ASSESSMENT OF CHROMIUM POLLUTION AT BAULA MINES, ORISSA

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BACHELOR OF TECHNOLOGY

IN

MINING ENGINEERING

BY

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2010
This is to certify that the thesis entitled “ASSESSMENT OF CHROMIUM POLLUTION AT BAULA MINES, ORISSA” submitted by Sri Basanta Kumar Kishan in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ABSTRACT

This study is conducted in and around one of the chromite mines of the Nuasahi-Baula igneous complex for assessing the Cr pollution. Hexavalent chromium was found between 0.002 and 0.006 ppm in groundwater and 0.008 to 0.036 ppm in mine discharges. The total chromium ranged between 0.002 and 0.007 ppm in groundwater and 0.009 to 0.042 ppm in mine discharge water. The goethite rich overburden material at chromite mines is an efficient sink for the chromate anion. Leaching experiments using a saline solution, phosphate solution and tap water showed that phosphate solution release more hexavalent chromium compared to other two solutions. These results can be useful in evaluating natural attenuation of fertilizer-derived pollutants in the agricultural land near chromite mines. From the mineralogy it was found that the laterite contains more goethite mineral compared to other minerals. The concentration of chromium is more in laterite than overburden and soil. The impacts of chromium on the environment depend on the percentage of chromium in exchangeable fraction. The study shows that percentage of chromium is less in exchangeable fraction and more in residual fraction in the study area. So the Cr bioavailability is low and toxicity is less.
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CHAPTER 1

INTRODUCTION & OBJECTIVE
1.1 INTRODUCTION

Chromium is a member of the transition metals, in group 6. Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm. Chromium exhibits a wide range of oxidation states. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable. From them +6 oxidation state is mobile in water and carcinogenic in nature. The locked up chromium in chromites that carry the major portion of the lithogenic Cr and the refractoriness of the mineral is an environmental blessing. If each of the Cr (III) atoms took up only one more atom of oxygen for conversion to a higher valance state, the entire atmospheric oxygen could be stripped out. However, before the earth attains such an anoxic disaster, life will be poisoned by Cr (VI) toxicity (Bartlett and James, 1986) as a result of Cr (III) to Cr (VI) conversion. Hexavalent Cr is known to be 100–1000 times more toxic than the trivalent form (Gauglhofer and Bianchi, 1991). In the hexavalent state, chromium exists as oxospecies such as CrO_3 and CrO_4^{2-} that are strongly oxidizing. Hexavalent chromium may exist in aquatic media as water soluble complex anions and may persist in water. Hexavalent chromium is a strong oxidizing agent and may react with organic matter or other reducing agents to form trivalent chromium. The trivalent chromium will eventually be precipitated as Cr_2O_3·XH_2O. Therefore, in surface water rich in organic content, hexavalent chromium will exhibit a much shorter life time. Any hexavalent chromium in soil is expected to be reduced to trivalent chromium which is lost from soil by aerial transport through aerosol formation and surface water transport through run off (www.epa.gov/iris/toxreviews/0144tr.pdf).

There has been an increasing demand for chromite ores in recent years. In the opencast mining processes, the chromite ore as well as waste rock material are dumped in the open ground without considering the environmental aspects and resulting in the oxidation of Cr (III) to Cr (VI). The result has been damage to the topography and leaching of chromium and other impurities to the groundwater as well as surface water bodies (Tiwary et al., 2005). Therefore, contamination of groundwater and soil in the vicinity of mines is expected.
1.2 OBJECTIVE

This thesis has the following objectives

- Concentration of Cr in mine discharges and ground water
- Mineralogy of the soil
- Desorption of the Cr (VI) form the lateritic soil
- Sequential extraction of the Cr
CHAPTER

2

LITERATURE REVIEW

CHROMIUM CHEMISTRY
NATURAL SOURCES OF CHROMIUM
POLLUTION OF WATER BY CHROMIUM
HARMFUL EFFECT OF Cr (VI)
Cr (VI) RETENTION BY MINE OVERBURDEN
LOCATION AND GEOLOGICAL SET UP OF NUASAHI-BAULA COMPLEX
2.1 CHROMIUM CHEMISTRY

Chromium has a unique geochemical behaviour in natural water systems. Under strong oxidizing conditions, chromium is present in the Cr (VI) state and persists in anionic form as chromate. Cr (III) is the most common form of naturally occurring chromium, but is largely immobile in the environment. Redox potential Eh-pH diagrams present equilibrium data and indicate the oxidation states and chemical forms of the chemical substances which exist within specified Eh and pH ranges.

![Figure 2.1: Eh-pH diagram for Chromium](Sources: http://www.epa.gov/nrmrl/pubs/625r00005/625r00005.pdf)

The Figure 2.1 implies that the boundary separating one species from another is distinct; the transformation is so clear cut. Concentration, pressure, temperature, and the absence or presence of other aqueous ions can all affect which chromium species will exist. A measure of caution must be exercised when using this diagram as site-specific conditions can significantly alter actual Eh-pH boundaries. Under reducing conditions, Cr (III) is the most thermodynamically stable oxidation state. However, Cr (VI) can remain stable for significant
periods of time. Cr (III) exists in wide Eh and pH ranges. Cr (III) predominates as ionic (i.e., $Cr^{+3}$) at pH values less than 3.0. At pH values above 3.5, hydrolysis of Cr (III) in a Cr (III)-water system yields trivalent chromium hydroxy species [$CrOH^{+2}$, $Cr(OH)_2^+$, $Cr(OH)_3^-$, and $Cr(OH)_4^-$] is the only solid species, existing as an amorphous precipitate.

2.2 NATURAL SOURCES OF CHROMIUM

Chromium is one of the earliest elements to be immobilized in solids by crystallization during differentiation of magma. Therefore it is normally concentrated in the ultramafic and ultrabasic rocks. Dunite, peridotite, pyroxenite, and serpentine contain Cr at levels of 2400 ppm (Matzat and Shiraki, 1974). The distribution of total Cr in natural groundwaters was investigated by Barnes and Langmuir (1978). They found total Cr thresholds, corresponding to the 97.7 percentile, of 10–19ppb for 647 groundwaters associated with carbonate rocks, sandstones (including quartzites, arkoses, grey wacks, and conglomerates), shales (comprising clays, siltstones, and slates), and felsic to intermediate igneous and meta-igneous rocks. By contrast, a total Cr above the threshold was found for 35 groundwaters coming from mafic and ultramafic igneous and meta–igneous rocks. In fact the worldwide average Cr contents of peridotites and basalts (1800 and 185ppm, respectively) are much higher than those of limestones (11 ppm), granites (22 ppm), sandstones (35 ppm), and shales (90 ppm; (Faure, 1992). However these data are insufficient to define the natural (background) concentrations of Cr (VI) and Cr (III) in waters, a facet of utmost importance due to their different toxicity. Concentrations of Cr (VI) reaching 12 ppb and Cr (III) 11 ppb were recently found in groundwaters interacting with ultramafic rocks (Robles-Camacho and Armienta, 2000), indicating that these lithotypes may cause natural pollution of waters in not only Cr (III) but also Cr (VI).

2.3 POLLUTION OF WATER BY CHROMIUM

Water pollution has been a serious threat to mankind since last few decades. The common polluting sources are domestic sewage, mine drainage, and industrial effluents. Natural weathering of rocks, which supplies a significant amount of toxic elements and compounds to surface as well as ground water acts as a background to the pollution effect. Metal pollution
of water by different sources has been studied by several workers. Chromium contamination from Sukinda chromite mine, leading to the pollution of river and groundwater has been reported by Godgul and Sahu (1995). Chromium pollution is caused mainly due to weathering of mafic or ultramafic rocks (Fantoni et al., 2002) and industrial waste (Singh et al., 2009).

In nature, the dispersion of pollutants is partly controlled by clay minerals, metal oxides and organic matter which acts as sinks for pollutants (Raymahashay, 1996). The surface charge of clay minerals is pH dependent. At pH below the zero point charge (ZPC), the surface is positively while the charge becomes negative at higher pH. As a result, anion exchange is more prominent at low pH whereas cation exchange capacity increases with increasing pH. Adsorption of positively charged metal ions on clay surfaces has been widely observed. The clay minerals which occur in soil profiles as well as stream sediments remove the pollutants when water containing toxic metals pass through them. Metal oxides and hydroxides like those of Al, Fe and Mn also act as scavengers of trace elements. The surface of the hydrous oxides has a positive charge at pH below ZPC and negatively charge at pH value. This enables them to adsorb the toxic elements in high as well, as low pH conditions. Lateritic soil and organic matter similarly remove ionic pollutants from waste water.

The geochemical cycle of Cr may also involve reduction of Cr (VI) to Cr (III) in the presence of ferrous (Fe$^{2+}$) iron and organic matter (Richard and Bourg, 1991) (Sedlak and Chan, 1997). This principle has been utilized to treat Cr (VI) – rich mine drainage with FeSO$_4$ which results in the precipitation of Cr (OH)$_3$. Moreover, biologically mediated Cr (VI) reduction in the presence of soil bacteria has been recommended as a method of Cr-removal (Ligy Philip, 1997). This process may be active in the top soil zone around chromite mines.

In Sukinda area, the lateralization process involving oxidation and alternation of the serpentines creates alkaline pore water which facilities the generation of Cr (VI) from the inert chromites and causes hazardous chromium pollution of water. Godgul and Sahu (1995) have found Cr (VI) in some quarry waters from Sukinda chromite field, above the permissible limit recommended by world health organization. The enhanced Cr levels of mine floor water samples in Sukinda according to them, are suggestive of the release of immobile Cr (III) after oxidation either from chromite or silicate and the likely movement of the oxidised species to the groundwater. The steady release of Cr from Sukinda into the Damsala river has been enhanced the Cr levels in the sediments and water of the Brahmani
river estuary near Dharma region of Bay of Bengal. So, while Cr (III) either in ultramafic rocks or in chromite deposits is rarely a danger to the environment, altered and oxidised chromite may pose a threat to the environment by dispersing significant quantity of Cr (VI) to the aqueous system. But this pollution effect is partly neutralized in nature by the presence of goethite in lateritic rocks present chromite mines. This is because goethite, a hydrated iron-oxide, carries a positive charge on its surface in its colloidal state, thereby adsorbing the negatively charged CrO$_4^{2-}$ from the ground water during its percolation through the rocks.

2.4 HARMFUL EFFECT OF Cr (VI)

Chromium (VI) is one of the most toxic water pollutant and is comparatively more toxic than trivalent compounds. Chromium and its compounds are known to cause cancer of the lungs, nasal cavity and paranasal sinus and is suspected of causing cancer of the stomach and larynx. Hexavalent chromium is transported into cells via the sulfate transport mechanisms, taking advantage of the similarity of sulfate and chromate with respect to their structure and charge. Trivalent chromium, which is the more common variety of chromium compounds, is not transported into cells. Cr (III) is considered to be essential to mammals for the maintenance of glucose, lipid and protein metabolism. Chromium can act directly at the site of contact or be absorbed into, or through, human tissue. Chromium (VI) can act as an oxidant directly on the skin surface or it can be absorbed through the skin, especially if the skin surface is damaged. Chromium absorbed into the blood does not accumulate in any organs at significant concentrations. In metabolism studies, injected and ingested chromium was found mainly in the liver, kidneys, and blood. Breathing in high levels of Cr (VI) (>2 µg/m3) containing dust particles in the form of compounds like chromic acid or chromium tri-oxide, can cause irritation to the respiratory system. The permissible limit of Cr (VI) in drinking water is 50µg/L and total Cr is 100µg/L (www.epa.gov/iris/toxreviews/0144tr.pdf).

2.5 RETENTION OF Cr (VI) BY MINE OVERBURDEN

Chromium is mined as its oxide ore chromite FeO.Cr$_2$O$_3$. Some of the largest opencast mines of India occur in the state of Orissa. Generally the chromite ore occurs in the form of discontinuous bands and lenses and confined to the altered dunite-peridotite, serpentinite has been extensively weathered by atmospheric and percolating ground water. The FeO
component of primary minerals like chromite, olivine and serpentine has been oxidized to

the group of Fe (III) like goethite, Fe$_2$O$_3$.H$_2$O and maghemite, $\gamma$-Fe$_2$O$_3$. These are the main

constituents of the thick laterite-limonite overburden over the ore body. It is apparent that

under the same oxidizing condition Cr (III) in chromite is mobilised into ground water as the

hexavalent CrO$_4^{2-}$ ion.

The overall process can be represented by a reaction of the type:

\[
\text{Chromite} + \frac{7}{2} \text{O}_2 + 5\text{H}_2\text{O} = \text{goethite} + 4 \text{CrO}_4^{2-} + 8\text{H}^+
\]

The situation is favourable for quantitative adsorption of the Cr (VI) anion on the positively
charged surface of goethite. The goethite is positively charged as the pH of water is below the
ZPC (Zero Point Charge) value of goethite. At ZPC the net charge on the mineral is zero
(Raymahashay, 1998). For Individual minerals, different authors have cited a variety of values
as shown in Table 2.1.

**TABLE 2.1: pH values at Zero point of charge for HFO minerals** (Equeenuddin et al., 2008)

<table>
<thead>
<tr>
<th>Minerals</th>
<th>pH at ZPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite, Fe$_3$O$_4$</td>
<td>6.5</td>
</tr>
<tr>
<td>Hematite, Fe$_2$O$_3$</td>
<td>5 to 9</td>
</tr>
<tr>
<td>Goethite, Fe$_2$O$_3$.H$_2$O</td>
<td>6 to 7</td>
</tr>
<tr>
<td></td>
<td>7.3 to 7.8</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
</tr>
<tr>
<td>Maghemite, $\gamma$-Fe$_2$O$_3$</td>
<td>6.7</td>
</tr>
<tr>
<td>Amorphous Fe(OH)$_3$</td>
<td>8.5</td>
</tr>
</tbody>
</table>

**2.6 LOCATION AND GEOLOGICAL SET UP OF BAULA-NUASAHI COMPLEX**

Deposits of chromite in Boula-Nuasahi area of Kendujhar district was discovered in 1942 and
mining started from 1943. The area around Nuasahi (21° 17' N: 86° 20' E) lies at the south
eastern fringe of Baula state forest and is connected to S.E railway and N.H.5 at Bhadrak
town by an all weather 45 kilometers long metal road passing through Bidyadharpur barrage
and Agarpara. The important features of the area include a dam on Slandi river and a
barrage at Bidydharpur. In Boula-Nuasahi sector, three mines are in active operation. Here, chromite is mostly lumpy and the wall rock is hard serpentine. Orissa Mining Corporation Limited (OMCL), a State Government undertaking is engaged in mining and processing of chromite ore in Keonjhar district of Orissa. Bangur Chromite mining lease of OMCL is located in Anandpur subdivision of Keonjhar district in Orissa. The total geological reserve of chromite ore in the lease-hold has been estimated to be 2.75 million tonnes (Mt).

The area around Boula-Nuasahi consists of older quartzites which include massive, ferruginous and micaceous varieties. The ultramafic body to the west of village Nuasahi extends for 3 kilometres in a NNW-SSE direction. This is a dyke like steeply incline body having distinct intrusive relationship with the older quartzites and epidiorite hills to the north. The ultramafic body has a maximum width about 1 kilometre in the middle tapering gradually towards north and south and mainly consists of serpenitised dunite-pridotite core and a subordinate amount of pyroxenite, almost in a bysmalith form. The Stratigraphy of Boula-Nuasahin igneous complex (Sahoo, 1963) is given in Table 2.2.

Table 2.2: Stratigraphy of Baula-Nuasahi igneous complex

<table>
<thead>
<tr>
<th>Recent to Pleistocene</th>
<th>Soil, Alluvium, Laterite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconfirmitry</td>
<td>Dolerite dykes</td>
</tr>
<tr>
<td></td>
<td>Granite</td>
</tr>
<tr>
<td>Precambrian</td>
<td>Granophyre</td>
</tr>
<tr>
<td>Ultramafics</td>
<td>Gabbro-anorthosite with Ti-V magnetite</td>
</tr>
<tr>
<td></td>
<td>Ore bodies Enstalite-Peridotite and dunite</td>
</tr>
<tr>
<td></td>
<td>With chrome ore</td>
</tr>
<tr>
<td>Meta sediments and metavolcanies</td>
<td>Quartzite, quartz-mica schist, quartz-sericite schist</td>
</tr>
</tbody>
</table>

Base not seen
CHAPTER 3

MATERIALS AND METHODS
3.1 SAMPLE COLLECTION

Mine discharges, ground water, soil and overburden were collected from the Nuasahi Boula chromite mines area in the month of December, 2009. Mine discharges were collected from the OMC quarry; ground water from the near by village; overburden from OMC dump site, and soil and laterite cover from the surroundings.

Soil and overburden samples were collected in the air tight polythene packet. Water samples were collected in the acid rinsed polyethylene bottles in duplicates. Non-filtrate part was used for measuring pH and Cr (VI) while filtrate part was acidified with HNO₃ to bring pH less than 2. The acidify part was used for the analysis of total Cr.

3.2 LABORATORY WORK

Soil and overburden samples were powered and sieved through (63 µm) for subsequent analysis.

Mineralogy of soil and overburden was studied using a Phillips PW-1710 X-ray diffractometer (XRD) employing CuKα radiation at 1.2º/minute scanning rate. Total concentration of Cr in soil and overburden was determined using Philips PW 2400 X-ray fluorescence from the press pellets.

Total Cr in mine discharges and ground water samples were analyzed using Atomic Absorption Spectrophotometer (PerkinElmer Analyst300). Hexavalent Cr was analyzed using the colorimetric method following Standard Methods (1985).

3.3 COLORIMETRIC METHOD

Stock solution of 1000 ppm Cr (VI) was prepared by dissolving 2.8 g of K₂Cr₂O₇ in 1000ml water. By diluting the stock solution, standard solutions of 0.05 ppm, 0.1 ppm, 0.2 ppm, and 0.4 ppm Cr (VI) was prepared for calibration purpose.
100 ml of solution was taken. 0.2 N H₂SO₄ was added to the solution and then, 2 ml of diphenylcarbazide solution was added and mixed thoroughly. The solution was kept for 5 to 10 minute. A red violet colour was developed. The absorbance at 540 nm wavelength was measured by spectrophotometer (EI-1305). A calibration curve was constructed by plotting absorbance value against concentration (Figure 3.1).

![Figure 3.1 Calibration curve for Cr (VI)](image)

**3.4 DESORPTION EXPERIMENT**

Cr (VI) was leached out from laterite soils into 1) a saline solution, 2) Phosphate solution 3) tap water. The samples were powdered and sieved between 230 and 200 mesh (0.065 to 0.074 mm) size. For desorption into saline solution, 1 g of sieved sample was stirred into 100 ml distilled water containing 1.74 gm NaCl and 0.05 gm NaHCO₃. This solution has pH 8 (Bisoi, 1990). After a contact period of 24 hours, the suspension was filtered through whatman 42 paper and Cr (VI) was determined in the clear solution by colorimetric method as outlined above. For desorption into phosphate solution, 1gm of sieved sample was stirred in 0.1M PO₄ solution prepared from KH₂PO₄.
3.5 SEQUENTIAL EXTRACTION OF CHROMIUM

An attempt was made to estimate the percentage of chromium associated with different fractions such as exchangeable, organic, Fe-Mn oxide, carbonate and residual fractions by sequential extraction procedure (SEP) (Figure 3.2).

Figure 3.2: Scheme of the selective sequential extraction (Tessier et al., 1979)
CHAPTER 4

RESULTS AND DISCUSSIONS
4.1 MINERALOGY OF LATERITE SOIL

Figure-4.1: XRD pattern of laterite sample.

X-ray diffraction pattern of the laterite soil is shown in Figure 4.1. It is observed that laterite is mainly composed of quartz, goethite, kaolinite and chromite with trace amount of mahgemite.

4.2 CHROMIUM IN WATER

Concentrations of Cr in various water bodies are given in Table 4.1. The pH of mine discharges ranges between 7.6 and 7.9 which is higher than the pH of ground water whose pH ranges between 6.7 and 7.2. Concentration Cr in mine and ground water ranges from 0.009 to 0.042 ppm and less than 0.001 to 0.007 ppm respectively. From the Table 4.1, it can be confirmed that most of the Cr occurs in the form of Cr (VI) due to very less difference in their respective concentration in both mine and ground water. The amount of Cr and Cr (VI) is below permissible limit in both type of water. The concentration of both total Cr and Cr (VI) in mine water is much higher than groundwater. This sharp decrease of the Cr concentration in ground water in comparison to mine water is apparently due to the retention of Cr (VI) in the from of CrO$_4^{3-}$ anion onto the positively charged surface of laterite which is mainly composed of goethite. Lateritic cover is very extensive in the mining area as shown in Figure 4.2. The adsorption occurs during percolation of groundwater through the lateritic soil.
cover. Similar kind of observation was earlier reported in near by Sukinda chromite mines (Raymahashay et al., 1998).

**TABLE 4.1: Dissolved chromium and pH in mine and ground water**

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Cr (VI) (ppm)</th>
<th>Total Cr (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mine Discharge water</td>
<td>7.7</td>
<td>0.011</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>7.6</td>
<td>0.014</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
<td>0.036</td>
<td>0.042</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>0.008</td>
<td>0.009</td>
</tr>
<tr>
<td>Ground water</td>
<td>7.5</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>0.006</td>
<td>0.007</td>
</tr>
</tbody>
</table>

**Figure 4.2: Development of laterite cover at the chromite mines**

### 4.3 DESORPTION EXPERIMENT

In order to estimate the amount Cr (VI) adsorbed in laterite soil, non-destructive desorption experiment was carried out. The concentration of Cr (VI) released after desorption using three different solution, namely, saline solution, phosphate solution and normal tap water is shown in Table 4.2 and Figure 4.3. It is observed that release of Cr (VI) increases with increase in contact time. Phosphate solution released maximum Cr (VI) followed by saline...
solution and tap water. This is possibly due to the similar specific adsorption mechanisms for both chromate and phosphate (Bartlett and James, 1988). Fendorf et al. (1997) showed that CrO$_4^{2-}$ form an inner sphere complex at the goethite-water interface. Hsia et al. (1993) also confirmed the inner sphere adsorption of chromate onto iron hydroxide. Chromate adsorption onto clay was suppressed in the presence of phosphate (Aide and Cummings, 1997). In the saline condition, like at the mixing zone with sea, increase in salinity causes desorption of metals and suppress the adsorption process (Maest et al., 1990). Mayer and Schick (1981) reported the removal of chromate is ineffective under very high salinity regime by the estuarine sediments.

**TABLE 4.2: Desorption of Cr (VI) from laterite soil into saline, phosphate solution and water**

<table>
<thead>
<tr>
<th>Day</th>
<th>Saline Solution(ppb)</th>
<th>Phosphate Solution(ppb)</th>
<th>Tap water(ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21</td>
<td>78</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>93</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>34</td>
<td>115</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>46</td>
<td>128</td>
<td>21</td>
</tr>
</tbody>
</table>

**Figure-4.3: Desorption of Cr (VI) in saline, phosphate solution and tap water at various period**
4.4 SEQUENTIAL EXTRACTION OF CHROMIUM

The concentration of Cr in soil, overburden and laterite cover provides just partial information of its potential impact. However, its association with various fractions is useful to assess the potential environmental and human health impact through mobilization. The metals mainly occur in soil, overburden and laterite through five major mechanisms, exchangeable (Exch), with organic matter (Org), with carbonates (Carb), with Fe-Mn oxides and hydroxides (Fe-Mn), and residual (Res). Metals in exchangeable fraction considered to be most mobile and readily available for biological uptake in environment (Gadde and Laitinen, 1974). The organic fraction represents metals held by complexation, adsorption, and chelation process. Under oxidising condition it release metals bound to those materials. Metals bound to Fe-Mn oxides and hydroxides fraction are unstable under reducing conditions. Metals bound to carbonates are sensitive to pH changes with the lowering of pH being associated with the release of metal cations. The residual fraction contains naturally occurring minerals which may hold trace metals within their crystal lattices and unlikely to be released from the soil and sediments thus it is considered to be chemically most stable and immobilized. Thus the bioavailability is low and toxicity is less.

Figure 4.4.: Total concentration of Cr in laterite cover, soil and overburden (OB)

Total Cr concentration in the study area in soil, overburden and laterite cover is given in Figure 4.4. It is observed that the concentration of Cr in laterite cover is much higher than overburden and soil. This is due to the presence of goethite in laterite. The concentration of chromium is also much higher than its crustal abundance, which is 126 ppm.
Fractionation result of Cr is given in Table 4.3 and Figure 4.5. Fractionation result indicates that Cr is mostly associated in residual fraction followed by Fe-Mn bound and carbonate and/or organic and exchangeable. So the overall chromium toxicity is less in Baula mines. However, if the area would change into the reduce condition in future then the Fe-Mn bound Cr is likely to release into solution and can pose severe Cr pollution.
CHAPTER 5

CONCLUSIONS
5. CONCLUSIONS

Based on the foregoing results and discussions, it can be concluded that hexavalent chromium was ranged between 0.002 and 0.006 ppm in groundwater and 0.008 to 0.036 ppm in mine discharges which are below the permissible limit. The total chromium ranged between 0.002 and 0.007 ppm in groundwater and 0.009 to 0.042 ppm in mine discharge water. This decrease in the concentration of Cr is apparently might be due to the retention of $\text{CrO}_4^{3-}$ anion on the positively charged surface of goethite during percolation of ground water through the lateritic cover soil. Goethite was found to be one of the major components of the lateritic soil in addition to quartz, kaolinite and chromite with trace amount of mahgemite. Desorption experiments indicates that Cr (VI) are well retained in the laterite soil and maxium Cr (VI) was released into phosphate solution. The experiment results will be helpful in evaluating the fertilizer derived Cr (VI) in the study area. Total Cr in the soil and overburden is very high in comparison to its crustal abundant. Fraction study of Cr in soil and overburden indicates that bioavailability of Cr is less, and mostly associated with residual fraction.
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