INVESTIGATION OF ALUMINA DISCHARGE INTO THE RED MUD POND AT NALCO'S ALUMINA REFINERY, DAMANJODI, ORISSA, INDIA

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Abstract

Around 14% of alumina gets discharged into the red mud pond from NALCO's alumina refinery. The minerals hosting alumina in red mud have been investigated using Optical microscope, Scanning Electron Microscope (SEM), Electron Probe Micro Analyzer (EPMA) and XRD. The minerals in red mud sample, as identified through integrated techniques, are: gibbsite, boehmite, goethite, silimanite, muscovite, garnet and kaolinite besides minor hematite, sodalite and rutile. The average particle size of red mud is ~8μm except isolated grains of gibbsite, goethite and garnet which are greater than 20μm in size. The gibbsite invariably contains up to 60 mole % of boehmite. The nodular goethite contains over 30-mol % of 'Al' in its lattice and termed as alumo-goethite. Around 34% of the Al_2O_3 is present in muscovite/silimanite/garnet. Studies reveal that most of the minerals in red mud have either alumina in their lattices or are undigested aluminium silicates that do not get dissolved during alumina refining, thus a considerable amount of alumina gets discharged through these phases into the red mud.

Introduction

Around 2 tons of caustic insoluble waste residue known as 'Red Mud' is generated from NALCO aluminium refinery at Damanjodi, Koraput district, Orissa for every ton of alumina produced. Aluminium metal is extracted from aluminium oxide phases that constitute only 38 to 60% of the original bauxite ore. The rest is made up of Fe_2O_3, SiO_2, TiO_2 and many other oxide phases. After dissolution of the bauxite in caustic soda, these impurities remain in suspended form which is separated out after being washed and then pumped in a slurry to the nearby pond called the Red Mud Pond. India accounts for about 2 Million tons of red mud per year of which is more than half the quantity is generated at the NALCO refinery. This industrial waste material poses tremendous environmental and disposal problems. Reduction in the quantity of red mud is possible only through their utilization in one form or another. However, the inherent complexity of red mud poses problem in its bulk utilization. Prior to going for bulk utilization of red mud rejects from the NALCO refinery, it needs in-depth characterization. Rao et al [1] have reported the characteristics of undigested sand rejects from the NALCO refinery. Only limited attempts have been made on the characterization of red mud sludge from this refinery [2-5].

Fine particles of red mud can be characterized only through selected instrumental techniques. The present paper describes the characteristics of NALCO red mud through scanning electron microscopy and electron probe micro-analysis with a view to finding out the reason for alumina discharge into the red mud pond during the alumina refinery process.

Materials and Methods

For this study, representative red mud sludge was collected from the red mud pond of NALCO alumina refinery. After washing and oven drying, the sample was sprinkled on double sided adhesive conducting tape, placed over the sample holder and studied under SEM (JSM 35CF) equipped with WDS & EDS systems. Compositional x-ray analysis was undertaken for selected minerals.

Chemical compositions of various phases were determined by an ARL-SEMQ-II electron microprobe in the Geochemisches Institute, Universitat Gottingen, Germany, which is equipped with six spectrometer and four different analyzing crystals. The operating conditions were 15 kV accelerating voltage and 15 nA sample current. ZAF - corrected representative mineral analyses are presented in Table -1.

Morphology and Mineralogy

In the red mud sample, about 35% by weight of solids contain less than 5-micron particles and the average size is found to be around 8 micron. However, a few independent grains > 20μm size (about 10%) are also present. Due to the very fine size, some of the particles appear coagulated.

Broad mineral species present in the red mud sample were identified through XRD (Philips). As can be seen from XRD pattern illustrated in Fig.1, the red mud sample contains gibbsite, boehmite and sodalite as alumina bearing; goethite and hematite as iron bearing and rutile as titanium bearing phases. Goethite, hematite, rutile, kaolinite and mica were recognized under optical microscope.

Some of these alumina bearing minerals were subsequently analyzed under electron micro-probe. Gibbsite and goethite are observed to be dominating phases in the red mud sample. Gibbsites occur in pseudo hexagonal or prismatic habit. Goethite is either flaky or nodular; the later showing bunches of rotund units. Presence of fine grains of rutile, ilmenite, and zircon are recorded in subordinate amount. In addition, flakes of kaolinite, mica, needles of sillimanite (as litho relics) and sub-rounded grains of garnet are also noticed.

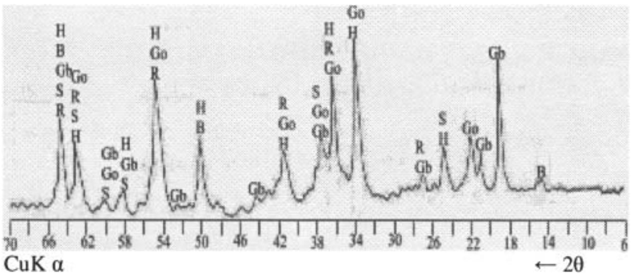

Fig.1: XRD pattern of Red-mud.
[H: Hematite, Go: Goethite, S: Sodalite, Gb: Gibbsite, R: Rutile, B: Boehmite]

Mineral Chemistry

A few selected mineral grains viz. gibbsite, goethite and kaolinite, muscovite (precursor minerals not completely replaced by alumina) from red mud were exposed under electron probe microanalyser (EPMA) to know the extent of alumina in them (Table 1-3). Most of the idiomorphic crystals appearing as gibbsite under scanning electron microscope are found to have undergone dehydroxylation containing up to 60 mole % of boehmite in solid solution (Table 1).

The nodular type of goethite contains alumina in its lattice (Fig. 2). Such alumina-rich goethite is termed as alumo-goethite by Jonas and Solymar [6]· Since goethite grains in the NALCO red mud are found to contain 30 mol % of alumina, it may be termed as alumo-goethite. 30 to 39% of Al_2O_3 are recorded in litho relict minerals like kaolinite and muscovite flakes (Table 2 & 3). Compositional maps of kaolinite, silimanite and garnet grains in red mud (Figs. 3-5) indicate that these minerals are not converted to gibbsite.

Table 1. Electron Probe Microanalysis Results of Selected Alumina-rich Grains from Red Mud

Compound,%	1	2	3	4
Al_2O_3	78.30	71.82	69.94	65.60
FeO	0.26	0.00	0.00	0.00
	0.04	0.00		
SiO_2	0.00	0.00	0.36	0.10
MgO	0.00	0.00	0.07	0.00
MnO	0.49	0.22	0.00	0.00
CaO	0.04	0.00	0.02	0.00
K_2O	0.00	0.00	0.00	0.00
Na_2O	0.00	0.00	0.00	0.04
TiO_2	--	--	0.00	0.01
AlOOH	69.44	49.90	35.65	2.35
$Al(OH)_3$	29.63	49.87	73.69	97.31
FeOOH	0.32	0.00	0.00	0.00
Other Oxides	0.93	0.23	0.66	0.34

Note: Column 1: Boehmite dominating; 2: Mixed boehmite-gibbsite; 3: Mixed gibbsite-boehmite; 4: Gibbsite dominating

Table 2. Electron Probe Microanalysis results of Kaolinite and Goethite

Compounds,%	1	2	3	4
SiO_2	45.859	43.834	0.795	0.70
Al_2O_3	39.228	38.009	0.957	18.48
FeO	0.145	0.049	85.012	52.63
MgO	0.076	0.058	--	--
MnO	0.000	0.018	--	--
TiO2	--	--	--	6.12
CaO	0.054	0.134	--	0.42
K_2O	0.025	0.033	0.013	--
Na_2O	0.203	0.064	--	--
Cr_2O_3	0.076	0.127	--	--
BaO	0.000	0.017	--	--
NiO	0.009	0.000	--	--
CaO	0.236	0.211	--	--
H_2O_{Calc}	--	--	12.20	21.44
	Based on 08 cation		Based on 1 cation	
SI	3.95	4.05	0.01	0.01
Total 1	3.95	4.05		
Al	3.98	3.90	0.015	0.30
Fe	0.01	--	0.974	0.62
Mg	0.01	0.01	--	--
Mn	--	--	--	--
Co	0.02	0.01	--	--
Total 2	4.02	3.93		
Na	--	0.01	--	--
K	0.03	0.01	--	--
Ca	--	--	--	0.01
Ti				0.06
Total 3	0.03	0.02	--	--

Note: Column 1 & 2: Kaolinite; 3: Goethite; 4: Alumo-goethite

Reasons for Discharge of Alumina Phases into Red Mud

After the soluble aluminium containing oxides and hydroxides are recovered in the Bayer process, other metal oxides present in the bauxite are disposed as a red mud material. However, discharge of alumina rich phases into the red mud pond, resulting loss in alumina recovery, is of great concern. Discharge of alumina to an appreciable extent (Av. Al_2O_3: 14%) into the red mud pond may be attributed to gibbsite containing boehmite in solid solution, alumo-goethite having 30 mol% of alumina in its lattice, needles of silimanite, specks of mica and garnet (litho-relict minerals) and minute kaolinite platelets recorded in the red mud. All such mineral phases do not get dissolved during the industrial treatment of bauxite with caustic soda and ultimately get into the red mud pond.

However, an in-depth study is necessary to improve the efficiency of digestion of all these phases during the Bayer process, so as to recover the alumina value from at least some of them. Volkov et al [7] reported that by increasing the amount of lime at 240° C, it is possible to completely break down alumino-goethite.

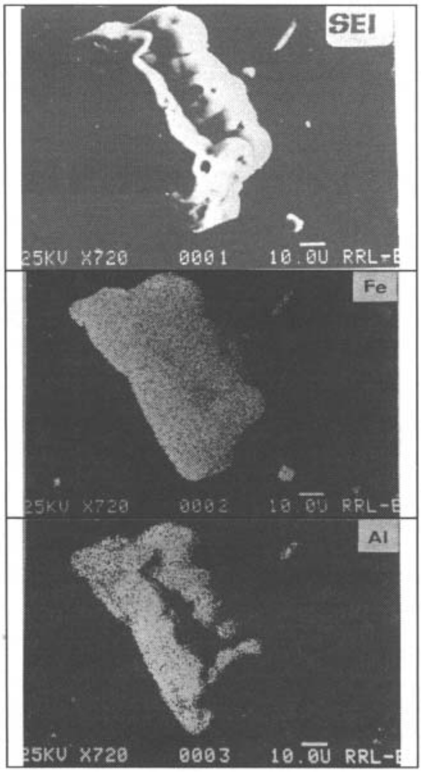

Fig. 2. Compositional X-Ray Map of Fe & Al in Alumo-goethite found in Red Mud. Image Map of Iron, Alumina confirms the Presence of significant Alumina in the Goethite Lattice

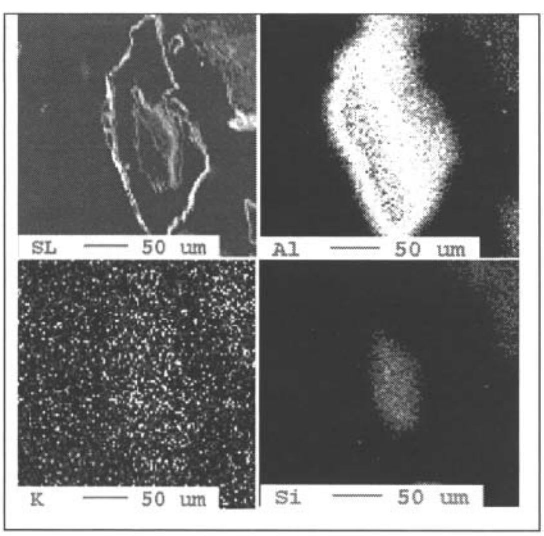

Fig. 3. Compositional X-Ray Map of K, Al & Si in a Litho Relict Observed in Red Mud. The Silica Rich Phase Still Occupies the Core Region and hence escaped leaching

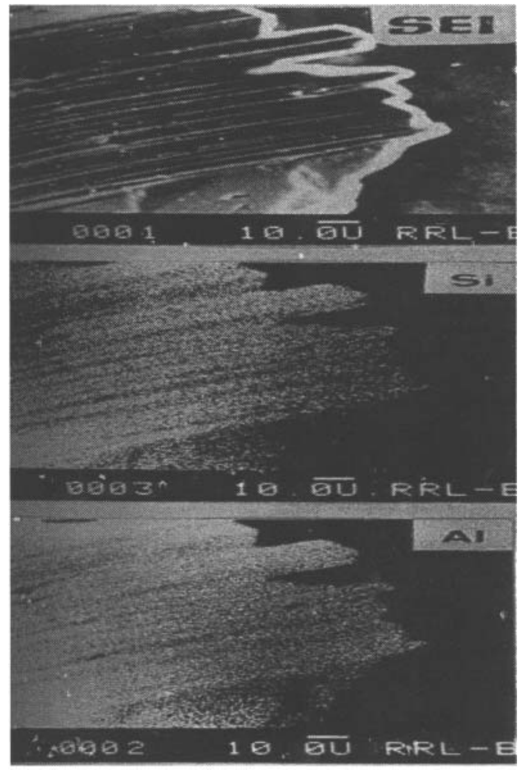

Fig.4. Compositional Map of Si & Al in Silimanite Grain Present in Red Mud. Presence of Silica and Alumina indicates its poor leaching during Bauxitisation Process

Table 3. Electron Probe Micro-analysis Results of Muscovite

	01	02	03	04
SiO_2	46.526	46.566	44.529	44.407
Al_2O_3	34.074	34.566	33.120	30.493
FeO	1.651	1.725	1.711	1.177
MgO	0.498	0.455	0.482	0.375
MnO	0.000	0.102	0.045	0.00
CaO	0.000	0.012	0.015	0.00
K_2O	11.697	10.270	10.734	10.304
Na_2O	0.400	0.441	0.455	0.426
TiO_2	0.214	0.350	0.355	0.248
BaO	0.000	0.00	0.00	0.076
Based on 14 cations				
Si	6.22	6.28	6.20	6.47
Al	1.78	1.72	1.80	1.53
Total 1	8.00	8.00	8.00	8.00
Al	3.60	3.78	3.63	3.72
Fe	0.19	0.19	0.20	0.14
Mg	0.10	0.09	0.10	0.08
Mn	--	0.01	0.01	--
Ti	0.02	0.03	0.04	0.03
Cr	--	--	--	--
Total 2	3.91	4.10	3.98	3.97
Na	0.10	0.12	0.12	0.12
K	1.99	1.78	1.90	1.91
Total 3	2.09	1.90	2.02	2.03

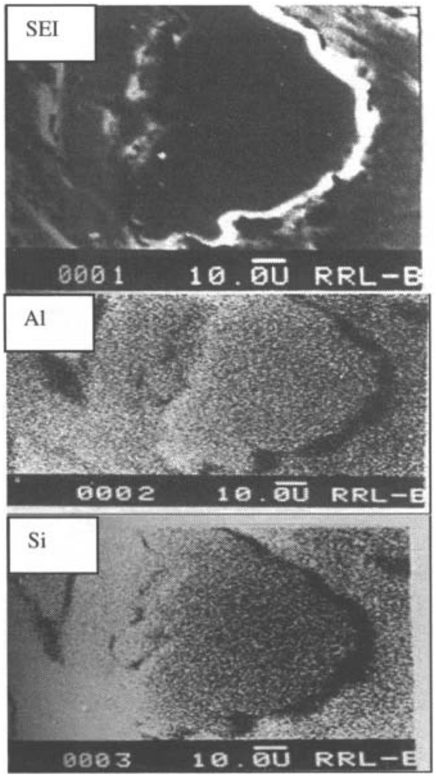

Fig. 5. Compositional Map of Si & Al in Relict Garnet Present in the in Red Mud

Conclusions

The red mud sludge from the NALCO alumina refinery at Damanjodi, Orissa, has been characterized using SEM-WDS and EPMA techniques. These are very fine grained muds, the average size being 8 micron. Different alumina containing phases such as alumo-goethite, sillimanite, kaolinite, mica and garnet were identified from their micro-morphology and in-situ chemical analysis, which contribute to the loss of alumina into the red mud. The presence of dehydroxylated grains of gibbsite probably indicates the higher temperature (than that for pure gibbsite) required for their dissolution.

The mineral chemistry of some of the constituent phases in red mud reveals the presence of lattice bound alumina which escapes the digestion stage in the Bayer's process, resulting in loss of alumina during the refining process at NALCO.

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