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Micro Pollutants in Red Mud Waste of Aluminium Plant

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The growth of the aluminium industry in India, the process details of an aluminium plant, and the genesis of red mud during the aluminium production have been described. Chemical analysis of a number of red mud samples collected at different points in the red mud ponds, at different periods, have been carried out, and the concentrations of the micro pollutants determined to assess their probable impacts on the soils and water of the adjoining areas.

KEY WORDS: Aluminium industry, mud samples, waste sample preparation, multielement determination, atomic absorption spectrophotometry.

INTRODUCTION

In bauxite reserves, India is ranking third on the global basis, with total deposits of ~330 million tons. Again, Madhya Pradesh ranks third in all the Indian states. Indian aluminium industry is, however, only 40 years old. The production of aluminium has grown steadily

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to the present installed capacity of 0.33 million tons. According to an estimate, the minimum national demand of aluminium by the end of the century is likely to touch 1.3 million tons against the present installed capacity of 0.33 million tons.¹ Aluminium smelters in India are presently located in Alwaye (Kerala), Hirakud and Angul (Orissa), Belgaum (Karnataka), Asansol (W.B.), Renukoot (U.P.), Mettur (T.N.) and Korba (M.P.).

The present studies have been carried out at Korba (Dist. Bilaspur M.P.) where an aluminium plant of a public sector undertaking (BALCO) is located. The bauxite for this plant is supplied from mines located at Amarkantak (Dist. Shahdol M.P.) and Phutakapahar (Dist. Bilaspur M.P.). The plant has an annual capacity of producing 200,000 tons of alumina and 100,000 tons of aluminium. The main raw materials consumed per annum, in tons, in the plant are: bauxite—550,000, caustic soda—2,000, fuel coal—40,000, lime—26,000, starch—200, coal—160,000, cryolite—2,000, aluminium fluoride—2,600, sodium fluoride—600, petroleum coke—4,500 and soda ash—500. The ore received from mines is crushed to 0.1 mm size in ball mills, and then mixed with caustic alkali to form a slurry which goes to a desilicator plant where silica reacts with sodium aluminate liquor and forms sodium aluminium silicate ($3\text{Na}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) \times H_2O . The slurry is then preheated to a temperature of 120–150°C and fed into a series of digesters, where the temperature increases up to 240°C under high pressure steam. In the process, alumina from the bauxite dissolves into caustic soda liquor forming sodium aluminate. The slurry then passes through flash tank to reduce the temperature to 115–125°C. The digested slurry then flows from flash tank to dilution tanks where separation of red mud from the aluminate liquor takes place by the process of settling. The amount of red mud formed depends on the Fe_2O_3 , SiO_2 and TiO_2 contents of bauxite. Undigested fractions of coarsely ground bauxite also leaves with the red mud.

The red mud separates in the settlers and the clear solution discharges at the overflow duct of the settler tank. The overflow goes to the aluminate liquor control filtration, and the underflow passes to red mud washers. Flocculents are used to speed up the settling of the red mud. The starch contents of the flocculents promote agglomeration of red mud particles and accelerate particles settling.

One ton of bauxite ore usually produces 0.05 tons of red mud waste, and this results into the disposal of 27,500 tons of the waste

each year at the plant site. The red mud is pumped into red mud ponds through pipe lines. The micro pollutants being studied here are: Cu, Ni, Co, Pb, Zn, Mn, Cd, Sb, Bi, Cr, Ba, Sr, Li, Ag, Mo and As. According to the classification of Wood² from the stand point of environmental pollution, Cu, Co, Ni, Pb, Zn, Cd, Sb, Bi, Ag and As fall under the category of very toxic and relatively accessible metals; Ba falls under toxic but very insoluble rare metals; Sr and Li fall under the category of non critical metals. Although Mn, Cr, and Mo have not been included in this classification, significant toxicological studies of these elements have appeared in recent years. Apart from the toxic effects, the relative quantities of these elements require to be taken into account to assess their capacities of affecting the adjoining soils and water with which they establish a sort of an equilibrium.

MATERIALS AND METHOD

Sample collection

Samples were collected from the red mud ponds which are located near Biligiri Nallah at the plant site. There are two red mud ponds, and two samples of the red mud, weighing 1 kg each, were scooped out from each of the ponds. After a duration of 30 days 4 samples were again collected from the same sampling sites. Four samples of the bauxite ore were also similarly collected.

Procedure

About 20 g quantity of each sample was dried in an oven at 110°C for 5 hours. 1 g weight of each sample was treated in a Teflon digestion bomb using 10 ml acid mixture of hydrofluoric acid, hydrochloric acid and nitric acid, placing in an oven at 180°C for 30 minutes.³ Thereafter the solutions were made up to 100 ml volume in a medium of 0.1 M EDTA to suppress the interference of phosphate, carbonate, iodide, fluoride and acetate.

Method

The analysis was performed on an Atomic Absorption Spectrophotometer (Varian Model AA 575). The operating conditions of the instrument for the respective metals have been shown in Table I.

TABLE I
Operating conditions of the atomic absorption spectrophotometer

Sl. no.	Metals	Wave length (nm)	Fuel	Support	Lamp current (mA)	Flame stoichio-metry	Spectral band pass (nm)
1.	Cu	324.7	C ₂ H ₂	Air	3.5	Oxidizing	0.5
2.	Co	240.7	C ₂ H ₂	Air	7.0	Oxidizing	0.2
3.	Ni	232.0	C ₂ H ₂	Air	3.5	Oxidizing	0.2
4.	Pb	217.0	C ₂ H ₂	Air	EDL ^a	Oxidizing	1.0
5.	Zn	213.9	C ₂ H ₂	Air	5.0	Oxidizing	1.0
6.	Mn	279.5	C ₂ H ₂	Air	5.0	Oxidizing	0.2
7.	Cd	228.8	C ₂ H ₂	Air	HCL ^b	Oxidizing	0.7
8.	Sb	217.6	C ₂ H ₂	Air	10.0	Oxidizing	0.2
9.	Bi	223.1	C ₂ H ₂	Air	10.0	Oxidizing	0.2
10.	Cr	357.9	C ₂ H ₂	Air	7.0	Reducing	0.2
11.	Be	234.8	C ₂ H ₂	N ₂ O	5.0	Reducing	0.7
12.	Ba	553.6	C ₂ H ₂	N ₂ O	2.0	Reducing	0.5
13.	Sr	460.7	C ₂ H ₂	N ₂ O	10.0	Strongly Oxidizing	0.5
14.	Li	670.8	C ₂ H ₂	Air	5.0	Oxidizing	1.0
15.	Rb	780.0	C ₂ H ₂	Air	20.0	Oxidizing	0.2
16.	Ag	3,281.0	C ₂ H ₂	Air	7.0	Oxidizing	7.0
17.	Mo	313.3	C ₂ H ₂	N ₂ O	7.0	Reducing	0.5
18.	As	1,937.0	C ₂ H ₂	Air	12.0	Oxidizing	7.0

^aElectrodeless discharge lamp.

^bHallow cathode lamp of cadmium.

During the calibration, the standard solutions of the metals were suitably diluted to match the concentrations of the sample solutions within the measurement sensitivity. Bi, Co, Cu, Ni, Pb, Sb, Zn, Ag, As, Cr, Mn, Li and Cd were determined using the air-acetylene flame. Nitrous oxide-acetylene flame was used in the determination of Ba, Sr, Mo in view of the low concentration and nondissociability of the compounds of the elements.^{4,5}

The results obtained have been shown in Table II.

RESULT AND DISCUSSION

The contamination of red mud by the toxic metals have been found in the following order: Cr, Mn, Pb, Sr, Cu, Ba, Mo, Sb, Bi, Zn, Co,

TABLE II
Analysis data^a of micro pollutants in the red mud

Sr. no.	Pollutants	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Mean value	Bauxite sample ^b
1.	Cu	49	50	55	58	69	66	63	60	53.8	49
2.	Co	19	22	20	25	23	24	24	21	22.3	26
3.	Ni	28	29	24	23	29	30	28	26	25.9	21
4.	Pb	65	66	68	70	72	79	75	73	71.0	47
5.	Zn	36	37	32	33	36	38	35	34	35.1	40
6.	Mn	139	142	149	148	158	162	151	156	150.6	69
7.	Cd	2	2	2	2	2	2	2	2	2.0	Nil
8.	Sb	40	43	45	46	45	43	48	47	44.6	60
9.	Bi	40	42	38	36	40	30	32	35	37.9	10
10.	Cr	760	750	710	740	770	750	680	730	748.8	260
11.	Be	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
12.	Ba	50	48	45	47	55	57	60	62	53.0	30
13.	Sr	60	58	60	57	52	55	58	56	57.1	20
14.	Li	2	3	3	2	3	2	3	2	2.5	2
15.	Rb	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
16.	Ag	19	27	23	24	28	25	27	24	22.1	26
17.	Mo	47	46	48	49	45	44	46	48	45.7	50.5
18.	As	4	4	4	4	4	4	4	4	4.0	3

^aIn mg/kg.
^bAverage of four samples.

Ag, As, Li and Cd. Be and Rb have been found absent. These micropollutants are in addition to Si, Fe, Al, Ca, Mg, Ti, V, SO_4^{--} , CO_3^{--} , Cl^- , PO_4^{--} , Na and K which have been studied and reported earlier as macropollutants.⁶ Out of the micropollutants studied here Cr, Mn, Pb, Sr, Cu, Ba, Mo and Sb have been found to be present in significant amounts. Taking into account the hazardous effects associated with these metals, it will be relevant to examine their impacts over the adjoining soils and water which are susceptible to contamination arising from leaching of the dissolved metals.

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