Extraction of Al and Rare Earth Elements from Boehmite-Kaolinite Bauxite by Ammonium Bisulfate High-Pressure Leaching

Dmitry Valeev[1] and Andrei Shoppert[2]
1. Senior research fellow
Laboratory of Sorption Methods, Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences, Moscow, Russia
2. Associate professor
Department of Non-Ferrous Metals Metallurgy, Ural Federal University, Yekaterinburg, Russia
Corresponding author: dmvaleev@yandex.ru

Abstract

Boehmite-kaolinite bauxite of the North Onega deposit (Arkhangelsk region, Russia) are currently not used to obtain sandy grade alumina due to the high content of silica (alumina/silica ratio, $\mu_{Si} < 3$). Acidic methods are the most promising for treatment this type of raw material. In this study, the bisulfate method was studied, which involves bauxite leaching, precipitation of ammonium alum, recrystallization for gibbsite precipitation and calcination for alumina production. This research studied the effect of temperature: 130 - 170 ºC, liquid to solid ratio: 8 - 12, and the leaching duration (5 - 90 min) to the Al, Fe, Ti, Li, Sc, Ga, REEs extraction degree. It is shown that the Al, Fe, Ga extraction degree is higher than 90%. Practically, all the silica and titania remain in the solid residue. REEs extraction degree are not more 70 - 80%. Solid residues after leaching were studied by XRD, XRF, SEM and ICP-MS to define the mechanism of leaching and the solubility of the Al-containing minerals - boehmite (AlOOH), kaolinite ($Al_4[Si_4O_{10}](OH)_8$), muscovite ($KAl_2[AlSi_3O_{10}](OH)_2$). The data obtained in this research will make it possible to create an effective technology for processing of high-silica bauxite in Russia.

Keywords: Bauxite, boehmite, kaolinite, high pressure leaching, ammonium bisulfate, rare earth elements.

1. Introduction

The worldwide method for alumina (Al_2O_3) production is the Bayer method, which involves the bauxite leaching by alkali (NaOH), precipitation of gibbsite ($Al(OH)_3$) from an aluminate solution, and $Al(OH)_3$ calcination at T = 1200 ºC. This method can be used when the alumina/silica ratios ($\mu_{Si} = Al_2O_3/SiO_2$) in bauxite above 7. These types of bauxite are mainly mine in Guinea, Jamaica, Guyana, and Australia. Silica contents in the Russian mined bauxites can be as high as 20-25 wt. %, which poses technological complications to their chemical treatments [1]. Currently, the bauxite deposits in the Northern Urals and Middle Timan are recovered by the technology combining sintering bauxites with sodium carbonate (Na_2CO_3) and limestone ($CaCO_3$) if μ_{Si} of bauxite < 7, for bauxite with μ_{Si} > 7 using the direct alkali leaching [2].

The Severoonezhsk Bauxite Mine (Arkhangelsk region, Russia) is not used for alumina production, due to the high content of chromium oxide (Cr_2O_3) up to 1 wt.%. High Cr_2O_3 content is a significant technological obstacle for the further bauxite treatments by sintering process, as the final product has a high likelihood of Cr^{6+}-contamination, which is toxic to humans and the environment. Therefore, it is impossible to use traditional alkaline methods for treatment this type of bauxite.

Previously, a hydrochloric acid (HCl) method for Severoonezhsk bauxite was studied: by preliminary roasting at T = 560 ºC [3] and atmospheric leaching or direct bauxite leaching in a high-pressure reactor at T = 170 - 180 ºC [4]. The aluminum extraction degree by both methods exceeded 90%. However, alumina obtained from crystals of aluminum chloride hexahydrate (ACH, $AlCl_3 \cdot 6H_2O$) did not correspond to the RUSAL requirements for particle shape and chlorine ion content [5]. Therefore, alkaline recrystallization of ACH is necessary to obtain alumina from $Al(OH)_3$ [6].

An alternative to HCl method can be the ammonium bisulfate (NH_4HSO_4) method. After aluminosilicate leaching process the aluminum ammonium sulfate solution is obtained. It is possible to precipitate $Al(OH)_3$ by ammonia (NH_3) gas sparging from this solution [7]. Thus, the problem of accumulation of impurities in $Al(OH)_3$ and further in Al_2O_3, the production of the spherical shape of Al_2O_3 powder, and the possibility of reusing the leaching reagent - ammonium bisulfate can be solved.

Previous research is devoted to the study of the roasting ammonium sulfate with aluminosilicates at T = 400 - 600 ºC and further water leaching [8]. To decrease the duration of the extraction process, reduce technological conversions and energy consumption, it is possible to use high-pressure reactors. Hu et al. [9] and Khamizov et al. [10] showed the possibility of using this equipment for leaching the coal fly ash, Middle Timan bauxite, kaolin, and nepheline. In this research, for the first time, the leaching of high-silica bauxite from Severoonezhsk deposit with μ_{Si} less than 3 by the mixture of $NH_4HSO_4 + H_2SO_4$ was studied.

2. Materials and Methods

2.1 Materials and reagents

Raw bauxite sample was collected from the Severoonezhsk Bauxite Mine (N62.573349º, E39.719039º). Analytical grade ammonium sulfate CAS No. 7783-20-2, sulfuric acid CAS No. 7664-93-9 (both from SigmaTek, Russia) were used in the leaching process. Distilled water was used to dilute leaching reagents and washing of solid residue after leaching. Chemical composition of raw bauxite is resented in Table 1.

Table 1. Chemical compositions of raw bauxite from Severoonezhsk deposit (Arkhangelsk region, Russia).

Main components, wt. %									
Al_2O_3	**SiO_2**	**Fe_2O_3**	**TiO_2**	**CaO**	**Cr_2O_3**	**MgO**	**Na_2O**	**K_2O**	**LOI***
53.30	17.80	6.52	2.57	0.68	0.52	0.75	0.04	0.23	15.60
Minor components, g/t									
Li	**Sc**	**Ga**	**Sr**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**
202	116	58	136	29	44	126	11	43	8.4
Eu	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Lu**	**Th**	**U**
2.0	8.6	1.2	7.0	1.3	4.1	4.1	0.6	16	5

*LOI – loss on ignition at 1000 ºC.

2.2 Experiments

Bauxite samples were leached by 40% NH_4HSO_4 + 3M H_2SO_4 mixture in a 50 mL high-pressure reactor (Deschem, China). The duration time at T = 130 - 170 ºC was 30 - 90 min. The liquid to solid ratio (L:S) varied from 8 to 12. Pulp after leaching was filtered, the solid residue was washed by heat water (90 ºC). The solid residue dried at 110 ºC for 2 h and analyzed by physical and chemical methods. The liquor after filtration was analyzed for major and minor metals content.

Bauxite also contains phases: gibbsite $Al(OH)_3$; muscovite $KAl_2[AlSi_3O_{10}](OH)_2$; hematite ($Fe_2O_3$); goethite FeOOH); anatase (TiO_2) whose peaks fit with the main phases. Gibbsite dissolves first by the leaching process, its peaks cannot be found on the solid residue samples. However, muscovite and anatase do not dissolve by the NH_4HSO_4 + H_2SO_4 mixture. During the dissolution of the main phases, these minerals begin to appear on XRD patterns. At 170 ºC, the main aluminum phase - boehmite, has completely dissolved. Undissolved aluminum is found in refractory minerals - kaolinite and muscovite. Therefore, the aluminum content in the solid residue is still high – 16.68 wt.% (Table 4).

Table 4. Chemical compositions of solid residue after bauxite 40% NH_4HSO_4 + 3M H_2SO_4 leaching (T = 170 ºC; L:S = 10; τ = 60 min)

Main components, wt. %									
Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	Cr_2O_3	MgO	Na_2O	K_2O	LOI*
16.68	59.79	0.87	9.69	0.02	0.25	0.03	0.11	0.60	11.57

*LOI – loss on ignition at 1000 ºC.

4. Conclusions

In this study, the bisulfate method of treatment of Severoonezhsk bauxite by high-pressure leaching was investigated. Using machine learning with ANNs for analysis of the Al and Sc extraction degree showed that at optimal parameters (T = 170 ºC; L:S = 10; τ = 60 min), aluminum goes into liquor for 90%, scandium for 75%. The distribution of REEs and other minor components of bauxite during the leaching process at T = 130 - 170 ºC is shown. The average extraction degree is 70-80%. The highest content of Li, Sc, and Ga in acid liquor is 14 mg/L, 8.5 mg/L, and 5 mg/L, respectively. XRD analysis of the solid residue after leaching at T = 110 - 170 ºC showed that the main aluminum-containing mineral - boehmite, almost completely dissolves at 170 ºC. In this case, all undissolved aluminum is concentrated in kaolinite and muscovite.

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6. References

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