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DISTRIBUTION OF HEXAVALENT CHROMIUM IN CHROMITE RESOURCES AND CHROME-BASED INDUSTRIES IN INDIA

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ABSTRACT

Accumulated seepage water from different chromite mine quarries of the Sukinda belt of Jajpur/Dhenkanal District and the Boula-Nuasahi belt of Keonjhar District were collected during premonsoon and monsoon periods. Samples were analyzed for hexavalent Chromium [Cr(VI)] and total chromium concentration. The study revealed variations in Cr(VI) and total chromium in the seepage water with location and time. Wastewater samples are from different chrome ore benification (COB) plants, chrome based metallurgical industries, and two chrome based chemical industries situated in Orissa, India also were collected to determine Cr(VI) and total chromium content. It was found that there was an absence of Cr(VI) in the effluent generated from ferro alloy plants but a very high concentration of Cr(VI) in other chrome based chemical plants.

INTRODUCTION

Chromium is a ubiquitous element occurring widely in environmental matrices including rocks, soils, sediments, air, water, and biological materials [1-7]. The most common ore is chromite in which metal exists in the trivalent form; the ore is present in commercial quantities only in a few countries, given in Table 1 [8].

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Table 1. World Reserves and Reserve Base of Chromite (By Principal Countries)

Country	Reserve (in thousand tons)	Reserve Base (in thousand tons)
World Total	13,61,000	6,778,000
USA	—	10,000
Albania	6,000	6,000
Brazil	8,000	16,000
Finland	29,000	29,000
India	59,000	77,000
Philippines	7,000	7,000
South Africa	9,59,000	55,36,000
Republic of Turkey	8,000	20,000
USSR (erstwhile)	1,29,000	1,29,000
Zimbabwe	1,41,000	9,27,000
Other Countries	15,000	21,000

Chromite (FeO Cr_2O_3) is the only commercial ore of chromium having economic importance. It is chiefly used in metallurgical, refractory, and chemical industries [8].

The geological resources of chromite in the country (India) include both recoverable reserves and conditional reserves. Recoverable reserves are part of in-situ reserves which can be recovered after allowing for the losses due to mining and grade dilution. Conditional resources are at present sub-economic and may become reserves with a favorable change in cost of production, selling price, technology, or market infrastructural facilities. In general, the resources estimated up to a depth of 100 meters have been categorized as reserve while those below 100 meters depth have been categorized as conditional reserve.

The total for all of India's geological resources of chromite ore is estimated at 182.5 million tons of 01.04.90, the break-down of which is given in Table 2 [8].

Within this in-situ reserve of 104.1 million tons the recoverable reserve has been assessed at 88.35 million tons. These deposits are located in Orissa, Karnataka, Moharastra, Bihar, Tamilnadu, Andhra Pradesh, and Manipur.

Orissas holds an important place in chromite reserves, accounting for more than 97 percent of the total reserve of chromite in India given in Table 3 [8].

These deposits are mainly concentrated in Sukinda valley of Jajpur and Dhenkanal district and Boula-Nuasahi belt of Keonjhar district (Figure 1).

The huge deposits of chromite and its subsequent mining is the main reason for establishment of quite a few chrome based metallurgical industries like Ferro-Alloy's plants and chrome based chemical industries.

Table 2. (Million Tons)

	Proved	Probable	Possible	Total
Total	34.9	83.5	64.1	182.5[a]
i) In-situ reserves	32.3	36.8	35.0	104.1
ii) Conditional Reserves	2.6	46.7	29.1	78.4

[a]The estimation is approximately down to a maximum depth of 200-250 m.

Table 3. Statewise Reserves of Chromite in India

State	Recoverable Reserves (in ,000 tons)
Total	88,350
Andhra Pradesh	67
Bihar	334
Karnataka	845
Maharastra	472
Manipur	2
Tamilnadu	240
ORISSA	86,390

The chromite mines situated in Sukinda and Boula-Nuasahi belt are mostly open cast. The ore is being mined out by the open pit method, both over-burden removal and extraction of ore are being done mostly by a semi-mechanized process [9]. However, few large mines have adopted a completely mechanized process for overburden removal and mining of ore. In the process of excavation and extraction of ore by the open pit method the groundwater seeps into the quarries/pits, because this zone is a dominant laterite-limonite profile constituting a very good aquifer with high porosity and permeability [10]. Flowing streams within the mining area is a source of profuse percolation of ground water into the mine [9]. Since the pits are required to be kept dry for further advancement of mining activities, the accumulated water of the pits/quarries is pumped out. This water is discharged either to a nearby stream or on land or used for irrigation.

In the case of industries, waste water is generated from various sources like process activities, washing, and slag quenching, which is generally discharged outside.

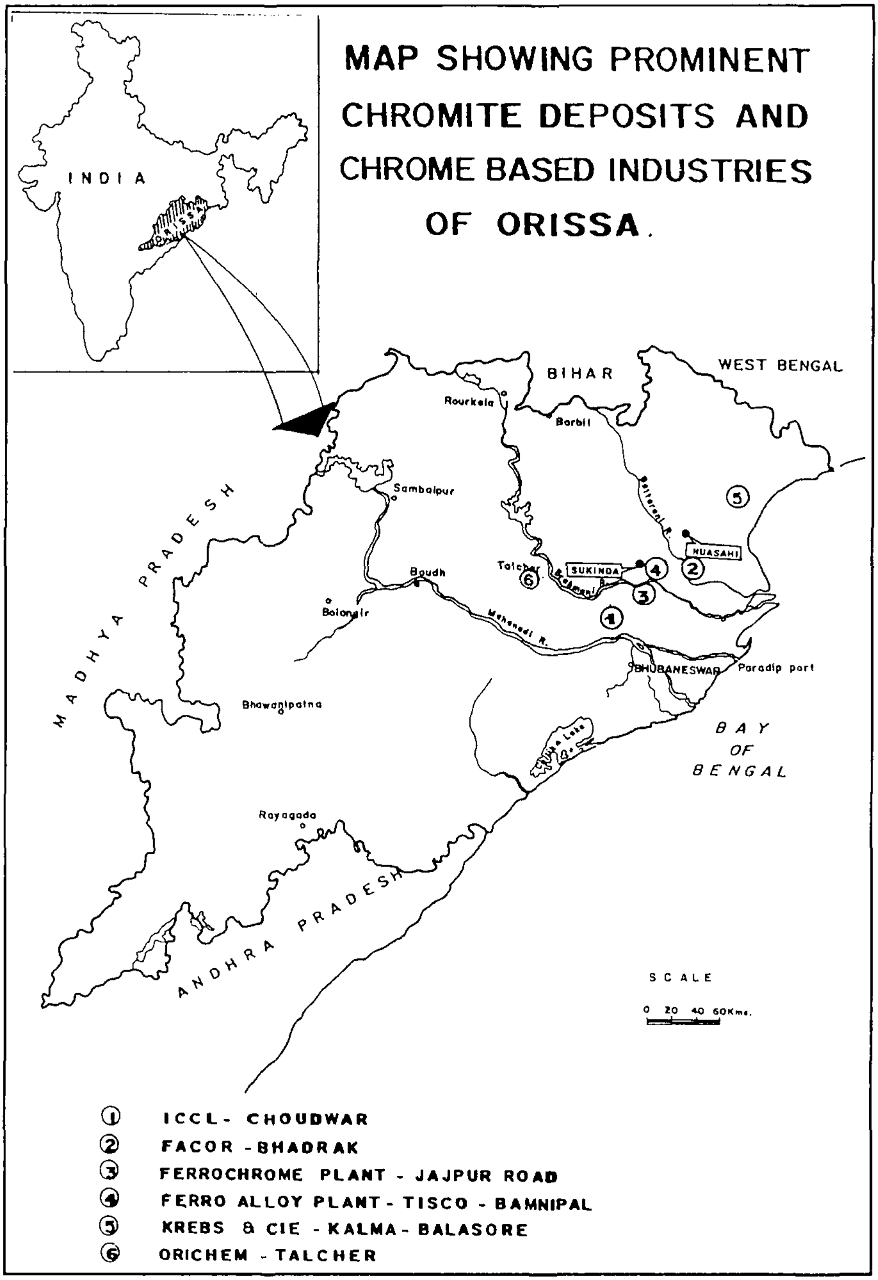


Figure 1. Map showing prominent chromite deposits and chrome-based industries of Orissa.

Recently we have reported the studies on removal of hexavalent chromium from industrial effluent as well as synthetic sample using a low cost adsorbent Kendu gum dust [11]. As Orissa holds an important place in chromite reserve, in the present study an attempt was made to determine the concentration of Cr(VI) in pumped out seepage water of the mines, tube well, and well water of the mining area and its variation with location and time. Further, an attempt was made to determine the presence of Cr(VI) in the generated wastewater in the process of production of charge Chrome/Ferochrome and basic chrome sulphate. The mine seepage water and industrial wastewater have also been analyzed for hexavalent chromium and total chromium.

LOCATION

The chromite fields of Sukinda and Boula-Nuasahi are fifty kilometers apart in an ENE-WSW direction, the latter being toward the east. The Sukinda valley is flanked by the Mohagiri range and Daitari range extending over an area of about 50 Sq km, bounded by latitudes N 21°59′ and 21°04′20″ and longitudes E85°41′10″ and 85°50′10″ [12]. The Damsala river flows through the center of the valley, contributing to the profuse percolation of ground water into the mines (Figure 2).

The Nuasahi field occupies an area of about 5 sq km, bounded by latitudes N 21° 15′ 35″ and 21° 18′ and longitudes E 86° 18′ 50″ and 86° 20′ [10]. The area consists of a cluster of low hills. The river Salandi flows in this area in a SE direction (Figure 3).

The chromite mines of the Sukinda and Boula-Nuasahi belts considered for the study are:

Sukinda Sector

Name of Mine	Sector	Type of Quarry
1. Kamarda	Private	Open cast
2. Saruabil	Private	Open cast
3. Sukrangi	Government	Open cast
4. Kaliapani	Government	Open cast
5. South Kaliapani	Government	Open cast
6. Ostapal	Private	Open cast
7. Bhimtanagar	Private	Open cast
8. Kalarangi	Government	Open cast
9. Kathpal	Government	Open cast
10. Kathpal	Private	Open cast and underground
11. Tailangi	Government	Open cast

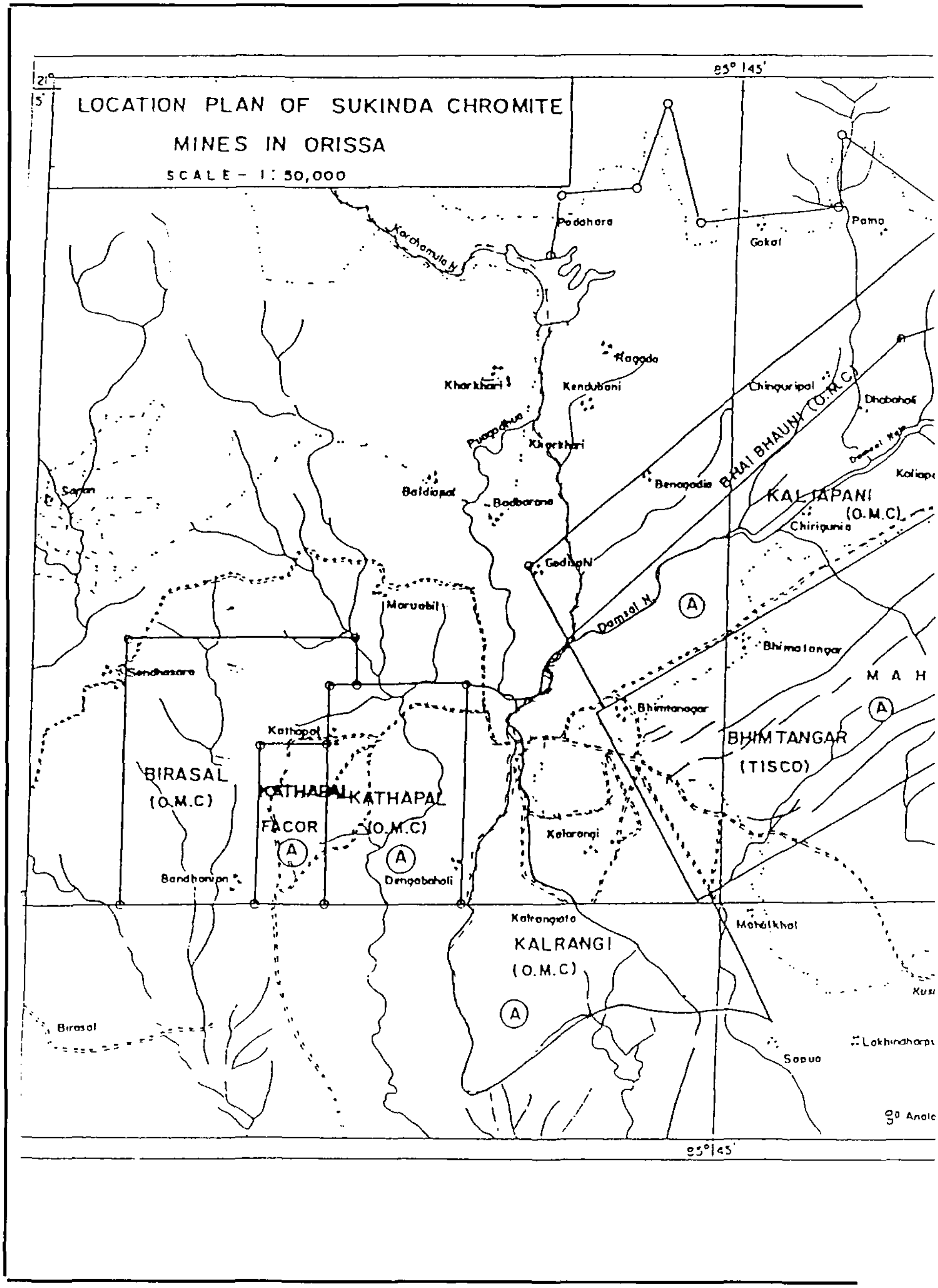
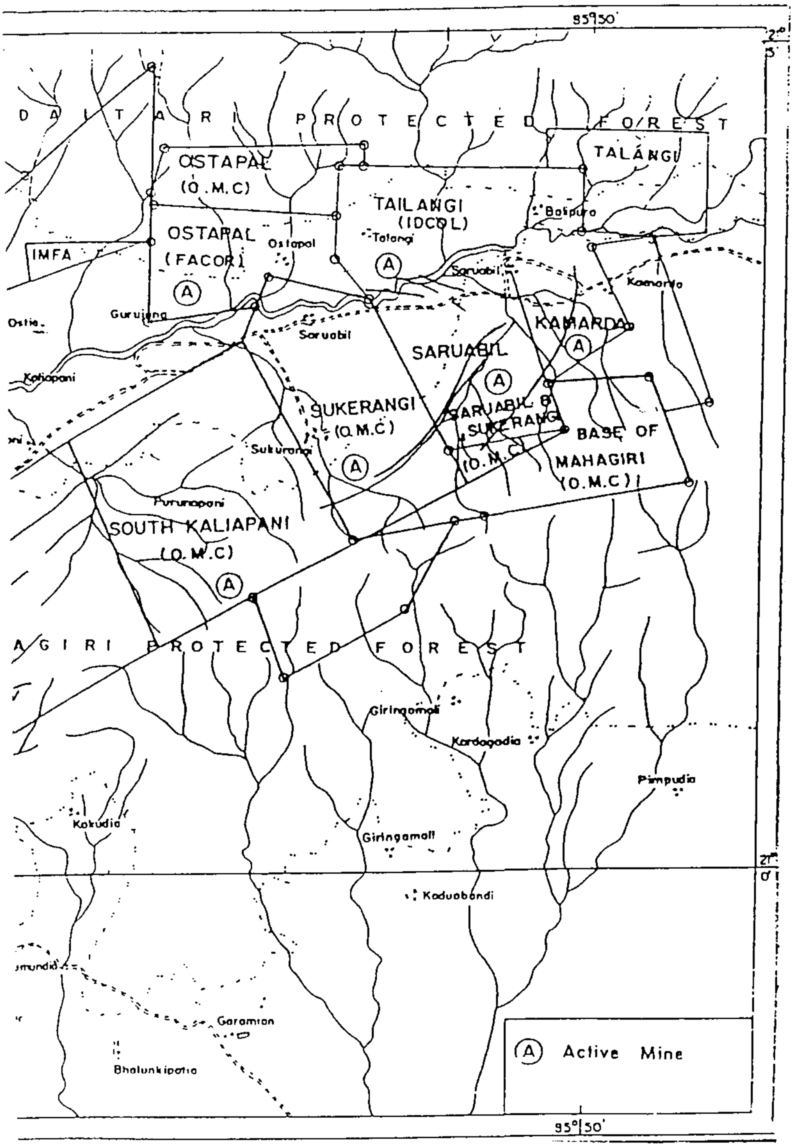


Figure 2. Locations of Sukinda chromite mines in Orissa.



85°50'
DALITARI PROTECTED FOREST
OSTAPAL (O.M.C)
TALANGI
TAILANGI (IDCOL)
OSTAPAL (FACOR)
IMFA
Ostapal
Talangi
Baliparo
Saruabil
Kamarda
Guruijang
Ostia
Saruabil
KAMARDA
SARUABIL
Kaliapani
SUKERANGI (O.M.C)
SARUABIL B SUKERANGI (O.M.C)
BASE OF MAHAGIRI (O.M.C)
Sukurangi
Purunapani
SOUTH KALIAPANI (O.M.C)
AGIRI PROTECTED FOREST
Giringamali
Kardagadia
Pimpudia
Kokudia
Giringamali
Koduabandi
Garamian
Bhalunkipatia
Active Mine
85°50'

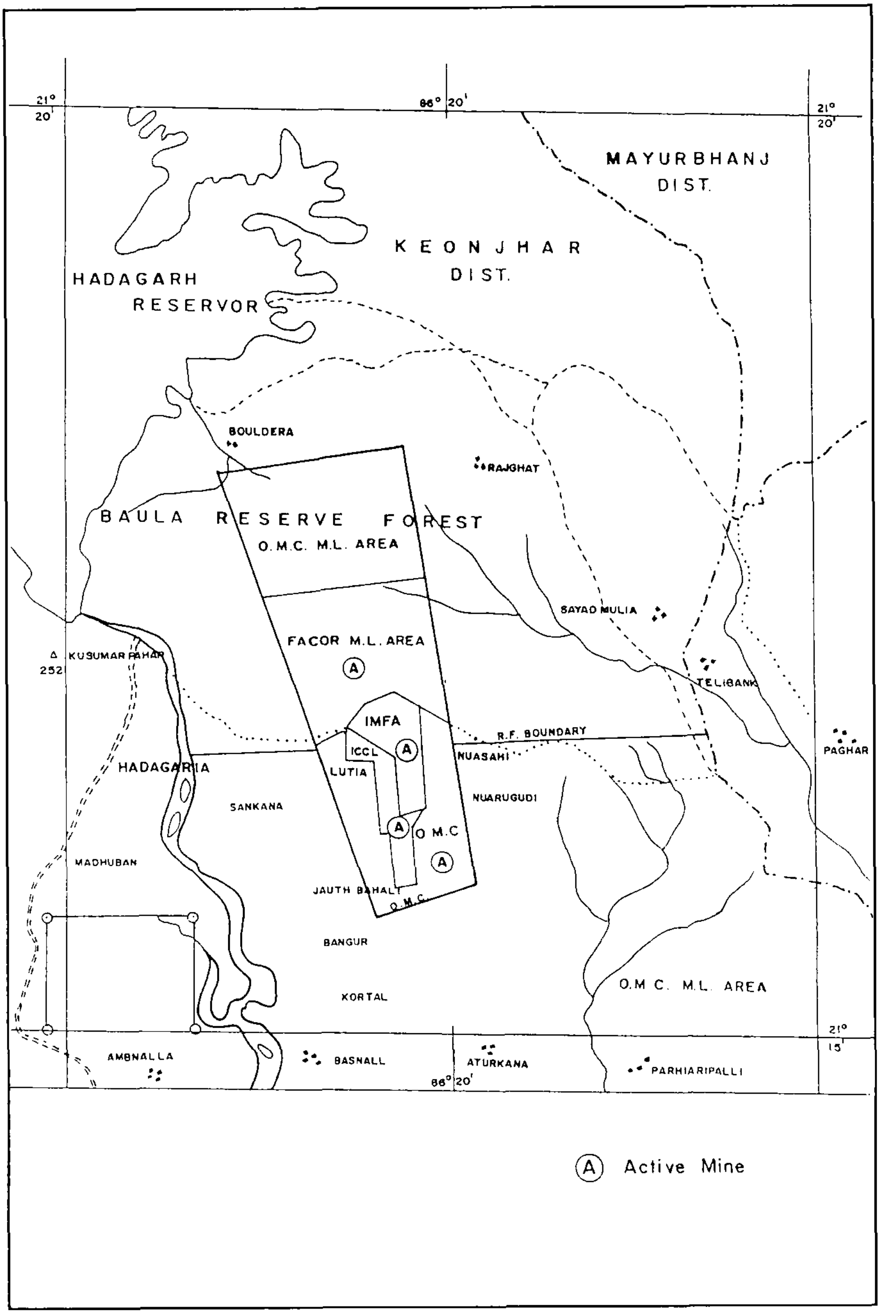


Figure 3. Locations of Boula chromite mines.

Boula-Nuasahi

Name of Mine	Sector	Type of Quarry
1. Boula Chromite Mine	Private	Open cast
2. Bangur Chromite Mine	Government	Open cast
3. IMFA Chromite Mine	Private	Open cast
4. ICCL Chromite Mine	Private	Open cast

INDUSTRY

Chromite is the basic raw material for metallurgical, refractory, and chemical industries.

The industries which have been included under the study are:

Company	Sector	Product	Location
1. ORICHEM Ltd.	Government	Basic chrome sulphate	Talcher, Angul
2. Krebs & Cie Pvt. Ltd.	Private	Basic chrome sulphate	Kalma, Balasore
3. FACOR	Private	Charge chrome	Bhadrak
4. ICCL	Private	Charge chrome	Choudwar, Cuttack
5. Ferro Alloy Plant, TISCO	Private	Ferro chrome	Bamnipal, Jajpur

MATERIALS AND METHODS

Water samples were collected in polyethylene bottles of 1.L capacity which were thoroughly cleaned with 1:1 HNO_3, rinsed several times with double distilled water and dried in an electric oven. Samples were collected in two different seasons (pre-monsoon and monsoon) from different mine quarry sites as shown in Figures 1, 2, and 3. Wastewater from the industries and benificiation plant were also collected once. These water samples were analyzed for hexavalent Chromium (Cr(VI)) and total chromium by standard techniques [13].

Hexavalent chromium is determined spectrophotometrically using 1,5-diphenylcarbazide [13]. GBC UV/VIS 911 spectrophotometer is used for spectrophotometric analysis. The presence of total chromium was determined by GBC 902 double beam Atomic Absorption Spectrophotometer.

Only analytical reagent grade chemicals were used for the analysis.

RESULTS AND DISCUSSION

The in-situ ore minerals being buried and compacted release only a little of the metals into the environment due to inertia of equilibrium. Mining activities not only expose the metallic minerals in equilibrium to natural reactive processes of oxidation, hydration reactive surface area due to excavation and reduction of particle size. Thus a large amount of heavy metals are released into the aquatic medium from mine drainage [14].

Water samples were collected in premonsoon and monsoon season from different mine quarry sites for determination of hexavalent chromium Cr(VI) and total chromium Cr(T). Analysis data are presented in Tables 4 and 5.

At Kathpal area the mine discharge water of both Kathpal (OMC) and Kathpal (FACOR) does not contain any hexavalent chromium except Maheswari Pit (FACOR) where hexavalent chromium has been observed to be 0.02 mg/L during monsoon only. The Cr(T) has been found to be in the range between 0.06-0.07 mg/L during premonsoon and between 0.09-0.2 mg/L during monsoon. In Kathpal mines of both the Orissa Mining Corporation (OMC) and the Ferro Alloy Corporation (FACOR) the ores are found to be lumpy in character and the reason for the absence of hexavalent chromium in water may be due to minimal chemical reaction of lumpy ore with underground water during mining. In addition, minimal chemical oxidation of lumpy ore occurs naturally to form hexavalent chromium.

Table 4. Sukinda Belt Mine Discharge Water

Sl. No.	Name of the Mines	Parameters			
		Pre-Monsoon		Monsoon	
		Cr(VI)	Cr(T)	Cr(VI)	Cr(T)
1.	Kamarda (B. C. Moahanty Mine)	0.15	0.46	0.26	0.82
2.	Tailangi (IDC)	0.14	0.28	0.25	0.46
3.	Saruabil (Mishrilal Jain)	0.17	0.28	0.32	0.42
4.	Ostapal (FACOR)	0.40	0.58	0.65	0.85
5.	Sukrangi (OMC)	0.05	0.11	0.08	0.12
6.	Kaliapani (OMC)	0.19	0.25	0.25	0.40
7.	South Kaliapani (OMC)	0.20	0.49	0.36	0.62
	Quarry (F)				
	Quarry (D)	0.50	0.59	0.60	0.85
8.	TISCO (Bhimtanagar)	2.62	2.65	3.2	3.21
	Quarry 10				
	Quarry 13	0.19	0.24	0.29	0.38
	Quarry 2	0.30	0.57	0.36	0.92
	Quarry 5	3.2	3.25	4.6	5.25
	(Not active quarry)				
9.	Kalrangi (OMC)	0.02	0.11	0.05	0.13
10.	Kathpal (OMC)	ND	0.07	ND	0.2
11.	Kathpal (FACOR)				
	Jungle Pit	ND	0.06	ND	0.09
	Maheswari Pit	ND	0.06	0.02	0.12

Note: ND = not detected. All values are in mg/L.

Table 5. Boula-Nuasahi Belt Mine Discharge Water

Sl. No.	Name of the Mines	Parameters			
		Pre-Monsoon		Monsoon	
		Cr(VI)	Cr(T)	Cr(VI)	Cr(T)
1.	FACOR Chromite Mine	ND	0.087	ND	0.16
2.	IMFA Chromite Mine	ND	0.082	ND	0.12
3.	ICCL, Chromite Mine	ND	0.083	ND	0.15
4.	Bangur Chromite Mine (OMC)	ND	0.86	ND	0.16

Note: ND = Not detected. All values are in mg/L.

Mine discharge water from all other mines shows the hexavalent chromium in the range between 0.02-4.6 mg/L during premonsoon and monsoon. However, the mine discharge water of each individual mine shows minor increase of hexavalent chromium concentration during monsoon period. Total chromium ranges between 0.06-2.65 mg/L during premonsoon and between 0.09-5.25 mg/L during monsoon. In this area from Kamarda Chromite Mine up to Kalrangi Chromite Mines the ores are mostly friable. There may be a significant amount of natural chemical oxidation and formation of hexavalent chromium.

In Boula-Nuasahi area the character of the ore is also lumpy. A very negligible quantity of chrome ore fines are found. This may be the reason why hexavalent chromium was not detected. Total chromium has been found to be the range of 0.082-0.86 mg/L during premonsoon and 0.12-0.16 mg/L during monsoon.

Water samples were collected once from different chrome ore benificiation plants, industrial waste water and ground water of surrounding areas of the industry. Samples were analyzed and the data are presented in Tables 6, 7, 8, and 9.

In the case of Ferro Alloy Plant/Charge Chrome plant the Charge Chrome/ Ferrochrome are produced by the reduction of chromite in an electrical arc furnace. No water is used in the process except for furnace cooling which is generally recirculated. In FACOR, Randia, Bhadrak, the slag contains some metal in it, therefore it is recovered by spraying water into the slag (while still hot) in the metal recovery plant. This water is discharged and does not contain hexavalent Chromium since the slags are stable and contain chromium in Cr_2O_3 form.

Hexavalent Chromium is found in chrome ore benificiation plant due to handling of large ore fines. During the process of benificiation the gangue materials of chrome ore fines are separated out so as to increase the grade of ore and these gangue or undesired materials are removed in the form of a slurry which is taken to the slime pond/tailing pond disposal area. This water contains

Table 6. Chrome Ore Benification Plant (COB Plant) Tailing Disposal Pond

Sl. No.	Name of COB Plant	Parameters	
		Cr(VI)	Cr(T)
1.	TISCO, Sukinda Mines	3.8	4.25
2.	FACOR, Boula Mines	0.006	0.015

Note: All values are in mg/L.

Table 7. Industrial Waste Water

Sl. No.	Name of the Industries	Source of Waste Water	Parameters	
			Cr(VI)	Cr(T)
1.	ICCL, Chowdwar	Slag & Metal Quenching	ND	ND
2.	FACOR, Randia, Bhadrak	Metal recovery plant	ND	ND
3.	Ferro Chrome Plant, Jajpur Road, IDCOL	Slag & Metal Quenching	ND	ND
4.	Ferro Alloys Plant, TISCO, Bamnipal	Slag & Metal Quenching	ND	0.118
5.	Krebs and Cie, Kalma	Gland Lekage, Cooling water, Washings	506.8	750
6.	ORICHEM, Talcher	Gland Lekage, Cooling water, Washings	750.4	844.5

Note: ND = Not detected. All values are in mg/L.

Table 8. Ground Water/Pond Water of Surrounding Places of Orichem

Sl. No.	Name of Sampling Points	Distance from the Industry	Parameters	
			Cr(VI)	Cr(T)
1.	Pond water near Tentulei village	Within 2 Km	1.25	1.26
2.	Tube well water near Tentulei village	Within 2 Km	ND	0.123
3.	Dug well of inside Tentulei village	Within 2 Km	ND	0.214
4.	Tube well water of Tentulei village	Within 2 Km	ND	0.034
5.	Tube well water of village Balaram Prasad	Within 2 Km	ND	0.049

Note: ND = Not detected. All values are in mg/L.

Table 9. Ground Water/Pond Water of Surrounding Places of Krebs and Cie

Sl. No.	Name of Sampling Points	Distance from the Industry	Parameters	
			Cr(VI)	Cr(T)
1.	Nirka pond at Kalma	Within 2 Km	ND	ND
2.	Kalma UP School Well	Within 2 Km	ND	ND
3.	Well water of Kalma near N.H – 5	Within 2 Km	0.3	0.67

Note: ND = Not detected. All values are in mg/L.

hexavalent chromium and which percolates down and mix with groundwater. In addition, overflow from slime pond/tailing pond is discharged to land which ultimately flows to a nearby stream. As seen from Table 6 the hexavalent chromium in the wastewater of COB plant of TISCO is 3.8 mg/L whereas wastewater of COB plant of FACOR contains 0.006 mg/L. Total chromium is in the range of 0.015-4.25 mg/L. In chrome salt manufacturing units waste water containing hexavalent chromium is a common problem. The liquid effluent is generally recirculated and excess water is discharged outside which contains hexavalent chromium in the range between 506.8-750.4 mg/L and chromium (Total) between 750-844.5 mg/L.

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