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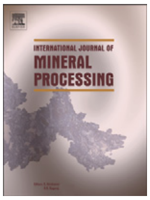

Extraction of lanthanum and cerium from Indian red mud

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ABSTRACT

Laboratory-scale experiments were conducted to recover lanthanum and cerium from Indian red mud in sulfuric acid medium. The method includes acid leaching of red mud pulp and subsequent liquid–liquid extraction of the leached metals with different organic extractants, in order to establish the technical feasibility of extraction and separation simultaneously. Maximum recovery of lanthanum (99.9%) was recorded with 3 M H_2SO_4 at ambient (35 °C) temperature, S/L ratio of 10 g/L and agitation rate of 200 rpm in 1 h time. While 99.9% cerium recovery was achieved at 75 °C and solid/liquid ratio of 10 g/L in 3 M H_2SO_4. Significant specificity for complete extraction of lanthanum, cerium and scandium by Cyanex 301 was noted as compared to the solvents such as DEHPA and Cyanex 272.

1. Introduction

At all the alumina plants, 1.0–1.6 tons of red mud is generated per ton of alumina and it is estimated that over 66 million tons of these toxic wastes is annually produced in the world. The global storage of red mud is currently estimated to be over 2.7 billion tons, with an annual growth rate of approximately 120 million tons (Klauber et al., 2011; Rai et al., 2012; Samal et al., 2013). In India, alumina plants have 1.692 million tons of annual capacity with aluminum metal production of 0.6 million tons per annum and generate about 2 million tons of red mud every year (Anand et al., 1996; Samal et al., 2013).

Red mud is a complex material whose chemical and mineralogical composition varies widely, depending upon the source of bauxite and the technological process parameters (Glenister and Thornber, 1985; Hind et al., 1999). It contains six major constituents, namely, Fe_2O_3, Al_2O_3, SiO_2, TiO_2, Na_2O and CaO and numerous minor/trace elements (as oxides) such as V, Ga, Cr, P, Mn, Cu, Cd, Ni, Zn, Pb, Mg, Zr, Hf, Nb, U, Th, K, Ba, Sr, and rare earths (La, Ce, Pr, Nd, Sm, Eu, HREE including Sc, Y) in varied ratio/distribution (Mohapatra et al., 2000; Agatzini-Leonardou et al., 2008; Raghavan et al., 2011; Tsakiridis et al., 2011; Samal et al., 2013). Although vanadium recovery from the sludge of the Bayer's process is in commercial operation, only a few processes are reported for extraction of scandium from red-mud, the residue generated from the bauxite digestion step (Fulford et al., 1991; Smirnov and Molchanova, 1997; Ochsenkühn-Petropulu et al., 2002; Zhou et al., 2008; Pandey, 2011). Pyrometallurgical reduction of iron from red mud was first reported by Qiu et al. (1995), which was followed by opting hydrometallurgical route to extract lanthanum and cerium by controlling the iron dissolution (Ochsenkühn-Petropulu et al., 1996). An analysis of the recent literatures indicates that there is no such simple method for recovery of lanthanum and cerium from Indian red mud (with very low concentration of rare earths), which possesses relatively different mineralogy as compared to the red mud generated elsewhere (Gupta and Bose, 1989; Mohapatra et al., 2012).

The aim of the present research work was to investigate the possibility of lanthanum (La) and cerium (Ce) recovery from Indian red mud, with sulfuric acid leaching, followed by liquid–liquid extraction in order to check the feasibility of their purification. The factors evaluated for optimization of leaching parameters were acid concentration/pH, temperature and solid to liquid ratio, followed by metal separation by solvent extraction. Complete study for solvent extraction is under progress and is not elaborated here.

2. Materials and methods

2.1. Raw material

Washed Indian Red Mud sample was used in this study. To ascertain the metal concentration, each sample after coning and quartering was analyzed under ICP-OES and characterized by XRD (Bruker D8™) and EPMA (JEOL™). Chemical Analysis using ICP-OES (Table 1) shows that red mud sample contains 70 ppm La and 110 ppm Ce as the major constituents of the rare earths. XRD analysis (Fig. 1a) indicates that allanite and dissakisite are the respective phases of lanthanum and cerium with dispersed phases of gibbsite, boehmite, quartz and iron oxides (hematite) as in Table 2. EPMA analysis (Fig. 1b) at 15 kV (800X) reveals sporadic distribution of lanthanum and cerium. It also reveals that concentration of

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Table 1
Chemical analysis of Indian red mud sample.

Constituent	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	V	La	Ce	Nd	Sc	Y
Analysis (%)	19.87	10.23	37.03	11.98	0.68	0.007	0.011	0.0005	0.005	0.001

alumina and silica determines the average spatial distribution of these rare earths, whereas at regions of high iron content, lanthanum and cerium concentration drops significantly.

2.2. Leaching experiments

The leaching of the metals was performed at different conditions by varying the parameters such as acid concentration/pH, temperature and solid/liquid (S/L) ratio. It may be noted that all the experiments were performed at ambient temperature (35 °C) in conical flask under orbital motion incubator shaker, while the experiments (at temp > 35 °C) were performed in a 3 neck glass vessel with heating and stirring provided by temperature controlled hot-plate (accuracy ± 1 °C) and magnetic stirring facility. To study the effect of acid/pH, NaOH was added in the sulfuric acid solution taken in different vessels, and acid concentration/pH values in each case were noted. Subsequent to attaining the desired temperature of the solution, a known amount of red mud sample was charged in the vessel for leaching. Aliquots were withdrawn at the desired interval during the course of experiments and then filtered, diluted and analyzed for rare earth metals by ICP-OES. To determine other metals, wet chemical method/ICP-OES was used. At the end of leaching tests, the slurry was filtered followed by in-situ washing with de-ionized water. The residue so obtained was dried at 100 °C in an electric oven and was analyzed for metal contents. Leaching experiments were carried out in three repetitions to check the consistency of results with a calculated deviation of ± 2–3%.

Since the concentration of lanthanum and cerium was low and may not be suitable for separation by precipitation, solvent extraction was performed using 3 different extractants (0.15 M of DEHPA, Cyanex 272 and Cyanex 301) to determine their efficiency and selectivity towards these metals.

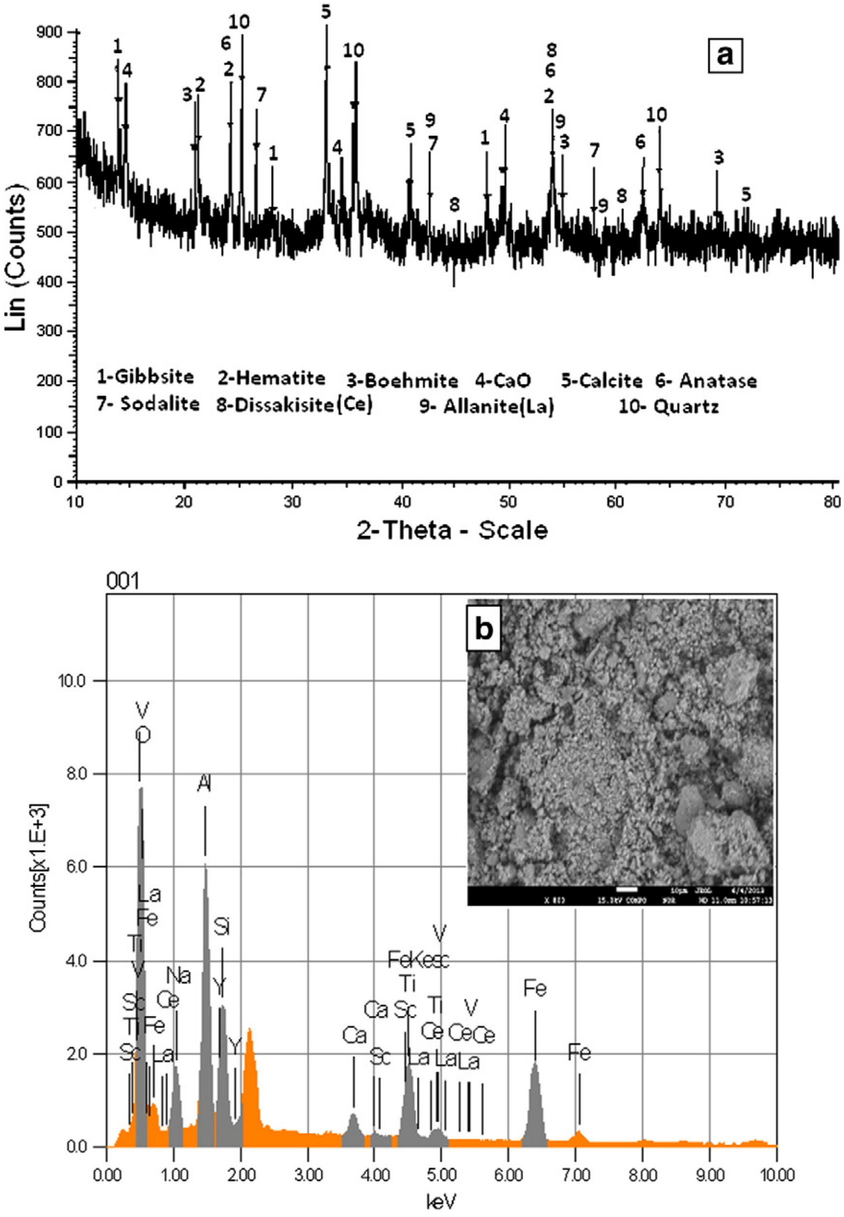

Fig. 1. X-ray diffractogram (a), and EPMA micrograph with EDS (b) of red mud sample.