

## Myth of Chromium Pollution from Chromite Mines with reference to Sukinda (How Green is the Sukinda Valley?)

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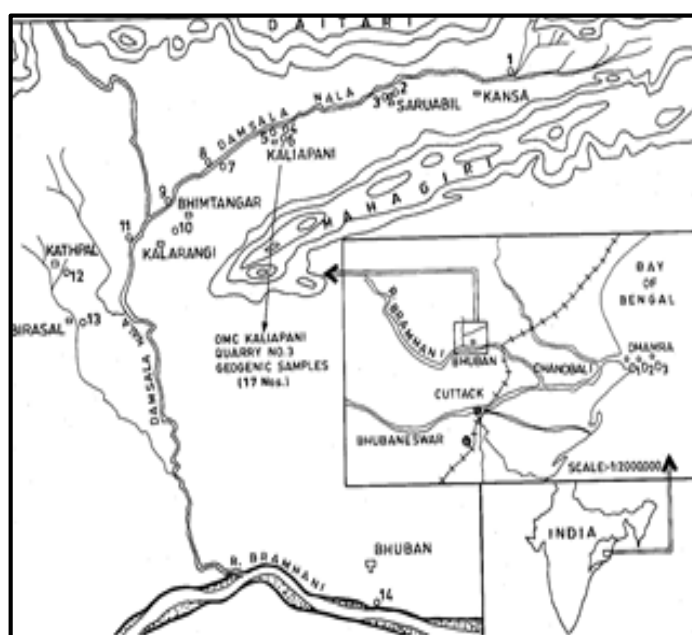
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**Abstract:** Large reserve of chromites and consequent mining activities has aroused fear of hexavalent chromium pollution in Sukinda valley in Orissa. Orthodox Geochemists deny chromium pollution around chromite mines because the mineral is refractory, extremely resistant to chemical weathering and the rogue element can only be mobilized into the environment either in industrial alkali fusion or to a limited extent under extreme Eh-pH environment. The later condition can be a possibility in deuteric alteration around chromite grains of podiform deposits during syn-kinematic serpentinization. However, the barrier to the natural mobilization of chromium from chromites and intracellular penetration of the rogue element into human tissue is prevented by certain biochemical mechanisms intrinsic to the element. The phobia of hexavalent chromium pollution has led to some stakeholders of mineral exploitation for the effluent treatment of mine face quarry waters. The present study attempts to look into the nature and extent of Cr- contamination of the waters of the Damsala stream flowing past the mining belt of Sukinda. A parallel study on effluent discharge from a chrome-chemical factory in Mumbai, which uses Sukinda chromites as raw material, shows large-scale dechromification of the effluent water along the discharge channel consequent to its passage through sprawling cattle shed in North Mumbai. The paper proposes the practice of a similar organic occupation in the mining belt to herald an identical mechanism of dechromification in Sukinda valley.

**Keywords:** Chromite, Pollution, Effluent study.

### Prologue

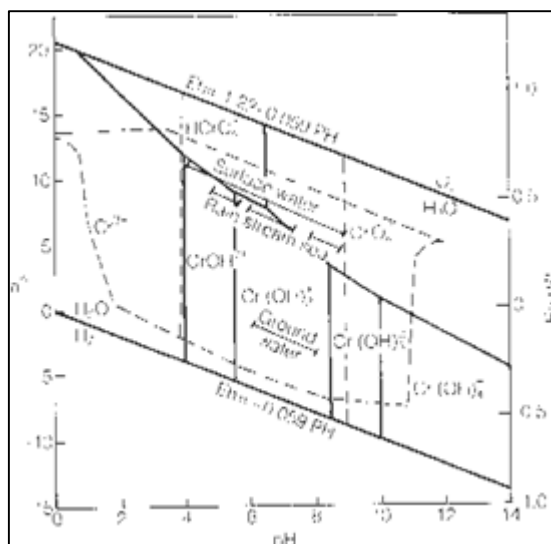
Of late, Sukinda valley in Orissa, India, is in limelight for its large chromites resource, mining, and mining related activities (Fig. 1). No doubt, pollution arising out of mining and mining related activities has reached to an extreme in the valley, Cr pollution in the region, because of the mere presence of a large chromite resource, is a matter of debate. Colored quarry waters, polarized scientific investigations, and media-hyped epidemiographic survey have blown up the issue out of proportion. Consistent and reliable analysis of Cr in ppb (parts per billion) level needs a dedicated laboratory and conventional Scientists are known to be biased. The observed color of the quarry water may likely be due to dissolved Fe and Mg chemicals which mimicry the yellowish tinge of Cr chemicals in a natural alkaline medium. Nasal septum perforation, a typical sign of Cr-toxicity is not reported from the region. Other indications like skin cancer can arise from entirely different routes. Nobody has reported Sidorosis or manganosis from the nearby Iron and Manganese Belts of Odisha. It is normal that when Covid is on the corner every sneeze is looked upon as a likely infection of the disease and with GHG shooting in the atmosphere, every hot summer, missing winter or a cyclone is considered to be an indicator of Global Warming.



**Fig. 1.** Map showing Chromite Mines in Sukinda Valley (Sample map: 1: 0.25 mln.).

### Discussion

The media hype of Cr- Toxicity is not an exception. Cr -Toxicity arises by the mobilization of Cr into the human environment, by its bioavailability and ingestion into the human metabolic system. Cr in a chromite deposit is not only bioavailable but also locked in the immobile state in a close-packed inverted Spinel structure. Every Chemist who analyses Chromites knows that even the strongest acid cannot dissolve the mineral. The only way to break the mineral structure is by severe alkali fusion at a high temperature which converts the Trivalent Cr to a Hexavalent state as done in chrome chemical manufacture. Cr can also be mobilized into the aqueous environment in strong chromic acids used in Tannery and electroplating baths and to some extent pumped into the flue gas emission of coal-based power plants. No such extreme conditions of high temperature and acidity can be expected in a chromite deposit or chromite mining. In other words, mobilization of Cr into the environment can take place only by industrial processing of Chromites and not by mere digging or mining of the mineral. No doubt, conventional Geoscientists emphatically deny Cr pollution around chromite mines. This of course is only partially true. When one looks into the stability fields of various Cr Species in Eh-pH diagram, Cr-6 has a small overlap on the regime of Natural water (Fig. 2). It means it is possible to have a restricted amount of Cr-6 in a natural environment at higher Eh-Ph conditions even in normal temperature and pressure. Leaching experiments carried out on chromite samples of Sukinda showed maximum leaching of Cr at alkaline pH, intermediate at acidic pH, and minimum leaching at the near normal environment. There are two types of chromite deposits, the Layered and the Alpine, either of them formed by differentiation from a dry ultramafic magma. Dry ultramafic magma with chromite bands when intrude into soft sediments of the mobile belt develops a positive vapor pressure gradient towards the intruding body, sucks in water vapor that produces serpentinization and syn-kinematic deformations in chromite layers. Observed under a microscope, deformation extends well into the mineral grains (Fig.3). Abrasion pH of olivine, pyroxene and serpentine is known to be highly alkaline. Oxidation and deuteric alteration of such chromite deposits develop pore fluid of high Eh- pH that could transform a part of the Cr-3 to a hexavalent state. That means Alpine chromite deposit in tropical regions is likely to pose environmental pollution during mining. The state of the art in Sukinda chromite deposits ought to be examined in this context.

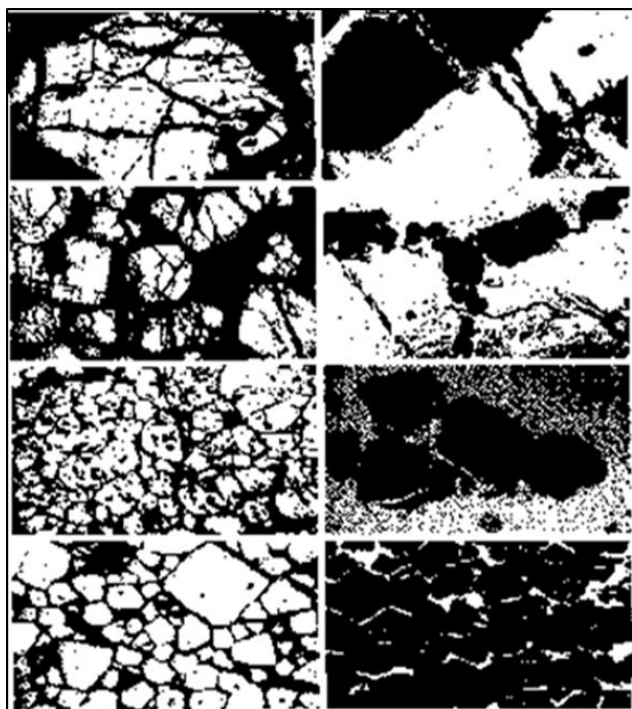


**Fig. 2.** Dissolved Chromium Species in System Cr + Water + O<sub>2</sub> at 250 C and 1 atm. (Baes and Mesmer, 1977; Hem, 1977).

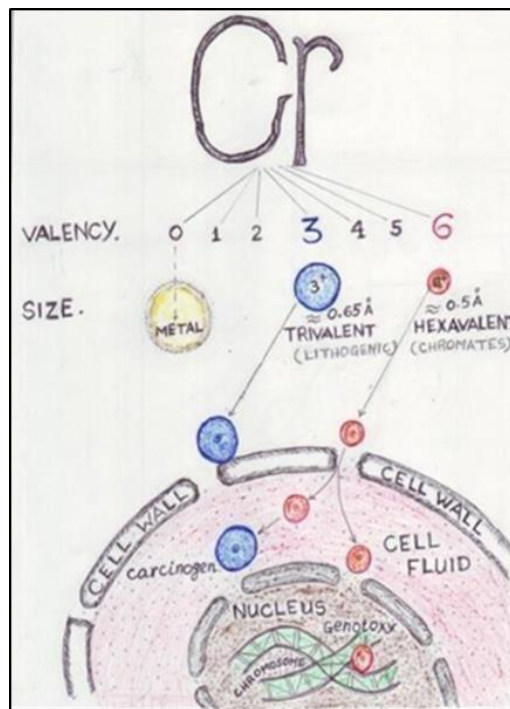
It is not just mobility and bioavailability; chromium must find a way into the human tissue to produce toxicity. Chromium is known to have 7 valence states, two of which are Cr-3 and Cr-6 are common in Nature. The most common and least mobile one with 3 of the outer electrons stripped out has a cationic dia. of about 0.65 Angstrom. With further removal of 3 more outer electrons, it attains a size of 0.5 Angstrom in Cr-6. The average pore diameter of cell-walls being of the order of 0.52 Angstrom, only Cr-6 can penetrate the cell and rest, even though ingested is easily expelled through urine or cuticular exudation. The reducing cellular fluid prevents the fugitive Cr-6 from further entry

into the nucleus by reverting it to larger Cr-3, failing which the Cr-6 enters the nucleus, produces DNA aberration and genotoxicity. The entrapped Cr-3 inside the cell or nucleus cannot be expelled out. Thus it is the entrapped Cr-3 that is responsible for all the Cr- related mutagenicity and not Cr-6 which is widely believed to be the toxic ion just because of its mobility and reduced size (Fig. 4).

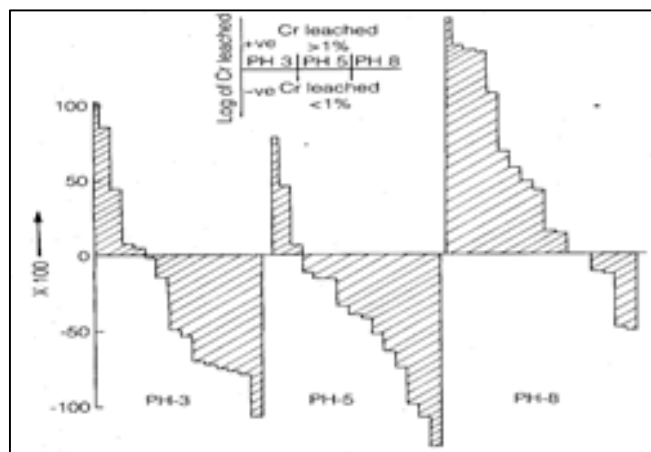
The fact that chromite deposits with immobile Cr-3, under a tropical Alpine environment can generate and release mobile Cr-6, led to a study of the Sukinda deposits for possible environmental pollution. To begin with, in chromite samples from Sukinda when subjected to leaching studies, the amount of Cr leached was found to be maximum at pH 8, intermediate at pH 3 and minimum at pH (Fig 5). Water samples from mine floors showed large Cr-6 concentration, as high as 1000 ppb (parts per billion), but samples along the Damsala stream draining the mine area showed erratic values but at lower concentrations due to (a) Dilution of the quarry discharges along its course and (b)Reduction conversion by organic materials, as the stream passes through dense vegetation. Almost ND (non-detectable) level of Cr in some of the village wells is due to the percolation of groundwater through laterite whose principal constituent goethite is a sponge or scavenger for Cr ions.



**Fig. 3.** Deformation fractures in Chromite grains seen under the microscope under Reflected (Left) and Transmitted (Right) lights.



**Fig. 4.** Entry of Chromium ion into Cell – A conceptual Model.



**Fig. 5.** Leaching results of Sukinda mine samples at pH 8, 3, and 5 (In microgram/gram).

Surface incrustation over detrital grains collected along Damsala stream was leached and analyzed for Cr, Al, Fe, and Mn. The incrustation is presumed to have precipitated as hydrolyzates from stream water, was confirmed by a positive relationship of Cr-Mn-Al. The Cr content of the leachate, 0 to 12 ppm, ought to have come from stream water by reduction conversion of Cr-6 received from mine discharge. The overall importance of leaching experiments on mine samples, analyses of natural waters and incrustation leachates clearly show that Cr, even if it is released from the chromite mines is prevented to travel far in the dissolved state because (a) The near-normal or slightly acidic nature of the surface and groundwater, (b) Reducing the environment encountered in some sections of the stream and (c) Presence of strongly absorbent goethite in the region. Detection of a high level of Cr in mine waters has led to some sort of chemical treatment of the mine discharges to mitigate Cr pollution. Effluent treatment is more effective in the point source of pollution where the contaminated stuff is collected for treatment. But when it comes to the non-point source of pollution like the sprawling mines and mineral deposits, remediation by effluent treatment is a technological hype, a marketing gimmick of process technology or “a placebo for environmental activists”. On the other hand, it may lead to the unwanted addition of chemicals to the discharge water.

### **Epilogue**

In the background of possible Cr pollution in the Sukinda region, the dechromification of mine water by chemical treatment ought to be supplemented by a wider approach to cover the entire mining belt for mitigation of a non-point source of pollution. A research project undertaken at IIT-Bombay to monitor Cr in the effluent discharge channel of a chrome chemical factory that uses Sukinda chromites discovered that when the open effluent channel passes through cattle sheds and slum areas, the channel water is extensively dechromified because of reduction precipitation of the dissolved chromate ions. It is felt that development of cattle sheds (Dairy practices), animal husbandry (Hatchery, Piggery), and allied organic trades (Fruiticulture, Floricultures, food canning, etc.) around the quarries and dumps undertaken by mine workers as a supplementary vocation or by corporate sectors in commercial scales, will not only mitigate the basic problem of Cr -pollution but also usher a parallel socio-economic development in Sukinda valley. An integrated approach of mineral excavation, and organic practices stated above for a balanced socio-economic development would counteract the negative impact of monotrack mineral excavation which has led to the spectre of Cr pollution and social upheaval in the Sukinda valley.

### **Acknowledgments**

The paper is a synoptic presentation of the Ph.D. work of G. Godgul (1994) under the supervision of the author.

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### **Appendix**

Consequent to the Reviewer's suggestion the following statements are appended to the Paper.

Sukinda chromite resources came to the limelight during the nineteen-fifties. Earlier studies by Geoscientists like K.L.Chakroborty of Jadavpur University (1965), Groups of Scientists of RRL, Bhubaneswar, led by R.K.Sahoo and Geologists of GSI, Bhubaneswar Circle, etc. emphasized on Geology, Mineralogy and Mining related issues of the deposits. By the mid-eighties, with Environment coming to the central stage of earth resources exploitation, several other Scientists and allied Technologists jumped into the problem of hexavalent chromium contamination of water and soil of the region consequent upon the large-scale mining of chromites in Sukinda valley. A select few of these studies are:

- Analytical Techniques and Geogenic Pollution of Chromium in Sukinda and dispersion of the rouge element around a chrome chemical factory, using Sukinda Chromites in Mumbai (A Doctoral study by Geeta Godgul . Thesis submitted to IIT-Bombay-1994).
- The Tata Iron & Steel Co. which virtually discovered the deposit in Sukinda, established an Effluent Treatment Plant at the quarry face using Ferrous sulphate Reductant and later by use of a natural reagent Terminalia Chebula (locally known as Harida) for removal of Cr-6 from Chromite concentrates ( Kapure, G & Mohan Rao,2008).
- Alok Prasad Das with Susmita Mishra (2010) reported the Biodegradation of metallic carcinogen Cr- 6 by an indigenously isolated bacterial strain of chromite mine soil samples of Sukinda. Later Sikha Singh (2011) carried out an assessment of Occupational Hazards for workers of chromite mines and associated metallurgical processes. Here, the mechanism of chromium carcinogenicity and intracellular toxicity leading to cell cycle arrest is more vividly presented as compared to that reported in the present paper by the author.
- Himadri Bhusan Sahoo of GSI, Karnataka Circle, presented an overview of the Geology, Mining, and Environment issues of Sukinda Chromites in relation to the economy and ecology of the region.
- Various stakeholders of the mineral property presently working in Sukinda valley, such as the TATAS, OMC, FACOR, IMFA, IDCOL, and others are seized with the issue of hexavalent chromium contamination in the region and down the Damsala river and the Directorate of Mines & Geology, Odissa, continues to have a watch over the environmental problem of chromium contamination. The twin volumes of Indian Bureau Mines, the Monograph on Chromites (2013) and the Mineral Year Book (2019) give a detailed account of the chromite deposits of Sukinda including the Environmental Impacts consequent upon the mining of the mineral deposits in Sukinda valley.

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