 mg/l. Effluents from different chromate and chemical factories in Tamilnadu, Maharashtra and Orissa are causing irreversible damage to the subsoil and surface water sources in adjoining areas and waste dumping sites. For example hexavalent chromium content in certain parts of Renipet in Tamilnadu has been found to be 550-1500 ppm (mg/l) in well water, 25-100 ppm in irrigation reservoirs and 4000 ppm (mg/l) in the soil making it unfit for domestic usages.

Some studies have provided that chromium may have a role to play in human health. Trivalent chromium Cr(VI) is considered an essential micronutrient for physiological activity. However, most of the interference on the effects on (a) Glucose metabolism, (b) lipid metabolism (c) life spans, (d) life growth & (e) life reproduction, were from studies on laboratory animals[13].

Most of the daily human chromium uptake is ranging 50-200 microgrammes which is through food in trivalent form, out of which a negligible portion that is 0.5 -3% is absorbed in the gastrointestinal tract and the rest exerted in Urine. The small ions of Cr(VI) get lodged in the perforations in the human cell water. After entering the cells, Cr(VI) ions get reduced in Cr(III) ions which are slightly bigger and then get stuck in the walls. The lethal usual dose for soluble chromite is considered to be 50 mg/kg of body weight. The clinical symptoms of acute toxicity are vomiting, diarrhea, blood loss into the gastrointestinal tract causing cardiovascular diseases. Exposure to small quantities of chromium can not be avoided due to indifference of the workers in chromium based industries. Toxic effects are produced by prolonged contact with airborne or solid or liquid chromium compounds even in small quantities. Prolonged exposure to Cr(VI) causes ulcers, skin irritation and allergic dermatitis. Exposure to chromite dust or Cr(VI) may cause perforation of nasal septums, corrosion of bronchopulmonary tract and lung cancers. In the kidneys, it causes tubular necrosis and may also damage the liver. Chromium exposure may even lead to brain damages[1998].

Several countries have irradiated regulatory measures where industries using chromite are located. For example, the Federal Republic of Germany has enacted an emission protection Law and a technical guidance for clean air (TA –Luft). As per TA-Luft, the mass of carcinogenic substances, for example, chromium (VI) compounds in respiratory form is restricted to 1mg/m³ (class II) [1000 mg/ m³]. The total dust concentration in emissions is limited to 20 mg/ m³ [20000 micrograms/ m³ ] and other inorganic material in dust form (Class III) to 5 mg/ m³ [5000 micrograms/ m³ ].

The maximum allowable concentration (MAK) of CrO₃ measured as CrO₃ in air of workplace is 0.1 mg/ m³[100 mg/ m³]. In the united States, the Clean Air Act amendments exacted in 1970 and set standards and formulated the steps to limit air pollution in ferrochrome industries. Such comprehensive database that considers all sources of chromium in the environment, the likelihood of its exposure to humans and post consequences to man and lower organisms from its absorption was published in USA in 1984 [7]. Such a database is essential in India also. It is desirable to evolve control and preventive measures at the planning stage of any chromium based industries. For, prevention is better than cure, very little or nothing can be done if the Cr(VI) has already reached the subsoil as usually happens near bichromate factories or chromite mine water discharge points. Sadly, similar situations have already happened in Tamil nadu, Maharashra, Orissa and some other places. There is some hope of the Cr(VI) content in water is low say, 8-10 ppm is not fit for domestic use and drinking purposes[2].

Under low acidic conditions Cr(III) is hydrolysed to insoluble hydroxide form and is easily retained in the soil matrix. The possibility of its getting back into solution thereafter is very small [11].

Chromium (VI) on the other hand is stable both acidic and alkaline conditions and is not retained in the soil matrix. It percolates through porous medium and even enter the subsoil water sources. Under slightly acidic conditions (pH is less than 4 ), Cr(VI) is reduced by organic matter like humus or biomass. This solubility of Cr(III)
hydroxide and the easy reducibility of Cr(VI) comes in handy to control when pollution due to chromium.

The insolvable hydroxides such as Cr III/Fe III are separated after flocculation or adsorbed on suitable adsorbents like cotton dust which is a good adsorbent of chromium. Just like coal dust, saw dust. Sodium sulphite is an other reductant, sulphant dioxid, sodium dioxid, sodium poly-sulphide can be used. Certain clay materials like calamite, chlorite and alpha quartz adsorb Cr(VI) from solution. The adsorption depends on pH. Furnace slag was used for the removal of Cr(VI) by adsorption in effluents. Inorganic oxides and oxyhydroxides are very good adsorbents for Cr(VI). Alumina in an adsorbent of Cr(VI). Cr(VI) is absorbed in some of the waste generated by thermal power plant or fertilizer plants. Fly Ash / China Clay mixture is effective in removal to Cr(VI) from aqueous solution. It is necessary that all chromium based industries must follow adequate safe guards(1998).

3.2 Enactment of Worker’s Compensation Laws and Occupational Diseases law
It has been observed by the authors that most of the management of the chromium based industries like cromite mining industries both private and Government have not implemented the Worker’s Compensation Laws. As per the research studies conducted, it has been proved that approximately 80 percent of all industrial disasters are preventable. Hence, the Worker’s Compensation Laws must be enacted in all industries in India.

The principle involved Worker’s compensation laws is that the worker injured or disabled in industry should be enabled, through proper medical treatment, to return to wage-earning capacity as promptly as possible and, while incapacitated, should receive compensation in lieu of wages, regardless of fault. The expenses of medical treatment and compensation should properly be borne by industry and become a part of the cost of its products. The laws generally provide that workers injured in industry shall be furnished the necessary medical treatment, and, in addition, compensation based on a percentage of their average weekly wages, payable periodically. Dependents of employees killed in industry are likewise compensated [8]. They have to be supplemented their worker’s compensation laws by providing comparable benefits in cases of incapacity or death due to occupational disease[6]. They make these provisions applicable only in case of specified occupational diseases; others make them of general application to cases of any disease directly attributable to the employment. Management of the industries may provide for compensation benefits in occupational-disease cases either by enlarging the scope of the worker’s compensation law, by separate legislative enactment, or by judicial constructions. The enactment of worker’s compensation laws has to be followed in many jurisdictions by more stringent provisions relating to factory inspections for the prevention of accidents in industry and of occupational disease. The enactment of worker’s compensation and occupational-disease laws will increase materially the cost of insurance to industry. The increased cost and the certainty with which it is applied have put a premium on accident-prevention work. This cost can be materially reduced by the installation of safety devices.

4 Conclusion
The above information details have provided us about the chromium pollution load in the environment. The studies have provided percentage composition of chromium element including Cr +3 and Cr +6 . As far as the case studies pertain to chromium leather tanneries are concerned in India, there were about 2,000 tanneries in our country having an annual processing capacity of 7,00,000 tones of hides and skins in the year 2000. About 80% of the tanneries have used chrome-tanning process[4]. The tannery process consisting of curing, soaking, liming, and unhairing, deliming-bating, deliming-washing, bating-pickling and chrome tanning. Chrome tanning process has used dichromate, sodium chromate and chromium sulphate having 50% basicity as raw material. This process has produced tremendous chromium wastes in wastewater. Out of the chromium compounds applied in chrome tanning process, that was about 69,000 tons annually in 1600 tanneries, (i) about 25 to 39% has been spent in waste water. Out of this, there was 45% in the form of Cr +6 salts and (ii) 61 to 75 % has been absorbed in the leather. Out of this about 45 % was in the form of Cr +6 salts. In this about 20 to 25 % chromium has been confined with the CCLC roller element. It is mentioned that about 80% of these leather tanneries have caused severe water pollution. This has polluted river bodies. This has caused ground water pollution.
contamination with toxic hexavalent chromium widely spreading all over India.

Chromium and its compounds are exclusively used in chromium based industries such as leather tanning, textiles, metallurgical industries, mechanical and mining engineering industries, chemical and metal finishing industries, ferrochrome, pigments, electroplating and photography. These generate considerable quantity of toxic chromium pollutants which contaminates 6000-18000 mg/kg (ppm) of total chromium (including hexavalent chromium) in air, water and soil environment [2]. This chromium pollution produces adverse health effects on the workers and those people who are exposed in the vicinity. They suffer from chromium based diseases such as chromium poisoning, ulcer, allergic dermatitis, lung cancer, liver necrosis, brain damage, premature death, liver and kidney problems. Several countries have initiated regulatory measures to control chromium pollution, but Indian companies have not initiated so far. It is essential to evolve control and preventive measures which are to be taken at the planning stages in these industries as prevention is better than cure, very little or nothing can be done if the toxic chromium reaches the air, water and soil environment[3].

Acknowledgement
The first author is thankful to WSEAS for the award of Post Doctoral Fellowship under the guidance of Prof. Nikos Mastorakis and for publication of this research inputs in one of the WSEAS proceedings /NAUN journals.

References: