

PROTON INDUCED X-RAY ANALYSIS OF SOIL AND WATER SAMPLES FROM CHROMITE MINE ENVIRONMENT FOR DETERMINATION OF TOXIC METAL ION CONTAMINATION

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Soil and water samples collected from chromite mine environment were analyzed by proton induced X-ray emission (PIXE) for determination of toxic metal ion concentrations. The soil samples were collected from an active mine quarry, overburden dumps, fallow, and cultivated lands adjacent to the mines. The water samples were collected from the mine quarry, natural stream, and ground water in the mining area. Different elements such as Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, and Zr were detected both in soil and water samples. The concentrations of Fe, Cr, and Mn in the samples were relatively high as compared to other elements. The concentrations of Cr in the soil and water samples collected from the chromite mine environment were found in the ranges of 792 to 33705 mg/kg and 4 to 308 µg/L, respectively. The concentration of all elements in the soil samples collected from the active mining sites, as well as from fallow and cultivated lands, exceeded their permissible limits. However, the concentration of Cr in the water samples of the mine quarry treated with ferrous alums, the Damsala Nala river upstream, and ground water outside the mining area was found within the permissible range.

Keywords: hexavalent chromium, metal pollution, proton induced X-ray emission, soil and water of mining area.

АНАЛИЗ ОБРАЗЦОВ ПОЧВЫ И ВОДЫ ВБЛИЗИ ХРОМИТОВЫХ ШАХТ НА СОДЕРЖАНИЕ ТОКСИЧНЫХ МЕТАЛЛОВ С ПОМОЩЬЮ ПРОТОННО-ИНДУЦИРОВАННОГО РЕНТГЕНОВСКОГО ИЗЛУЧЕНИЯ

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УДК 543.422.8

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(Поступила 10 января 2017)

С помощью протонно-индуцированного рентгеновского излучения (PIXE) проведено определение концентрации ионов токсичных металлов в образцах почвы и воды, собранных вблизи хромитовых шахт. Пробы почвы взяты из действующего карьера и прилегающих к шахтам отвалов, залежей и возделываемых земель. Пробы воды получены из карьера, естественного потока и грунтовых вод в районе добычи. В образцах почвы и воды обнаружены различные элементы, в том числе Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb и Zr. Концентрация Fe, Cr, Mn высокая по сравнению с другими элементами. В образцах почвы и воды, собранных вблизи хромитовых шахт, концентрации Cr 792–33705 мг/кг и 4–308 мкг/л. Концентрация всех элементов в пробах почвы, собранных на участках активной добы-

чи, а также на залежах и обрабатываемых землях, превысила допустимые пределы. Однако концентрация Cr в пробах обработанной железными квасцами воды из карьера шахты, взятых вверху по течению реки Дамсала-Нала и грунтовых вод за пределами района добычи, находилась в допустимых пределах.

Ключевые слова: шестивалентный хром, загрязнение металлами, протонно-индуцированное рентгеновское излучение, почва и вода из района добычи полезных ископаемых.

Introduction. Metal contamination of soil and water in mining and industrial areas is a serious environmental problem, contributed mainly by mining and industrial activities. Mining operations such as excavation of ore and minerals and disposal of overburden soils provide sources of metal contamination in and around mining environment [1]. Occurrence of toxic metal ions in environment is detrimental to all forms of living organisms. Most of the metals are known to be cytotoxic, mutagenic, and carcinogenic to human and living organisms in relatively low concentrations. Metal pollution has become a serious concern in many parts of the world and warrants immediate attention for their detoxification through appropriate bioremediation technology. Sukinda valley, spreading over 420 km² in the Jajpur District of Odisha (India), is the richest field of chromiferous mass of India accounting for 97% of chromite ore deposits of the country. Several chromite mines are operational in this region practiced through opencast mining system. Extensive mining of chromite ore for the last several years in the Sukinda region has resulted in contamination of soil and water by chromium and other metal ions [2]. Besides, huge deposition of overburden soils causes leaching problems in nearby mining areas. The toxicity of metal ions on the environments mainly involves many different species of the same metal, which can vary greatly in toxicity [3]. Since metals are nondegradable and tend to accumulate in soil, they pose a serious ecological risk due to the contamination and leaching problems [4]. Thus, the metal pollution in the soil ultimately affects the flora, fauna, and microbiota of this region.

In the present study the soil and water samples from a chromite mine and its adjacent areas were analyzed by proton-induced X-ray emission (PIXE) in order to determine the concentration of different metal ions. PIXE is a powerful, nondestructive ion beam analysis technique routinely used to determine multi-elemental concentrations at parts per million (ppm) and parts per billion (ppb) levels in different sample types [5]. The intensities of emitted X-rays for each element denote the concentration of these elements in the sample. The availability of low-energy accelerators has made PIXE an attractive alternative to other conventional multi-element analytical methods and it has been used for analysis of environmental, geological, archeological, and biological samples [6–10].

Materials and methods. Seven soil samples (CS-1–CS-7) were collected from the chromite mine environment of Sukinda, Odisha (Fig. 1). Out of seven samples, two samples (CS-1 and CS-2) were collected from an active mine quarry, two samples (CS-3 and CS-4) from overburden dumps, one sample (CS-5) from a fallow land near the mine area, one (CS-6) from a forest soil nearby the mining area, and one sample (CS-7) from a cultivated land soil. Random soil samples were collected in triplicate from each of the sampling sites, placed in sterile polythene bags, and brought to the laboratory in sealed condition following the methods of Zobell [11].

Seven water samples (CW-1–CW-7) were collected from the mine and its adjacent areas. Out of these seven samples, CW-1 and CW-2 were collected from a water discharge point from the mining quarry being treated with ferrous alums, while CW-3 and CW-4 were collected from the active mine quarry. The water samples CW-5 and CW-6 were collected from downstream and upstream points of Damsala Nala, and CW-7 was collected from ground water outside the mining area.

The metal ions of the soil and water samples collected from the chromite mine area were analyzed by proton induced X-ray emission (PIXE). The soil samples were oven-dried at 60°C and then powdered using a mortar and pestle. The powdered samples (150 mg) were mixed with extra pure graphite (70:30), and then pellets (1 mm thick and 10 mm diameter) were made using a tabletop pelletizer (pressure 100–110 kg/cm²). Pellets of soil standards from the National Institute of Standards and Technology (NIST, USA) were also prepared following the same technique. Water samples were prepared by the method described by Aprile-si et al. [8]; 50 mL of the water sample was taken, and 200 µL of 1000 ppm palladium, as PdCl₂, was added in to it, which served as an internal standard and also as a co-precipitant. The solution was maintained at pH 9 by using an ammonia solution. Saturated sodium diethyldithiocarbamate, (NaDDTC, C₅H₁₀NaS₂·H₂O) (2.5 mL) was added to the solution, which resulted in precipitation of the metals as their respective carbamates. The precipitate was then filtered out by vacuum filtration (millipore vacuum filtration unit) on 25 mm diameter nucleopore membranes of 0.4 µm pore size. A thin uniform layer was formed on the membrane. This mem-

brane was used as the target for the PIXE measurements. Using only the chemicals mentioned we also prepared a sample to be used as a positive control (blank) along with the NIST water standard [SRM.1643d]) following the same procedure [8]. The soil and water samples collected from each sampling site were prepared in triplicate for the analysis. Apart from running triplicates, each sample was bombarded at three points to account for sample inhomogeneity, if any.

The targets so prepared with the above method were mounted on a scattering chamber maintained at a pressure of 10^{-6} Torr, and the targets were exposed to a 2 mm diameter collimated beam of 3 MeV protons from a 3 MV Pelletron tandem accelerator at the Institute of Physics, Bhubaneswar, India. The beam current of the accelerator was controlled between 1.5 and 3.0 nA to maintain a count rate of 400–600 cps during collection. The multiple target ladder of the scattering chamber on which the targets were mounted was oriented at 45° to the beam axis. During analysis, the characteristic X-rays thus produced from the target were detected by an EG & G Ortec Si(Li) detector (active area: 30 mm², Be window thickness: 12.7 μ m and resolution: 145 eV Mn X-ray) placed at 90° to the beam axis. The instrument was so adjusted that the X-rays were allowed to fall on the detector through a 25 μ m Mylar window fixed to the detector port of the scattering chamber. The detector had a resolution of 145 eV at 5.9 keV Mn X-rays and the elements range was from Al to U (hundreds of eV to 50 keV). Finally data were collected in a PC based MCA in the 2K channel mode for a given preset live time. The system was calibrated for the identification of the X-ray peaks using a ²⁴¹Am radioisotope standard X-ray source.

Statistical analysis of the data from soil and water samples was carried out for comparison using Generalized Linear Model, ANOVA procedure and Duncan's multiple range tests [12].

Results and discussion. *Metal analysis of soil samples.* The PIXE-analyzed metal contents of the soil samples collected from the Sukinda chromite mine and its adjacent area are presented in Table 1. Figure 1a shows the PIXE spectrum of the soil samples collected from the chromite mine, Sukinda. The elements were detected and identified by their characteristic *K* and *L* X-ray lines. The spectra were analyzed for quantitative elemental estimates using a GUPIX 96 software [13]. Samples were analyzed in triplicate to check the reproducibility of the results. The metal analysis results for the soil samples showed very high metal concentrations in the order of Fe>Cr>Mn>Ni>Ti>Zr. The results indicated a higher concentration of the metal ions of the active mine quarry and its adjacent areas, which exceeded the maximum permissible levels. The World Health Organization (WHO) permissible limits for these metals in soil are as shown in Table 2. The concentration of Fe and total Cr in the active mine quarry soil samples of CS-1 was found to have the highest values of 194939±8209 and 33705±4665 mg/kg, respectively. The overburden soils CS-3 and CS-4 also exhibited relatively higher Cr concentrations, i.e., 12718±2193 and 24759±700 mg/kg. On the other hand, the soils collected from the mine adjacent areas such as fallow land (CS-5), forest soil (CS-6), and cultivated land (CS-7) exhibited comparatively lower concentration of Cr such as 1964±422, 10111±3530, and 792±21 mg/kg of Cr, respectively. The soil analysis from Boula-Nuasahi chromite mine of Odisha carried out by Dhal et al. [14] revealed that chromium was the only principal metal that was found in the range of 0.27 to 19.3 % in the soil samples. Another study carried out by Kien et al. [15] has reported a very high

TABLE 1. Metal Concentration (mg/kg) of the Soil Samples from the Sukinda Chromite Mine and Its Adjacent Areas Collected during 2011 as Estimated by the PIXE Analysis

Metal	Standard	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Ti	3948.5	–	–	–	–	5447.0± 115.0 ^b	4410.4± 183.2 ^b	5583.0± 596.0 ^b
Cr	99.1	33705.0± 4665.0 ^e	23048.0± 1254.0 ^d	12718.0± 2193.0 ^c	24759.0 ±700.0 ^d	1964.0± 422.0 ^{ab}	10111.0± 3530.0 ^{bc}	792.0± 21.0 ^a
Mg	651.8	2790.0± 103.3 ^c	2924.0± 116.0 ^c	3458.0± 378.0 ^{cd}	3695.0± 228.0 ^d	1276.0± 158.0 ^{ab}	1442.0± 83.0 ^b	649.0± 87.0 ^a
Fe	28573.8	194939.0± 8209.0 ^c	161215.0± 4944.0 ^c	311997.0± 44316.0 ^d	185681.0± 4509.0 ^c	33238.0± 5253.0 ^a	92415.0± 1424.0 ^b	25799.0± 3612.0 ^a
Ni	35.9	2376.0± 126.0 ^b	3411.0± 114.0 ^c	1853.0± 371.0 ^b	2324.0± 105.0 ^b	–	552.0±31.0 ^a	–
Zr	111.1	–	–	–	–	–	–	643.0±20.0 ^b

“–” Not detected. The data represent mean ± S.E of replicates (*n* = 3). Means bearing different superscripts in a row differ significantly (*P* < 0.05) by Duncan's multiple range test.

TABLE 2. Permissible Limits of Some Metal Ions for Soil According to World Health Organization [15]

Metals ions	Maximum permissible limit, mg/kg
Titanium	–
Chromium	0.05
Manganese	12
Iron	0.3
Nickel	6.5
Zirconium	–

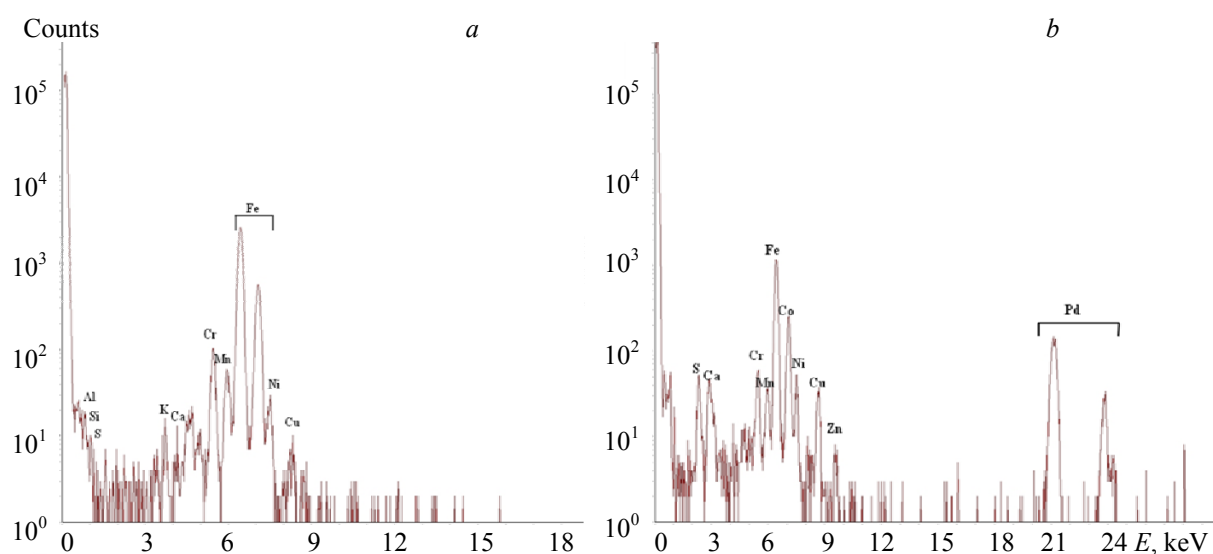


Fig. 1. A typical PIXE spectrum of the soil (a) and water (b) sample of Sukinda Chromite mine, Odisha.

concentration of Cr to the tune of 5750 mg/kg from the soil samples collected around a chromite mine in Vietnam. Apart from the Cr, Ni was found in the soil samples collected from the active mine quarry and its adjacent area in Sukinda as another most toxic metal ion. The concentration of Ni was found in the range between 552 ± 31 and 3411 ± 114 mg/kg. The PIXE study carried out by Copaja et al. [16] reported relatively higher concentrations of different metal ions such as Cu, Zn, Al, Fe, Mn, and Pb in the river basin sediments in Chile attributed to mining activity in the vicinity of rivers.

As evident from the present investigation, chromite mine soils contain generally high concentration of different types of metals as contaminants, and the active mining sites is more polluted with metals in comparison to the mine adjacent sites. The level of metal toxicity decreased with increase in the distances from the active mining sites. Most of the metal ions are predominantly found as oxyanion species. Different types of metal pollutants, when incorporated into soils, lead to changes in the chemical speciation [17]. The toxicity of various metals depends to a large extent on its speciation and also the metal bioavailability [17].

Metal analysis of water samples. Data in Table 3 represents metal contents of the water samples collected from the active mine and its adjacent areas from Sukinda as analyzed by PIXE. A typical PIXE spectrum of the water sample analyzed is shown in Fig. 2b. The concentrations of the metal ions found in water samples collected from the active mine quarry and its adjacent area are in the order of $\text{Fe} > \text{Mn} > \text{Cr} > \text{Co} > \text{Ni} > \text{Zn} > \text{Cu}$. The concentration of Fe in the water samples ranged between 124 ± 1 to 17373 ± 2 $\mu\text{g/L}$. The total Cr contents of the water samples collected from the active mine quarry, CW-3 and CW-4, were 288 ± 2 and 308 ± 1 $\mu\text{g/L}$, respectively, whereas the total Cr contents of the natural stream of Damsala Nala was found to be in the range between 24.7 ± 1.3 to 73.0 ± 0.9 $\mu\text{g/L}$. Most of the metal contents of CW-1 (discharge point from the mining quarry being treated with ferrous allums), CW-6 (upstream of Damsala Nala), and CW-7 (ground water outside from the mining area) were found to be within the permissible range. The World Health Organization permissible limits for some metal ions in water are presented in Table 4 [18]. It is anticipated that elevated levels of heavy metals found in and around the chromite mine

water due to discharge and dispersion of heavy metals into water sources may eventually lead to health risks [19]. Dhakate et al. [20] have reported that the levels of most of the metals in the water sample collected from the groundwater are within the permissible limit for drinking water except for slightly higher concentration of Cr(VI) found in the few water samples of the mine seepage and Damasal Nala of Sukinda chromite mine. Earlier studies on the hexavalent chromium content of the seepage water samples collected from different locations of the Sukinda valley were found to be in the range of 0.19 to 3.12 $\mu\text{g}/\text{mL}$ [21]. Oyuntsetseg et al. [22] have assessed the concentration of Mn, Cu, Ni, Zn, As, Sr, and Pb in surface soils, human hair, and potable water samples around the small-scale mining areas, Mongolia, using the PIXE technique, which is in agreement with the present investigation. This study also reported the presence of Mn, Fe, and Ni at higher concentrations than that of the WHO safe limits in drinking waters from mining areas.

TABLE 3. Metal Concentration ($\mu\text{g}/\text{L}$) Analysis of Water Samples from the Chromite Mine and Its Adjacent Area of Sukinda, Odisha

Metal	Standard (NIST)	CW-1	CW-2	CW-3	CW-4	CW-5	CW-6	CW-7
Cr	23.3	10.0 \pm 1.0 ^b	92.3 \pm 2.0 ^c	288.0 \pm 2.0 ^f	308.0 \pm 1.0 ^g	73.0 \pm 1.0 ^d	25.0 \pm 1.0 ^c	4.0 \pm 1.0 ^a
Mg	38.2	7958.0 \pm 1.0 ^g	273.0 \pm 2.0 ^b	488.0 \pm 1.0 ^e	650.0 \pm 1.0 ^f	338.4 \pm 4.0 ^c	65.3 \pm 1.0 ^a	361.5 \pm 1.0 ^d
Fe	96.1	17373.0 \pm 2.0 ^g	1492.0 \pm 3.0 ^c	5939.0 \pm 2.0 ^f	5485.0 \pm 3.0 ^e	1535.0 \pm 3.0 ^d	124.0 \pm 1.0 ^a	342.0 \pm 1.0 ^b
Co	25.9	246.0 \pm 2.0 ^d	17.0 \pm 1.0 ^b	38.0 \pm 1.0 ^c	17.5 \pm 1.0 ^b	38.0 \pm 1.0 ^c	3.5 \pm 0.0 ^a	7.0 \pm 1.0 ^a
Ni	61.5	223.0 \pm 0.5 ^e	100.0 \pm 1.0 ^c	235.0 \pm 1.0 ^f	261.5 \pm 2.0 ^g	215.3 \pm 3.0 ^d	20.3 \pm 0.5 ^b	7.0 \pm 1.0 ^a
Cu	22.3	2.0 \pm 0.0 ^a	8.0 \pm 1.0 ^c	3.0 \pm 0.0 ^{ab}	2.5 \pm 0.3 ^{ab}	4.0 \pm 0.0 ^b	2.6 \pm 0.0 ^{ab}	3.0 \pm 0.5 ^{ab}
Zn	76.9	111.0 \pm 2.0 ^c	8.0 \pm 1.0 ^a	382.0 \pm 2.0 ^e	158.0 \pm 2.0 ^d	27.0 \pm 1.0 ^b	546.1 \pm 2.0 ^f	623.0 \pm 1.0 ^g
Ld	17.2	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl

Bdl – Below detection level, the data represent mean \pm S.E of replicates ($n = 3$). Means bearing different superscripts in a row differ significantly ($P < 0.05$) by Duncan's multiple range test.

TABLE 4. Permissible Limits of Some Metal Ions for Drinking Water (WHO 1993)

Metals ions	Maximum permissible limit, $\mu\text{g}/\text{L}$
Chromium	50
Manganese	500
Iron	100
Cobalt	–
Nickel	20
Copper	2000
Zinc	15000
Lead	100

Mining of chromite ore provide an obvious source of contamination of different metals including chromium, since different metals usually occur along with chromium in the chromite mine soil and water [23]. Previous reports have stated that the heavy metal pollution of water is a significant environmental problem, and different heavy metals (Cr, Ni, Mn, Cd, Co, Fe, Pb, etc.) contaminated water coming from different mining sources have toxic effects on humans and the environment. Among the different heavy metals, nonessential metals like Cd and Pb are sometimes found in soil, water, and air and may be highly poisonous for plants, animals, and humans [24]. Similarly, Ni has been implicated as an embryotoxin and teratogen, while Cr and Hg are reported to be cytotoxic, carcinogenic, and mutagenic to animals and human beings [24]. Metals can be dissolved from mining sites through the action of acid runoff or can be washed into streams as sediments [25]. Most of the water bodies in the coal mining area of Jaintia Hills, Meghalaya, have been found to contain high concentrations of various metals. These metals can be toxic to fish and other aquatic organisms when present dissolved in high concentrations [25]. Briefly, it can be inferred that the heavy metal contamination of soil and water in adjoining areas of mines is a well-known environmental threat, and the present study around the Sukinda mines, Orissa, India clearly reflects the potential danger of these contaminants that can lead to serious consequences towards environmental peril and health risks.

Conclusion. The PIXE analysis of the chromite mine soil samples collected from Sukinda, India, shows that Cr, Fe, Mn, and Ni contents of the soil and water samples exceeded the WHO permissible limits. The amount of Cr in most of the water samples was found to be above the acceptable limit. The concentration of

Fe dominated in the both soil and water samples followed by Cr and Mn. Apart from Fe and Cr, other toxic elements like Cu and Zn were also detected in the water samples, but they were within the safety limit. The present work data reflects high levels of pollution in both soil and water due to metal contamination in the active mining areas around Sukinda mines in comparison to its adjacent areas.

Acknowledgment. Financial support from UGC-DAE, CSR, KC, Kolkata to carry out this research is thankfully acknowledged. The authors are grateful to the authorities of the College of Engineering and Technology, Bhubaneswar, Biju Patnaik University of Technology, Odisha for providing the laboratory facility to the first author.

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