Kaolinite clays as a source of raw materials for the aluminum industry of the Republic of Kazakhstan

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Abstract

Kaolinite clays can serve as an additional source of alumina in the Republic of Kazakhstan. The most promising is the Alekseevsky kaolinite deposit. To obtain high-quality kaolinite and quartzite products, it is necessary to develop special enrichment techniques, since no satisfactory results were achieved when using standard methods of gravitational enrichment of kaolinites. The paper presents the results of studies of the effect of preliminary chemical activation during the processing of kaolinite clays of the Alekseevsky deposit. Previously, the method of preliminary chemical activation of raw materials in a solution of sodium bicarbonate has proven itself well in the processing of various mineral raw materials. It was determined that during the preliminary chemical activation in a solution of sodium bicarbonate, changes occurred in the phase composition of the kaolinite fraction: the content of muscovite decreased almost twice; the phase of sodium aluminosilicate was formed. The dependence of the yield of Al₂O₃ in the kaolinite fraction on the temperature of chemical activation, duration, and the ratio of L:S and the concentration of the sodium bicarbonate solution during chemical activation. The optimal mode of preliminary chemical activation of kaolinite clay of the Alekseevsky deposit has been established: the temperature is 150 °C, the duration is 120 minutes and the concentration of sodium bicarbonate solution is 120 g/dm³. A basic technological scheme is proposed for the processing of kaolinite clays.

Keywords: kaolinite, quartzite, silicon module, chemical activation, chemical enrichment, product yield, technology.

Introduction

The constant decline in the production of high-quality bauxite is an impartial basis for the use of alternative alumina-containing raw materials; however, high operating costs, energy intensity, and low efficiency of the known methods of mining, enrichment, and processing of such raw materials restrain their use in production.

The world production of alumina is based mainly on the processing of high-quality bauxite by the Bayer method [1-4]. According to this method, the processing involves bauxite with a flint modulus of more than 7 units.

The Republic of Kazakhstan has no bauxite deposits that are suitable for direct processing by the Bayer process.

Geological exploration in Kazakhstan has identified various types of aluminum raw materials such as bauxite, nepheline syenite, alunite, and iron-aluminum ore. Only bauxite is used industrially. Bauxite deposits and ore occurrences are grouped in several bauxite-ore regions: West Torgaysky, East Torgaysky, Central Torgaysky, Mugodzharsky, Tselinogradsky, Ekibastuzsky, and Prichimkentsky, differing in geological and morphological features and the scale of mineralization. Commercial deposits are known in the first three regions [5].
The structure of Aluminum of Kazakhstan JSC includes the Pavlodar Aluminum Smelter (PAS) which is the only alumina producer in the Republic of Kazakhstan with an annual capacity of 1,500,000 tons of Al₂O₃, and the Kazakhstan Electrolysis Plant which produces about 250,000 tons of aluminum in ingots per year. The raw materials used by PAS are mainly low-quality bauxites of the Krasnooktyabrsky deposit, which are located in the Kostanay region, with a low flint modulus and an increased content of iron and carbonates [6, 7].

Currently, the Krasnooktyabrsky deposit has reserves of about 80 million tons of bauxite. Mining is performed at the Ayatsky and Krasnogorsky bauxite mines.

At the beginning of 2021, the total bauxite reserves of the Ayatsky mine and the Krasnogorsky mine were 29.194 million tons and 47.094 million tons, respectively [8-11].

Thus, the available bauxite reserves can be enough for PAS to be operated at the existing capacities for no more than 15 years; given that the bauxite processing technology includes the redistribution of the release of ferrous sand in the amount of 10-12% of the total mass, the period of supply of raw materials will be further reduced. Since the remaining bauxite deposits in Kazakhstan do not have sufficient reserves, it is necessary to switch to alternative sources of aluminum raw materials.

The world practice has experience in the industrial processing of nepheline raw materials in the Russian Federation: Leningrad region, Pikalevo; Krasnoyarsk Krai, Achinsk Alumina Refinery. These enterprises are currently working unstable due to the difficulties in sales of silicate products. The Republic of Kazakhstan has the Kubasadyrskoye deposit, one of the largest deposits of nepheline syenite in the world, located in the Kostanay region and having total forecast resources of up to 1.7 billion tons.

One of the leading places in alternative raw materials sources of alumina belongs to kaolinite ores. The world volume of kaolinite ores is estimated at 16 billion tons [12]. Modern mining and processing of kaolinite raw materials have an established infrastructure, are provided with raw materials and in the future can be adapted to the production of alumina and by-products. Currently, kaolinite is mined in the USA, UK, China, Ukraine, Russia, Kazakhstan, the Arab Republic of Egypt, etc. [13].

There are some studies performed to extract alumina from kaolinite by high-temperature firing and effective separation of alumina and silica minerals.

Work [14] is aimed at studying the effect of thermal reactions of kaolin at different sintering temperatures on the mechanisms of phase transformation and microstructural changes, the mechanism of self-decomposition, as well as the efficiency of extracting aluminum oxide from kaolinite using the lime-agglomeration process.

Agglomerates were obtained at temperatures between 800°C and 1400°C, then subjected to a leaching process (S:L = 1:5) with sodium carbonate solution (120 g/dm³); the final productive solutions contained alumina.

It was found that 1360°C is an optimal sintering temperature for the induction of a solid-phase reaction between clay and carbonate components, which results in maximum alumina recovery equal to 80.49%. Under optimal sintering conditions, kaolinite was dehydroxylated and converted to metakaolinite, while calcite was decomposed to calcium oxide. The new phases formed have reacted to form calcium aluminate, which are considered to be highly efficient and generating precursor phases in the recovery of alumina.

The article [15] describes the process of extracting alumina from aluminum slag using a safe alkaline sintering process.

Aluminum slag which causes numerous disposal problems is a useful resource for extracting alumina.

For slag grinding, aluminum nitride (AlN) decomposition, and salt removal, an experimental unit was developed. Then, the desalted slag was calcined with NaOH and leached under optimal conditions, and the kinetics of dissolution of aluminum oxide and silica was evaluated.

The leach residue was used to produce the mineral ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) with calcium-based compounds (including CaO and CaSO₄) to avoid problems associated with solid waste disposal during the leaching process.

Aluminum hydroxide Al(OH)₃ precipitated after carbonization was calcined at 900°C for 2 hours to obtain γ-alumina.

It is noted that the activation temperature equal to 1000°C; Na₂O/Al₂O₃ molar ratio equal to 1.4; leaching temperature equal to 60°C, process time equal to 40 minutes and liquid/solid ratio in leaching (ml/g) equal to 25/1 are optimal for 86.7% alumina recovery with a purity of more than 98%.

The results of studying the leaching kinetics showed that the dissolution of aluminum oxide and silicon dioxide is controlled by the process of diffusion of
layers with an apparent activation energy of 11.4010 kJ mol$^{-1}$ and 2.0556 kJ mol$^{-1}$, respectively.

The work [16] studied the effect of different calcination temperatures on the phase transformation of minerals in coal gangue and optimal conditions for alkaline leaching of coal waste after calcination. Based on the results, the following conclusions were drawn.

Phase transformation of kaolinite during high-temperature roasting occurs as follows: kaolinite (A/S = 0.85) → metakaolin (A/S = 0.85) → spinel (A/S = 1.13) → mullite (A/S = 2.55), where A/S is the weight percentage of alumina to silica. Phase transformation releases the active silica mineral which can be dissolved in an alkaline solution and separated from the desilicate residue.

The optimum calcination temperature of coal gangue should be maintained at the level of 1050 ± 50°C. Lower calcination temperatures will result in the incomplete release of the active mineral silica and the formation of the cristobalite phase instead of active silica formed at high calcination temperatures.

Under conditions of desiliconization with an alkali concentration of 90 g·L$^{-1}$ and solid content of 320 g·L$^{-1}$, the optimum leaching temperature is 85°C and the leaching time is 60-80 minutes. The modulus of the resulted sodium silicate solution can reach 1.1, the ratio of aluminum oxide to silicon dioxide in the desilicated residue is 1.6-1.7, and the Na$_2$O content is about 4-5%.

In the Republic of Kazakhstan and near the city of Kokshetau, the Alekseyevskoye kaolinite deposit developed by Arai Pro LLP is the most promising. At the deposit, the balance kaolin reserves of categories B, C$_1$, and C$_2$ are 13.665, 67.228, and 174.261 million tons, respectively. The average stripping ratio is not more than 1 m$^3$/t.

At present, Arai Pro extracts about 300 thousand tons of raw kaolin, which is exported to the Russian Federation. The relatively high content of REE reaching 1% is one of the advantages of the kaolinite of the Alekseyevsky deposit, where the bulk is represented by erbium.

We are developing a technology for complex waste-free processing of kaolinite from the Alekseyevsky deposit to obtain alumina concentrate, a wide range of popular kaolinite products for use in the production of fine ceramics, pharmaceuticals, cosmetics, and high-purity quartz products.

To create a cost-effective technology for the processing of kaolinite clays, the proposed method provides for the operation of preliminary chemical activation of the feedstock at the head of the process. It will allow, with further gravitational enrichment, to effectively isolate high-quality kaolinite and quartz products and significantly reduce the flow of materials supplied for sintering. Preliminary chemical activation is a key operation of the proposed technology. It enables not only to increase the efficiency of gravity concentration but also has a positive effect on further hydrochemical processing. When developing the technology in the research, it was taken into account that the optimal modes of preliminary chemical activation and processing depend on the characteristics of the feedstock.

The purpose of the research was to increase the efficiency of the complex processing of kaolinite clays in Kazakhstan due to the preliminary chemical activation of clay in a sodium bicarbonate solution.

**Experimental part**

The research used X-ray fluorescence, chemical, X-ray phase, and thermal analyzes. X-ray fluorescence analysis was performed on a Venus 200 wave dispersion spectrometer (PANalyical B.V., Holland).

Samples were chemically analyzed using Optima 2000 DV, an optical emission spectrometer with inductively coupled plasma (USA, Perkin Elmer). Semi-quantitative X-ray phase analysis was performed on a D8 Advance (BRUKER) diffractometer using copper Cu–K$\alpha$ radiation at an accelerating voltage of 36 kV and a current of 25 mA. Thermal analysis was performed on STA 449 F3 Jupiter, a synchronous thermal analysis instrument. The results obtained from the STA 449 F3 Jupiter were processed using the NETZSCH Proteus software.

**Discussion of the results**

A representative sample of a kaolinite clay from the Alekseyevsky deposit, provided by Arai Pro LLP and corresponding to the company standard 101240014515-01-2019 was the initial product for the research.

The appearance of a sample of kaolinite clay is loose whitish sand with a density of 2.06 g/cm$^3$, bulk density 1.36 kg/cm$^3$, pH 7.7, with an average grain size of 2 mm. Chemical composition of the kaolinite clay sample from the Alekseyevsky deposit (wt %): Al$_2$O$_3$ 26.9; SiO$_2$ 56.6; Fe$_2$O$_3$ 0.537; Na$_2$O 0.07; SO$_3$ 0.028; K$_2$O 1.31; LOI: 14.555, silicon...
module ($\mu_s$) 0.47. The silicon modulus ($\mu_s$) is determined by the mass ratio of Al$_2$O$_3$:SiO$_2$.

X-ray phase analysis of a sample of kaolinite clay indicates the presence of the following minerals (wt %): kaolinite 31.1; quartz 67.5 and muscovite 1.1.

Figures 1 and 2 show the results of thermal analysis of a sample of kaolinite clay from the Alekseyevskoye deposit.

![Figure 1 - Heating curves of a kaolinite clay sample from the Alekseyevskoye deposit](image1)

![Figure 2 - Cooling curves of a kaolinite clay sample from the Alekseyevskoye deposit](image2)

The DTA curve showed an intense endothermic effect with maximum development at 167.8°C. An even more intense endothermic effect with maximum development at 566.6°C was also noted. On its ascending branch, one more endothermic effect with an extremum at 575°C was noted. They are developed against the background of an intensive decrease in the weight of the sample, which can be seen from the course of the curve. In addition to endothermic effects, strong and weak exothermic effects with peaks at 993.8°C and 647.2°C, respectively, were recorded. Additional endothermic effects with extrema at 172.2°C, 539.8°C, 555.9°C, 649.3°C can be noted on the dDTA curve.

Kaolinite or hydrated halloysite (endellite, a kaolin group mineral) is the main phase of the sample. Its manifestation is associated with endothermic effects (-)167.8°C, (-)566.6°C, and exothermic effect is (+)993.8°C. The endothermic effect with an extremum at 575°C on the DTA curve and endothermic effects with extrema at 539.8°C, 555.9°C on the dDTA curve can be a manifestation of the dehydration of aluminum hydroxides, may be boehmite, diaspora with various degrees of grinding. In addition, the combination of the endothermic effect with an extremum at 167.8°C and the exothermic effect with a peak at 993.8°C on the DTA curve can be a manifestation of the clay mineral allophane (mAl$_2$O$_3$nSiO$_2$pH$_2$O). The combination of the endothermic effect with an extremum at 167.8°C and an exothermic effect with a peak at 647.2°C can be interpreted as a manifestation of the opal SiO$_2$nH$_2$O. In superposition, in the temperature range of 500 - 600°C, the decomposition of the siderite impurity is also possible. These effects may be due to the polymorphic transformation 2CaO·SiO$_2$.

Sieve analysis of a representative sample of kaolinite clay from the Alekseyevskoye deposit was performed (table 1).

<table>
<thead>
<tr>
<th>Size</th>
<th>Yield, %</th>
<th>Na$_2$O</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>TiO$_2$</th>
<th>SO$_3$</th>
<th>K$_2$O</th>
<th>LOI</th>
<th>μSi</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.05</td>
<td>51.97</td>
<td>0.03</td>
<td>23.47</td>
<td>60.85</td>
<td>0.69</td>
<td>0.48</td>
<td>2.5</td>
<td>0.09</td>
<td>0.61</td>
<td>11.28</td>
<td>0.386</td>
</tr>
<tr>
<td>-0.05+0.02</td>
<td>44.69</td>
<td>0.068</td>
<td>29.89</td>
<td>46.65</td>
<td>0.597</td>
<td>0.19</td>
<td>0.79</td>
<td>0.028</td>
<td>1.31</td>
<td>20.477</td>
<td>0.641</td>
</tr>
<tr>
<td>-20 + 10 μm</td>
<td>3.05</td>
<td>0.09</td>
<td>32.07</td>
<td>48.09</td>
<td>0.631</td>
<td>0.313</td>
<td>0.57</td>
<td>0.23</td>
<td>1.48</td>
<td>16.526</td>
<td>0.667</td>
</tr>
<tr>
<td>-10 μm</td>
<td>0.29</td>
<td>0.176</td>
<td>30.35</td>
<td>46.59</td>
<td>0.689</td>
<td>0.24</td>
<td>0.53</td>
<td>0.26</td>
<td>1.39</td>
<td>19.775</td>
<td>0.651</td>
</tr>
</tbody>
</table>
For further research, a fine fraction with a particle size of 0.05 mm was isolated by washing with running water at room temperature.

Chemical composition of fine clay fraction (wt%): $\text{Al}_2\text{O}_3$ 31.2; $\text{SiO}_2$ 51.6; $\text{Fe}_2\text{O}_3$ 0.53; $\text{CaO}$ 0.43; $\text{Na}_2\text{O}$ 0.095; $\text{MgO}$ 0.2; $\text{SO}_3$ 0.02; $\text{K}_2\text{O}$ 1.5; $\text{TiO}_2$ 1.05; $\text{Cl}^-$ 0.02; LoI: 13.355; $\mu_{\text{si}}$ 0.6. Content of rare earth elements: Ce 0.44376; Dy 0.00056; Er 0.19488; Eu 0.00298; Gd 0.01049; Ho 0.00125; La 0.00623; Lu 0.00008; Nd 0.00023; Pr 0.02006; Sc 0.00229; Sm 0.00547; Tb 0.00710; Tm 0.00191; Y 0.00048; Yb 0.00034; $\Sigma$REM 0.69811. The fines yield was 41.4%.

The phase composition of the fine fraction is presented (wt %) by kaolinite 63.2; quartz 21.6 and muscovite 15.3.

The chemical composition of the coarse fraction $+$ 0.05 mm is as follows, wt%: $\text{Al}_2\text{O}_3$ 7.65; $\text{SiO}_2$ 65.5; $\text{Fe}_2\text{O}_3$ 0.68; $\text{CaO}$ 0.29; $\text{Na}_2\text{O}$ 0.031; MgO 0.08; $\text{SO}_3$ 0.05; $\text{K}_2\text{O}$ 0.39; $\text{TiO}_2$ 0.9; LoI: 24.413; $\mu_{\text{si}}$ 0.12. Content of rare earth elements: Ce 0.65758; Dy 0.09495; Ho 0.00195; Gd 0.01485; Er 0.00076; La 0.00638; Lu 0.0004; Nd 0.00051; Pr 0.02981; Sc 0.00131; Sm 0.0002; Tb 0.00349; $\Sigma$REM 0.81686.

The phase composition of the coarse clay fraction is represented by 100% quartz. To determine the optimal conditions for the preliminary chemical activation of kaolinite clay, the process was performed in a solution containing 40÷120 g/dm$^3$ NaHCO$_3$ at a L:S ratio of 2÷10.0 and temperatures of 90÷230°C using a thermostated unit with 6 autoclaves rotating through the head with a working volume of 250 cm$^3$ (Figure 3); the activation duration was 30÷300 minutes. The maximum content of sodium bicarbonate in the solution was 120 g/dm$^3$, taking into account its solubility limit. The initial weight of a kaolinite clay sample was 25.0 g.

X-ray phase analysis of the kaolinite fraction of clay after chemical activation under optimal conditions is represented by kaolinite 54.8%, quartz 28.0%, muscovite 8.0%, sodium aluminosilicate 5.5%, and magnetite 3.7%. The analysis of the results showed that after preliminary chemical activation of the clay:

- the yield of kaolinite fraction increased from 48.03% to 76.39%;
- dispersion increased, the class yield was 0.02 microns (increased from 3.34 to 11.7%);
- the yield of $\text{Al}_2\text{O}_3$ in the kaolinite fraction increased by 30.6%. The yield of $\text{Al}_2\text{O}_3$ in the quartz fraction was only 5.67% after activation.
The effect of preliminary chemical activation of kaolinite clays from the Alekseyevsky deposit of the Republic of Kazakhstan in a sodium bicarbonate solution on the qualitative separation of kaolinite and quartz fractions was studied. The yield of the kaolinite fraction after clay activation increased from 48.03% to 76.39%.

As a result of activation, the phase composition of the kaolinite fraction has changed: the percentage of the kaolinite fraction decreased; new phases of muscovite and sodium aluminosilicate appeared; the amount of quartz increased. A decrease in the content of a chemically stable fraction of kaolinite in clay will increase the efficiency of processing when extracting Al₂O₃.

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Каолинитті сزادар Қазақстан Республикасының алюминий алмасуы үшін шыққа келтіріледі

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Каолинитті саздар Қазақстан Республикасының алюминий және кремнеземдік балшықтарының басты маңыздылығын алады. Алматы, Қазақстан. ORCID ID: 0000-0003-1474-8354, Email: bagdaulet_k@mail.ru

Аннотация
В качестве дополнительного источника для получения глинозема в Республике Казахстан могут служить каолинитовые глины. Наиболее перспективным является Алексеевское месторождение. Для получения высококачественной каолиновой фракции, необходимы разработки новых технологий обогащения. Ранее этот способ был применен в рудах каолинитового оборудования, но результаты хотя и приближенные, но не удовлетворительные.

Каолинитовые глины как источник сырья для алюминиевой отрасли Ресооблик Казахстан

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Reference


