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.

The Al and Sc extraction degree were analyzed using machine learning with artificial neural networks (ANNs) included in the «Statistica 13» software.

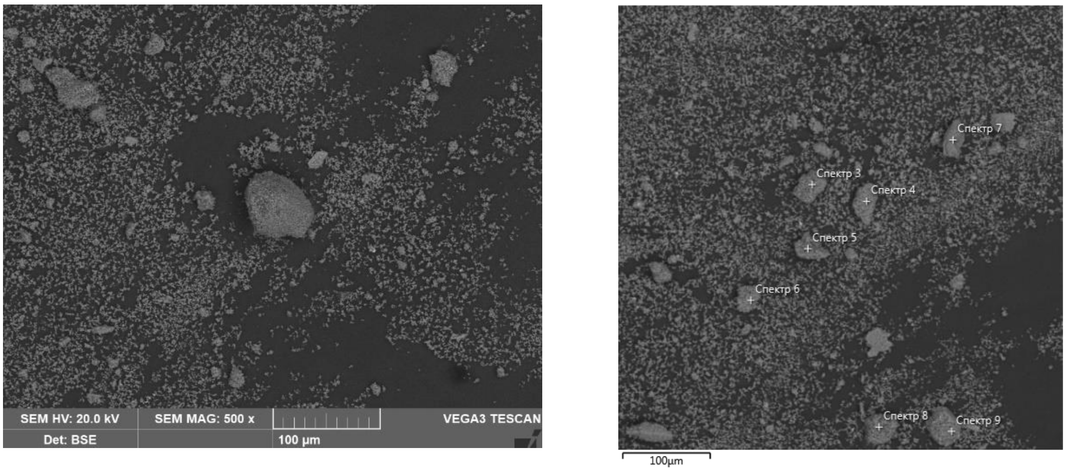
2.3 Analytical methods

Mineralogy of the bauxite samples were measured by X-ray diffraction (XRD) using a Difrei-401 X-ray diffractometer (JSC Scientific Instruments, Saint Petersburg, Russia) using a Cr-Ka radiation source and a 2θ range from 5º to 140º with 30 min exposure time. The operating mode of the X-ray source was set to 25 kW/4 mA. The mineral phases were analyzed by Match! 3 software. The surface morphology and elemental composition of bauxite sample after 40% NH_4HSO_4 high-pressure leaching was investigated by scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDX, Vega III, Tescan, Czech Republic). Chemical composition of raw bauxite and solid residue after leaching were analyzed by X-ray fluorescence (XRF) on AXIOS-Advanced spectrometer (PANalytical B.V., Netherlands). The metals concentrations in liquor after bauxite leaching were measured by X Series II inductively coupled plasma (ICP-MS) quadrupole mass spectrometer (Thermo Scientific, Germany) equipped with a concentric nebulizer and a quartz cyclonic spray chamber cooled by a Peltier element (2 ºC). Measurements of elements in the analyzed solutions were carried out using the software of the PlasmaLab spectrometer.

3. Results and discussion

3.1 High-pressure leaching of bauxite by $NH_4HSO_4 + H_2SO_4$ mixture

In first experiments, we used only 40% NH_4HSO_4 as reagent to extract Al and other metals. However, using this method, the ammonium alum ($NH_4Al(SO_4)_2$) precipitates from liquor during the leaching process. Crystals of $NH_4Al(SO_4)_2$ are very small (1-2 μm) and cover the entire surface of solid residue particles (Figure 1 a,b and Table 2). These crystals cannot be separated from the solid residue of bauxite even by hot water filtration. So, we applied the method from Xu et al [9], in which the mixture of two reagents ($NH_4HSO_4 + H_2SO_4$) was used for leaching process.



(a) **(b)**

Figure 1. The SEM images of the solid residue after 40% NH_4HSO_4 leaching (a) particles appearance; (b) spectrums for EDX analyze.

Table 2. The elemental compositions [wt. %] of the solid residue after 40% NH_4HSO_4 bauxite leaching (see Figure 1b).

Spectrum	O	Al	S	N	Si	Fe	Cr	K
3	63.1	15.7	10.2	4.6	4.0	2.3	-	-
4	57.0	17.8	15.2	4.5	1.1	4.1	0.3	-
5	58.4	14.9	12.8	5.0	4.7	3.9	0.3	-
6	60.3	16.3	9.4	8.0	4.0	2.0	-	-
7	61.4	15.4	7.8	5.4	6.8	2.1	-	1.1
8	63.1	16.3	11.4	4.9	2.1	2.2	-	-
9	62.5	14.9	8.3	8.0	4.5	1.8	-	-

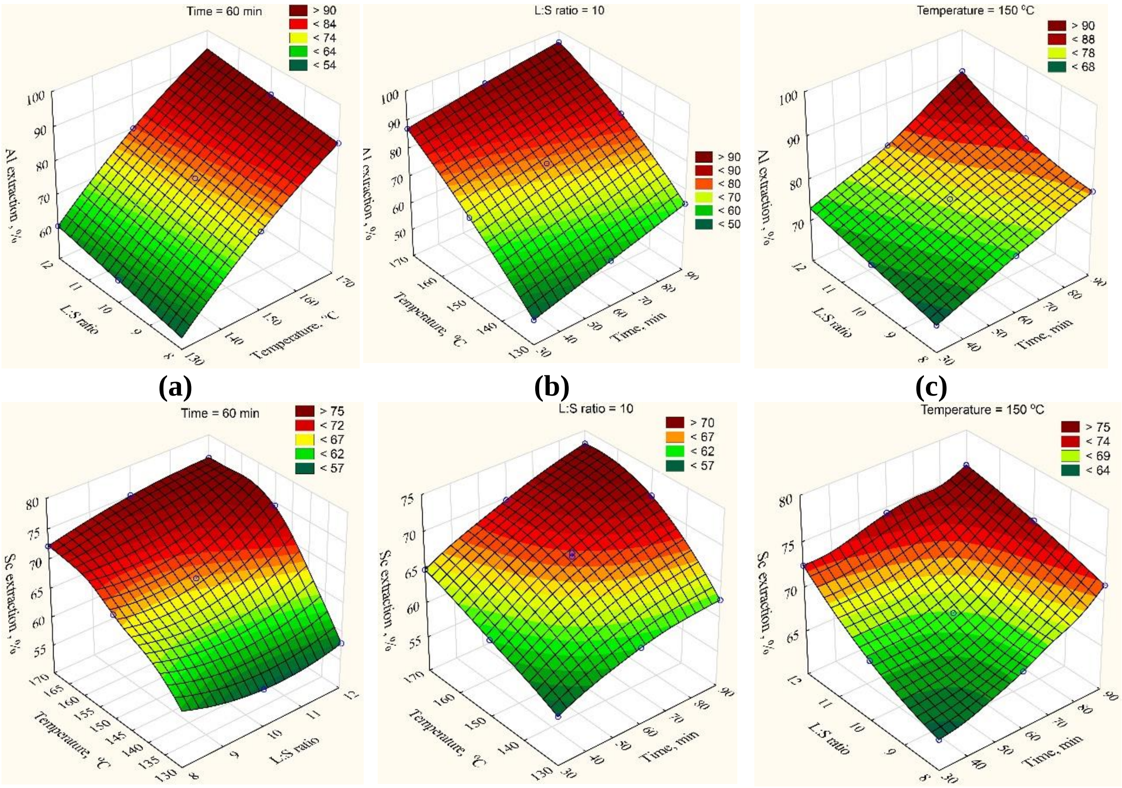
To reduce the number of experiments and to identify the mutual influence of various factors on each other, a full factorial design method was used. The matrix of experiments and the value of the yields of solid residue after leaching are shown in Table 3. The concentration of leaching reagent in all experiments was 40% NH_4HSO_4 + 3M H_2SO_4 (50%/50%) to exclude $NH_4Al(SO_4)_2$ precipitation.

Table 3. The matrix for planning experiments.

№	Time, min	L:S ratio, mL/g	Temperature, ºC	Yield of solid residue, %
1	90	10	150	32.40
2	90	12	150	29.04
3	60	10	150	35.23
4	30	12	150	42.12
5	60	10	150	35.57
6	30	8	150	43.30
7	90	8	150	39.10
8	90	10	170	27.93
9	60	8	170	36.58
10	60	8	130	54.20
11	60	12	170	25.88
12	60	12	130	50.28
13	90	10	130	48.80
14	30	10	130	54.83
15	30	10	170	32.83

Xie et al. [11] and Shokri [12] showed that the use of machine learning provides more accurate models than traditional mathematical methods. The results of the Al and Sc extraction degree were analyzed by machine learning with ANNs. The best results were obtained by the architecture MLP (a multilayer perceptron) 3-9-1, where the first digit is the number of input neurons, the second is the number of hidden neurons, and the last is the number of output neurons. High convergence of experimental data and values predicted using the resulting network is obtained ($R^2 = 0.987$). The response surfaces predicted by the ANN for Al and Sc extraction depending on the temperature, leaching time and the S:L ratio are shown in Figure 2.

As can be seen from Figure 2, the leaching temperature is the main factor for increasing the extraction of Al and Sc. Decreasing the L:S ratio to 7 or below also leads to $NH_4Al(SO_4)_2$ crystal precipitation from acid liquor. The maximum Al and Sc extraction degrees at optimal parameters (T = 170 ºC, τ = 90 min, and L:S ratio = 10) were more than 90% and 75%, respectively. The chemical composition of the acid liquor was, g/L: Al – 24.6; Fe – 6.0 g/L; Cr – 0.36; Ti – 0.11; Si – 0.31. Chromium (Cr) in liquor had a non-dangerous valence (+3), the Fe, Cr, Ti, Si extraction degrees were 92%, 70%, 5%, and 1.7% respectively.

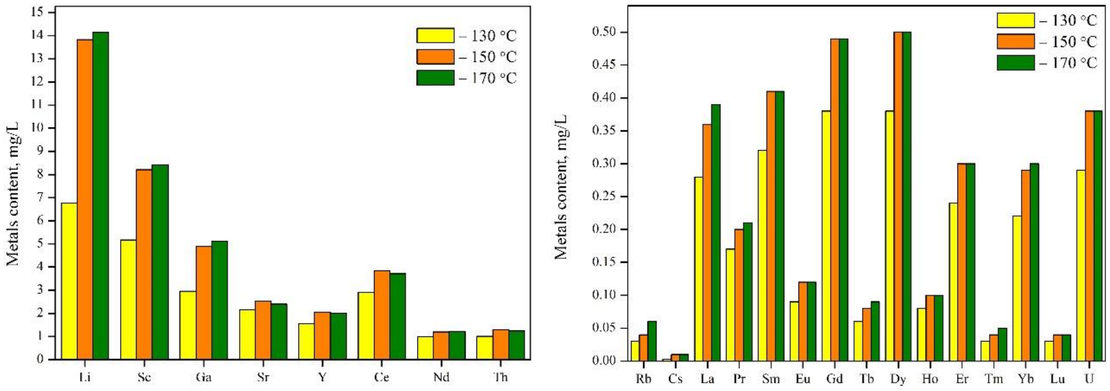


(a) **(b)** **(c)**

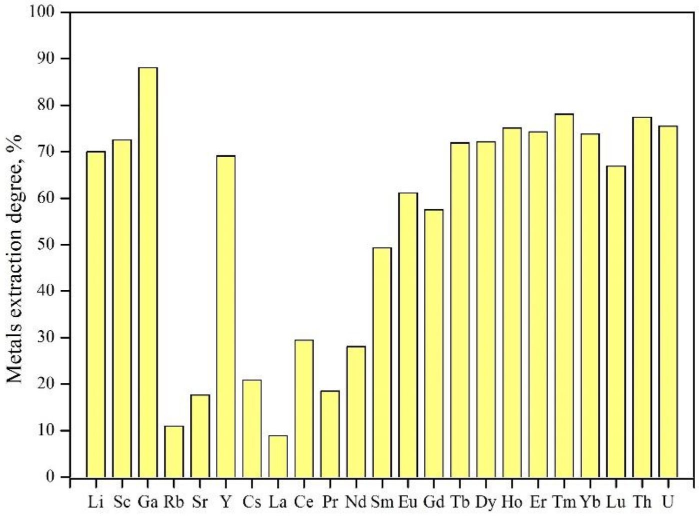
(d) **(e)** **(f)**

Figure 2. Neural network response surfaces for: (a) Al extraction degree at leaching time 60 min; (b) Al extraction degree at L:S ratio = 10; (c) Al extraction degree at T = 150 ºC; (d) Sc extraction degree at leaching time 60 min; (e) Sc extraction degree at L:S ratio = 10; (f) Sc extraction degree at T = 150 ºC. Blue points are the experimental data.

In this study, the behavior of bauxite micro-components during the leaching process was analyzed. Figure 3 shows the content of the metals depending on the leaching temperature. The highest content of micro-components in an acidic liquor is observed for lithium (Li), scandium (Sc), gallium (Ga), and cesium (Ce) (Figure 3a). The REMs content does not exceed 0.5 g/L for gadolinium (Gd) and dysprosium (Dy), the content of other metals is significantly lower (Figure 3b). The average extraction degree for these metals is 70-80%, gallium is recovered most completely ~90%. The acid liquor after bauxite leaching further can be used for Li, Sc, and Ga extraction by solvent extraction or resin sorption methods.



(a) **(b)**



(c)

Figure 3. Chemical compositions of minor components in acid liquor after bauxite leaching at T = 130-170 ºC, L:S = 10 and τ = 90 min (a) - Li, Sc, Ga, Sr, Y, Ce, Nd, Th contents; (b) – Rb, Cs, La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U; (c) – metals extraction degree at T = 170 ºC, L:S = 10 and τ = 90 min.

The solid residue after leaching process was investigated by XRD and XRF methods. The raw bauxite consists mainly of boehmite (AlOOH), kaolinite ($Al_4[Si_4O_{10}](OH)_8$) and quartz (SiO_2) (Figure 4).

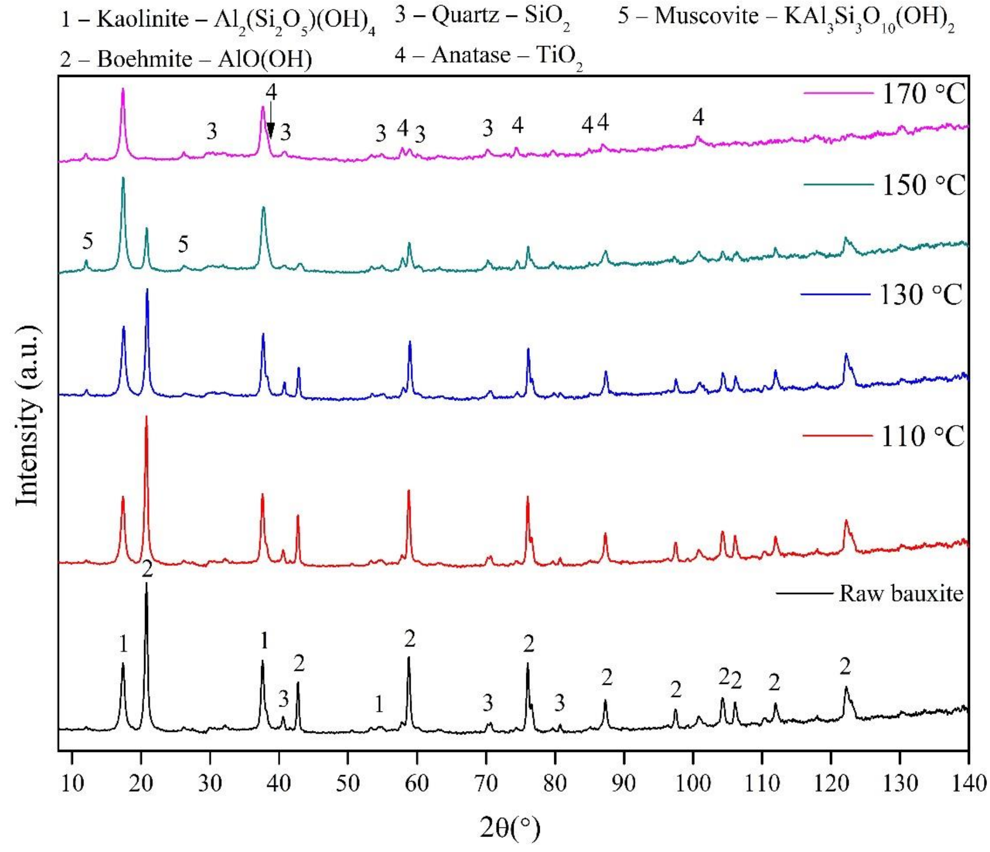


Figure 4. XRD patterns of the raw bauxite and solid residue samples after 40% NH_4HSO_4 + 3M H_2SO_4 leaching at T = 110-170 ºC (L:S = 10; τ = 60 min).

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.

5. Acknowledgements

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