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Extraction of Alumina from high-silica bauxite by hydrochloric acid leaching using preliminary roasting method

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Abstract. A process of dissolution Severoonezhsk deposit boehmite-kaolinite bauxite by hydrochloric acid, as well as the processes that occur during open-air calcination, were investigated. A dehydration process has been studied, and the basic phase transformation temperatures were identified. Temperature and time of calcination influence on bauxite dehydration speed were determined. It is shown that the preliminary calcination increases the extraction ratio of alumina into solution up to 89%. Thermodynamic modelling of physical and chemical processes of bauxite decomposition by hydrochloric acid and the basic forms of aluminium speciation in solution were obtained.

1. Introduction

Russia is the world leader in aluminum production, but the bulk of the raw material (~70% of bauxite and alumina) are imported from abroad (Australia, Jamaica, Guyana, Guinea). Shipments of aluminum ore from distant deposits are questioning production profitability due to constant increase in expenses for freight ships and transportation by rail. The total length of some logistic chains (mine - alumina refinery - aluminum plant) may exceed 15 thous. km. High political risks and the issue of raw materials security in the country make this problem even more acute [1].

Huge reserves of low-grade and non-traditional for alumina production aluminum-containing materials, such as high-silicon bauxites [2–3], kaolin [4], anorthosite [5] and coal fly ash [6–9], can serve as an efficient source of raw materials. Researches in this area are essential and extensively developing in countries with developed aluminum industry, e.g. Canada [10] or China [11-14].

Due to development of new corrosion-resistant materials (alloys based on Ta, Zr, Nb), durable equipment for alumina refinery can be produced [15–16].

The use of acid decomposition offers great opportunities for efficient complex processing of alternative raw materials to produce alumina [17], rare or rare-earth metals [18–19], silicon-based materials [20], and a reagent for the water purification [21] that will lead to a significant increase in competitiveness of domestic enterprises. Therefore, the main task of this work was to develop an efficient method of acid leaching which could be applied to raw materials available in Russia.
2. Experimental

Acid leaching was carried out in a round-bottom flask placed in a heating flask. The bauxite samples used in the experiments were of two types, both milled to a particle size of 0.1 mm: the original sample and the sample calcined at a temperature of 700°C. Calcination was performed in muffle furnace (HTC 03/18/3N/PE, Nabertherm, Germany) in open corundum crucibles, heating time to temperature of 560-750°C was 30 min., sample weight was 10 gr., and the time - 3.5 h.

Bauxite was leached by 20% hydrochloric acid with mechanical stirring at 110°C for 1-5 hours. Then the solutions were separated from the solid precipitation (Si-stoff) using a vacuum filter. The Si-stoff was washed with distilled water and then dried in an oven at 110°C for 2 h. The resulting solutions, washing water and Si-stoff were analyzed for Al, Fe and Si by ICP-OES (Optima-4300 DV of PerkinElmer Instruments, USA). The Si-stoff was characterized by X-ray diffraction (Ultima IV, Rigaku, Japan) for identification of crystalline phases. To determine the change in mass of bauxite and temperature of phase transitions of minerals included in bauxite, we used the simultaneous thermal analyzer STA 409 Luxx (Netzsch, Germany).

The study of Al-Si-Fe-Cl-C-N-H-O-e system was studied by the method of minimizing thermodynamic potentials. Researches were performed with the help of «Selector» software [22]. The basis of the simulation was based on the concept of ion-complex structure of acidic aluminum-containing solution.

The list of substances potentially possible in equilibrium included 71 dependent component, including: 8 condensed phases, 51 components of aqueous solution and 12 components of gas phase. All thermodynamic properties were taken from the «Selector» database: a_Sprons98, s_Sprons98, g_Reid, s_Yokokawa [23−25].

3. Results and discussion

In the present work, domestic high-silicon Severoonezhsk deposit bauxites (Arkhangelsk region) have been used as a raw material. To date, the main direction of processing these bauxites is the production of refractory materials. Processing of the raw material for alumina will let to meet the needs of basic aluminum smelter of the European part of Russia (Kandalaksha, Nadvoitsy, Volkhov and Volgograd aluminum Smelter) in metallurgical alumina.

According to XRD (figure 1a) the main mineral components in Severoonezhsk bauxite are boehmite AlO(OH) ~ 41.5%, kaolinite Al$_2$Si$_2$O$_5$(OH)$_4$~ 25%, gibbsite Al(OH)$_3$~ 8%, hematite Fe$_2$O$_3$ ~ 4%, goethite FeOOH ~ 5%, anatase TiO$_2$ ~ 3%. The chemical composition of bauxite is 50 % Al$_2$O$_3$; 20.0 % SiO$_2$; 7.94 % Fe$_2$O$_3$; 2.94% TiO$_2$; 0.88 % CaO; 0.86% Cr$_2$O$_3$; 0.52% MgO; 16.86% loss after calcination. Due to a high silicon content, this bauxite is considered to be a low-grade and therefore has a low silicon module ($\mu_{Si} = 2.5$).

The results of leaching of bauxite by 20% hydrochloric acid at 110°C show that the extraction ratio of aluminum is not more than 23% in case of a process duration of 5 h. (the obtained solutions are composed of 10.6 g/l Al, 7.69 g/l Fe, and 0.01 g/l Si). The process is uneven, the first two hours are characterized by the most intensive leaching due to a complete dissolution of the easily dissolved by hydrochloric acid minerals such as gibbsite, goethite and hematite. Kaolinite and boehmite thus dissolve slightly, which is confirmed by X-ray diffraction (figure 1b).
In order to increase the extraction ratio of aluminum bauxite precalcination was used, that allowed us to transfer low-soluble boehmite and kaolinite into the acid-soluble forms $\gamma$-Al$_2$O$_3$ and Al$_2$Si$_2$O$_5$, respectively.

This is confirmed by thermodynamic modeling of the solubility of certain minerals by hydrochloric acid. Subsequently, the calculation results were compared with experimental data. It is found that the solubility of aluminum-containing minerals in chloride solutions at 25°C decreases (figure 2). Thermodynamic calculations have shown that increasing solubility of aluminum-containing minerals caused by change in the ionic composition of the solution. In particular, there is a relative decrease in the concentration of cationic and hydroxide complexes of Al, while the concentrations of chloride and chlorohydrate complex compounds of aluminum increase [26].

To determine the temperature of dehydration and related phase transitions, thermogram of the original bauxite during a linear heating to 1300°C in air was taken (figure 3).
Figure 3. Effect of temperature on the weight change (TGA) and differential scanning calorimetry curve (DSC) of the original bauxite.

It shows two distinct endothermic peaks at 260-300°C and 500-560°C. According to XRD at the first stage (at 300°C), constitutional water is removed in the form of OH-ions from gibbsite and goethite, and at the second (at 560°C) - from boehmite and kaolinite to form γ-Al2O3 and irregular metakaolinite Al12Si2O7. Thus, after calcination of bauxite at optimal conditions the phase composition is the following: γ-Al2O3 – the main phase, metakaolinite Al12Si2O7, hematite Fe2O3 and a small amount of anatase TiO2.

Figure 4 shows the dependence of the dehydration rate on the temperature and duration of calcination. To remove the constitutional water completely, it is required to hold it from 30 min. at 700°C to 3 h. at 560°C. Temperature increase up to 750°C does not lead to a substantial increase in the dehydration rate. The maximum concentration of removed water is 14.5% of the total mass of the bauxite. Based on the data the optimal calcination parameters are temperature of 700°C and time of 30 min. Calcined bauxite was leached by 20% hydrochloric acid under the same conditions as the original. Figure 5 shows that the extraction ratio of aluminum in the solution has reached 89% after 4 h., which leads to an increase in the content of the main components in solution: 42.2 g/l Al, 9.25 g/l Fe, and 0.02 g/l Si.

Figure 5. Effect of leaching time on the degree of extraction of aluminum (η, %): 1 - original bauxite; 2 - calcined bauxite.

Figure 6. Distribution of chemical forms of aluminum in hydrochloric acid solutions after leaching the original (a) and calcined (b) bauxite: 1-Al³⁺; 2-AlCl₄⁻; 3 - AlCl₃.
Physicochemical modeling of the process of decomposition of bauxite by hydrochloric acid to determine the main forms of aluminum in solution is based on the experimental data (figure 5). As a result, the equilibrium component composition of hydrochloric acid solutions was determined. The basic compounds of leaching of original bauxite at 110°C are $\text{Al}^{3+}$ and $\text{AlCl}_4^-$, $\text{AlCl}_3$ concentration is estimated to be $10^{-3} \div 10^{-4}$ mol/kg H$_2$O (figure 6a). Other forms do not have a significant effect on the solubility of aluminum since their concentration is less than $10^{-6}$ mol/kg H$_2$O.

Using calcined bauxite increases the concentration of aluminum in the solution due to the formation of chloride aluminum forms. As shown in figure 6b, the basic form of the aluminum in solution becomes $\text{AlCl}_4^-$.4

4. Conclusion
It is found that precalcination of Severoonezhsk bauxite at 700°C for 0.5 h leads to a significant increase of the extraction ratio of aluminum in solution (89%), using leaching by hydrochloric acid, in comparison with leaching of uncalcined bauxite (23%). It has been shown that increasing of the extraction ratio of aluminum caused by the change of the phase composition of bauxite after calcination. This is a result of dehydration of low-soluble minerals, which are a part of bauxite, and occurs in two steps (at 260-300°C and at 500-560°C). As a result, soluble in hydrochloric acid phases $\gamma$-$\text{Al}_2\text{O}_3$ and metakaolinite are formed. The equilibrium composition of hydrochloric acid solutions was determined by the method of thermodynamic modeling. It is found that the increase in the aluminum concentration in the solution is due to the formation of chloride form $\text{AlCl}_4^-$, which along with $\text{Al}^{3+}$, is a main form of aluminum in solution.

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