



# Article Selective Processing of the Kaolinite Fraction of High-Silicon Bauxite

Sergey Gladyshev <sup>1</sup>, Symbat Dyussenova <sup>2</sup>, Yerkezhan Abikak <sup>1</sup>, Nazym Akhmadiyeva <sup>1</sup>,\*, Leila Imangaliyeva <sup>1</sup> and Arina Bakhshyan <sup>2</sup>

- <sup>1</sup> Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty 050010, Kazakhstan; gladyshev.sergey55@mail.ru (S.G.); abikak.erkezhan@mail.ru (Y.A.); leila.imangalieva@mail.ru (L.I.)
- <sup>2</sup> Department of Metallurgy and Mineral Processing, Satbayev University, Almaty 050010, Kazakhstan; dusenova\_s@mail.ru (S.D.); arinasmolkova@gmail.com (A.B.)
- \* Correspondence: akhmadiyeva141@gmail.com

Abstract: When processing low-quality gibbsite-kaolinite bauxites, technologies that involve different methods of mechanical and chemical enrichment with the separation of a difficult-to-utilize fine kaolinite fraction for disposal are used. Before production, problems related to waste storage and disposal arise. To solve the problem of utilization, it is necessary to develop an effective technology for the selective processing of the kaolinite fraction. The efficiency of the technology will depend on the quality of pretreatment of raw materials prior to processing for Al<sub>2</sub>O<sub>3</sub> extraction. Preliminary preparation of kaolinite fraction is associated with the maximum removal of excess silica during chemical enrichment by treatment with an alkaline solution. The presence of silica reduces the quality of final alumina products and requires a large consumption of reagents during the desiliconization of aluminate solutions. During the chemical enrichment of kaolinite fraction in alkaline solution, a serious problem of the co-dissolution of  $Al_2O_3$  with silica arises. The solution to this problem can be the transformation of phase composition with the transformation of kaolin into a chemically resistant compound corundum, which will create conditions for the selective removal of silica. Kazakhstan's alumina refinery, Pavlodar Aluminum Smelter, processes low-quality gibbsite-kaolinite bauxite from the Krasnogorsk deposit. To improve the quality of bauxite, preliminary gravity enrichment is carried out to separate the kaolinite fraction to a quantity greater than 50%. The purpose of this work was to study the possibility of the selective processing of the kaolinite fraction via various techniques, including preliminary thermal transformation, through sintering, chemical enrichment, autoclave leaching in a circulating aluminate solution, and low-temperature desiliconization, to obtain a solution for decomposition. As a result of this study, the possibility of obtaining a corundum phase after sintering at a temperature of 900–1000 °C was established, which made it possible to obtain 58.8% chemical enrichment through the extraction of SiO<sub>2</sub> into solution. Further use of the enriched kaolinite fraction in autoclave leaching in a circulating aluminate solution with low-temperature desiliconization made it possible to obtain an aluminate solution with a caustic modulus of 1.65–1.7, which is suitable for decomposition.

**Keywords:** bauxite; kaolinite fraction; thermal transformation; roasting; chemical enrichment; leaching; caustic modulus

# 1. Introduction

The Pavlodar aluminum plant (PAP) currently handles low-quality gibbsite–kaolinite bauxite from the Krasnogorsk deposit in the Republic of Kazakhstan. The chemical composition of bauxite is not stable; it varies spatially among different areas and in vertical sections. The main aluminum-containing mineral is gibbsite (Al(OH)<sub>3</sub>), which is found in three forms: amorphous (gibbsite gel), cryptocrystalline, and crystalline [1]. Among



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). other minerals, small amounts of aluminum-containing boehmite ( $\gamma$ -AlO(OH)) and diaspore (AlO(OH)) are present. Boehmite and diaspore under leaching conditions at atmospheric pressure and a temperature of approximately 100 °C are not processable and are sources of Al<sub>2</sub>O<sub>3</sub> loss in the Bayer process. Minerals containing silicon include kaolinite (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O, the main silicon-containing material of bauxite), quartz (SiO<sub>2</sub>), and chamosite ( $(Fe,Al,Mg)_6(SiA_{14})O_{10}(OH)_8$ ). During leaching, kaolinite interacts with alumina-alkaline solutions to form a precipitate of sodium hydroalumina silicate. Thus, kaolinite is a harmful impurity in bauxite processing via the Bayer method [1,2]. Quartz under conditions of bauxite leaching at atmospheric pressure in a temperature range of 100–150 °C is inert and does not enter the solution. Chamosite is a kaolinite mineral; it also does not dissolve and becomes sludge. Iron-containing minerals include haematite  $(Fe_2O_3)$ , goethite (FeOOH), aluminogoethite, magnetite (Fe<sub>2</sub>O<sub>3</sub>·FeO), and pyrite (FeS<sub>2</sub>). These minerals are practically insoluble in the process of low-temperature bauxite leaching, but they are sources of sulfides and sulfates. When interacting with alkaline solutions, pyrite forms iron trioxide, sodium sulfide, and polysulfide, which leads to the loss of alkalis. The carbonate minerals include siderite (FeCO<sub>3</sub>) and calcite (CaCO<sub>3</sub>). Siderite interacts with alkaline solutions, which leads to decausticization due to the formation of carbonate alkali. Calcite decomposes with alkali to form calcium hydroxide and soda. When processing low-quality bauxite, carbonate and sulfur components accumulate in the circulating solutions and are constantly removed by evaporation of a part of the solution to induce crystallization to obtain a soda-sulfate mixture. Bauxite contains the titanium mineral anatase, which can serve as a source of alkali loss due to the formation of sodium hydrotitanates. In addition to the listed minerals, bauxite contains a significant amount of organic substances, which negatively affect all technological stages of the Bayer process of production [3–5]. The mineralogical and chemical composition of the gibbsite–kaolinite bauxite of the Krasnogorsk deposit determines the degree of Al<sub>2</sub>O<sub>3</sub> extraction achieved (i.e., 70%) using the Bayer method at the PAS. Approximately 30% of the  $Al_2O_3$  remains in the sludge (red mud) in the form of aluminosilicates. To increase the extraction of alumina, red mud is processed via an energy-consuming, environmentally harmful sintering technique.

To reduce the negative impact of impurities on the technological stages of the Bayer process, the PAS introduced two bauxite enrichment schemes at the grinding stage: a scheme for removing the kaolinite fraction and a scheme for removing ferruginous sand. The ballast fractions containing a large proportion of the bauxite impurities are discarded into the dump before they have time to react with the alkaline solution to form products harmful to the processing steps.

The presence of large quantities of kaolinite in Kazakhstan bauxite is a serious obstacle to increasing the efficiency of alumina production at the PAS because of the slowing of the leaching process and a decrease in the level of aluminum oxide extraction in the Bayer process [1]. An increase in the kaolinite content in processed bauxite leads to an increase in the loss of aluminum and alkalis in the form of sludge during the desiliconization of aluminate solutions. The finely dispersed sodium hydroalumina silicate formed during desiliconization negatively affects the settling of red mud and disrupts the thickening and washing regime, increasing the amount of sludge entering the sintering shop. The development of technological solutions for the removal of the kaolinite fraction using Bayer processing is an urgent task of scientific and practical importance.

Various methods of mechanical and chemical purification of bauxite are used to preliminarily remove clay minerals (such as kaolinite) from bauxite ore [6]. Bauxite ore of a specific grain size is usually wet-screened on vibrating or curved screens. In this case, clay minerals with high silica contents are collected into a small fraction (<1.7 mm) and removed from the ore. In reference [7], a combination of a drum washer and a cyclone was used to remove quartz. The possibility of removing clay from Egyptian bauxite via ultrasonication and drum and water jet washing was investigated [8]. The beneficial effects of ultrasonication were noted.

In the enrichment of low-quality bauxite, in addition to the removal of silicate minerals (kaolinite, quartz, etc.), great attention has been given to the reduction of iron or calcareous impurities, mainly by gravity concentration [9]. Concentrating gibbsite via reverse froth flotation is performed in order to obtain a metallurgical-grade Brazilian bauxite concentrate. Tailings from an industrial plant have undergone attrition scrubbing and desliming; the quartz silica contained in the tailings has undergone flotation. The optimum pH is around 10.0 [10]. However, since the difference in density between bauxite and silicate minerals is relatively small, the gravity enrichment method is rarely used.

Magnetic separation is mainly used for iron removal and rarely for silica removal [11]. To improve the efficiency of magnetic separation, microwave energy was applied to magnetize the sintering of high-iron bauxite via iron shavings as a reducing agent [12]. Magnetic sintering of the bauxite sample was carried out with the addition of 20-40% chips at temperatures ranging from 870 to 880 °C. The alumina content in the nonmagnetic fraction increased to 87.5%, compared with 53.6% in the original sample. Hydrocyclone and magnetic separation were used to reduce the iron content [13], which increased the iron content of the separated magnetic fraction from 52% to 70% Fe<sub>2</sub>O<sub>3</sub>. In [14], the process of prereduction roasting of bauxite feedstock prior to enrichment by magnetic separation was modeled to determine the optimum temperature, mass ratio of carbon to bauxite residue, and duration. Under optimum conditions, an almost complete conversion of haematite to iron-magnetic phases (>99 wt%) was obtained. In [15], the removal of iron in the form of magnetite from bauxite ore was investigated via carbothermal reduction and magnetic separation. Using microwave-assisted reduction roasting of bauxite feedstock via lignite followed by wet magnetic separation, a feedstock suitable for the production of sponge or iron castings was obtained [16].

Studies of the flotation enrichment of bauxite ores have been performed. Flotation separation (direct or reverse), followed by flocculation as an effective pretreatment method, is the main technology for bauxite enrichment. One study [17] provides an overview of the main stages of the flocculant technology used in the alumina refining process. Notably, many advances in enrichment have been associated with the introduction of liquid- or emulsion-based flocculants, which have become widespread in industry. The advantages and disadvantages of various flocculant technologies for the precipitation of a difficult-to-fill bauxite leaching residue, red mud, were reviewed. In [18], polyacrylate and hydroxamate flocculants were used to separate bauxite residue from the leaching solution. In addition to flotation and reverse flotation, selective flocculation, which is a new method, has been used to solve the problem of bauxite dewatering in China [19]. The method of the selective flocculation of bauxite using hydrolyzed polyacrylamide as a flocculant was tested and evaluated. As a result, a concentrate with a high  $Al_2O_3$  content of 65.75% was obtained through the selective flocculation of bauxite. In [20,21], different approaches to the selective flotation of bauxite ores under different conditions were proposed, and prospects for further studies were outlined. In [22], flotation experiments were conducted using a collector (Hidroxamate-Cytec) to reduce the iron content. As a result, a concentrate containing 3.74% Fe<sub>2</sub>O<sub>3</sub> and 60.00% Al<sub>2</sub>O<sub>3</sub> with a recovery of 40.87% was obtained.

Improving kaolinite-bearing bauxite by preroasting is a potential method for removing silica from ore and incorporating it into the Bayer process. Caustic soda consumption is significantly reduced if precalcined bauxite is used in the Bayer process [6]. The disadvantage of this method is its relatively high cost. When heated, kaolinite undergoes structural changes and phase transformations. In a temperature range of 530–570 °C, kaolinite turns into metakaolinite, which has a relatively high reactivity. At higher temperatures (approximately 980 °C), the crystalline structure is destroyed, and amorphous silica and various transition phases of aluminum are formed. The primary role of the calcination process prior to leaching is to create a significant difference in solubility between the amorphous silica and aluminum particles from kaolin in a weak alkaline solution.

Several methods have been combined to achieve the enrichment of low-quality bauxite, including preliminary chemical activation, gravity enrichment, roasting, and chemical enrichment [23]. As a result of chemical activation in a solution of sodium bicarbonate, a change in the phase structure of bauxite occurs, which subsequently ensures a high degree of separation of the coarse gibbsite fraction (CGF) from the high-silica fine kaolinite fraction (FKF) during gravitational enrichment. The separated CGF is then subjected to roasting followed by chemical enrichment in an alkaline solution. As a result of the operations performed, conditioned bauxite with a silicon modulus of more than seven is obtained, which meets the requirements for processing via the simplest and most economical Bayer method.

Thus, by using preenrichment, it is possible to improve the quality of bauxite by separating high-silica (kaolinite) and high-iron materials. Additionally, the large amount of material released during enrichment results in an urgent need for its disposal. The amount of allocated FKF at the PAS is more than 50%, and the quality of bauxite is deteriorating.

The purpose of this work was to study the possibility of the selective processing of high-silica alumina-containing kaolinite fraction extracted as a result of the gravitational enrichment of low-quality gibbsite–kaolinite bauxite from the Krasnogorsk deposit of Kaza-khstan, including preliminary thermal transformation by roasting, chemical enrichment, autoclave leaching in a recycled aluminate solution, and low-temperature desiliconization combined with obtaining the solution necessary for aluminum hydroxide extraction from the decomposition of aluminum hydroxide.

#### 2. Materials and Methods

#### 2.1. Methods of Analysis

A chemical analysis of the samples was performed on an Optima 2000 DV optical emission spectrometer with inductively coupled plasma (PerkinElmer, Shelton, CT, USA), and an X-Ray fluorescence analysis was carried out on a Venus 200 PANalyical BV wavedispersive spectrometer (PANalyical BV, Almelo, The Netherlands).

The X-Ray phase composition of the samples was investigated on the X-Ray diffraction apparatus BrukerD8 Advance device using copper radiation at an accelerating voltage of 36 kW and a current of 25 mA. The sample, which was ground to a particle size of 0.056 mm, was placed in a cuvette pretreated with alcohol. The sample was evenly distributed throughout the cuvette, compressed, and placed in the apparatus. The International Centre for Diffraction Data ICDD PDF-2 2023 database was used to confirm the accuracy of phase identification.

The infrared analysis was carried out on an FTIR spectrometer (Avatar 370) with a spectral range of 4000–300 cm<sup>-1</sup>. Samples in the form of tablets were prepared by pressing 2 mg of sample and 200 mg of KBr. The spectrum of KBr was used for comparison. Baseline correction was performed automatically. The transmission ESP attachment was used to carry out the analyses.

A differential thermal analysis (DTA) was performed using an STA 449 F3 Jupiter (Munchen, German) synchronous thermal analysis instrument.

The caustic modulus  $\alpha_k$  was determined from the ratio of Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> × 1.645.

The silicon modulus ( $\mu_{Si}$ ) of the samples was determined from the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio.

Na<sub>2</sub>O<sub>ta</sub>—sodium oxide with total alkali.

Na<sub>2</sub>O<sub>ca</sub>—sodium oxide with carbonate alkali.

Na<sub>2</sub>O<sub>cu</sub>—sodium oxide with caustic.

#### 2.2. Experimental Methods

Thermal transformation was carried out in a tubular rotary kiln, which allows for uniform sintering as a result of mixing.

Sintering was carried out at a temperature of 900–1000 °C for 2 h.

Chemical enrichment (desiliconization) of the sintered FKF was carried out in a thermostated glass by stirring in a solution containing  $100 \text{ g/dm}^3 \text{ Na}_2 O_{cu}$  at a temperature of  $100 \,^{\circ}\text{C}$ , with a liquid-to-solid ratio of 6 and a duration of 2 h.

Autoclave leaching of enriched FKF was carried out at 240 °C for 2 h with a liquid-to-solid ratio of 2 in solutions containing 118.3 g/L of  $Al_2O_3$ ,  $Na_2O_{ta}$  (256.7 g/L),  $Na_2O_{ca}$ 

(30.7 g/dm<sup>3</sup>), and Na<sub>2</sub>O<sub>cu</sub> 226.0 (g/L) and a caustic modulus of  $\alpha_k = 3.14$  units. The dosage of the circulating solution was determined based on the calculation of the solution at  $\alpha_k - 1.48$ .

Desiliconization of the diluted autoclave-stirred leaching slurry up to an Na<sub>2</sub>Ocu content of 120 g/dm<sup>3</sup> was carried out at a temperature of 105 °C and a duration of 24 h.

The solution was forwarded to decomposition for  $Al(OH)_3$  extraction. The alkaline solution was recycled and returned for leaching after it was evaporated to 300 g/dm<sup>3</sup> of Na<sub>2</sub>O.

# 3. Results and Discussion

## 3.1. Analysis of the Original Sample

The initial raw material for the research was FKF isolated using gravitational enrichment at the PAS from gibbsite–kaolinite bauxites from the Krasnogorsk deposit [1]. The percentage (fraction yield) of the FKF with respect to the mass of the original bauxite was greater than 50%.

The FKF chemical composition in mass % was as follows:  $Al_2O_3$  40.26;  $SiO_2$  25.15;  $Fe_2O_3$  19.39;  $Na_2O$  0.187;  $TiO_2$  2.5; others 12.63; and  $\mu Si$  1.6.

The X-Ray phase composition of the FKF suggests that the sample was composed of gibbsite, kaolinite, iron titanium oxide, goethite, and halloysite (Figure 1).



Figure 1. X-Ray image of the FKF.

The infrared spectrum of the FKF is presented in Figure 2.

In the infrared spectrum of the original FKF sample, vibration modes at 3621, 3527, 3450, 3394, 3376, 1637, 1104, 1033, 968, 799, 748, 670, 558, 540, 471, and 428 cm<sup>-1</sup> are characteristic of the gibbsite  $\gamma$ Al(OH)<sub>3</sub> phase; those at 3695,3668, 3652, 3621, 1637, 1104, 1033, 1010, 936, 914, 799, 696, 540, 471, and 428 cm<sup>-1</sup> are characteristic of the kaolinite Al<sub>4</sub>[(OH)<sub>8</sub> | Si<sub>4</sub>O<sub>10</sub>] phase; those at 914, 799, 670, 578, 471, and 428 cm<sup>-1</sup> are characteristic of the goethite  $\alpha$ -FeOOH phase; those at 3695, 3621, 1637, 1104, 1033, 1010, 914, 696, 540, 471, and 428 cm<sup>-1</sup> are characteristic of the halloysite Al<sub>4</sub>[(OH)<sub>8</sub> | Si<sub>4</sub>O<sub>10</sub>](H<sub>2</sub>O)<sub>4</sub> phase; and those at 578 and 343 cm<sup>-1</sup> are characteristic of the anatase TiO<sub>2</sub> phase.

The study of the FKF using the thermal method of analysis (Figure 3) showed the presence of gibbsite, iron hydroxide, kaolinite, and coarse crystalline siderite. Intense endothermic effects with maximum development were recorded on the DTA curve at





Figure 2. Infrared spectrum of the FKF.



Figure 3. Thermogram of the initial gibbsite-kaolinite bauxite sample from the Krasnogorsk deposit.

The combination of an endothermic effect with an extremum at 557 °C on the DTA curve and a weak exothermic effect with a peak at 989.9 °C on the dDTA curve may be a manifestation of kaolinite. The combination of the same endothermic effect with an exothermic effect with a peak at 897.8 °C on the dDTA curve may reflect the presence of coarse crystalline siderite. Coarse crystalline siderite at 557 °C on the DTA curve indicates the dissociation of FeCO<sub>3</sub> into FeO, Fe<sub>3</sub>O<sub>4</sub>, and CO<sub>2</sub>. The endothermic effect, with an extremum at 557 °C on the DTA curve, reflects the release of water associated with hydroxyl groups. Additionally, amorphization of the substance occurs at this temperature. The exothermic effect, with a peak at 989.9 °C on the DTA curve, reflects the crystallization of shullite–3Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. After dehydration, kaolinite forms amorphous Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and metakaolinite.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \tag{1}$$

The FKF sample analysis using analytical techniques of XRF supported the aforementioned analyses, while gibbsite, kaolinite, goethite, and halloysite minerals phases identified using FTIR matched the identification made by XRD well. It is concluded that the traditional analytical methods of XRF, XRD, DTA, and FTIR assisted with the mineralogical composition understanding of FKF in the present study.

Selective processing for the FKF of high-silicon bauxite was carried out via various methods, including preliminary thermal transformation, chemical enrichment, autoclave leaching in a circulating aluminate solution, and low-temperature desiliconization, to obtain a decomposition solution (Figure 4).



Figure 4. Technological scheme for processing the FKF.

# 3.2. Prethermal Transformation

The purpose of conducting the preliminary thermochemical transformation was to produce a chemically stable aluminum-containing corundum phase, which prevents the transition of  $Al_2O_3$  into an alkaline solution and ensures the maximum dissolution of amorphous  $SiO_2$  during the chemical enrichment of the FKF. The scheme of the thermochemical transformation of aluminum hydroxide during sintering is shown in Figure 5.

|            | 200 °C          | 300-400 °C                           | boehmite and         | 1 500 °C                                 |
|------------|-----------------|--------------------------------------|----------------------|--|
| $AI(OH)_3$ | deh             | ydration                             | amorphous<br>alumina | -  |
|            | 600-900 °C<br>► | $\gamma$ - $Al_2O_3$ and - amorphous | 1000-1100 °C         | beginning of transition to               |
|            |                 | oxide residue                        |                      | $\alpha$ -Al <sub>2</sub> O <sub>3</sub> |

Figure 5. Thermal transformation reactions of aluminum hydroxide.

Physicochemical studies of the composition of the material obtained as a result of sintering the FKF samples were carried out, Table 1.

| Description         | Weight a  | Content, %                     |                  |                                |                   |                  |       |      |  |
|---------------------|-----------|--------------------------------|------------------|--------------------------------|-------------------|------------------|-------|------|--|
| Description         | weight, g | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | TiO <sub>2</sub> | Other |      |  |
| Initial fraction    | 100       | 40.26                          | 25.15            | 19.39                          | 0.07              | 2.50             | 12.63 | 1.60 |  |
| roasting at 900 °C  | 86.1      | 46.72                          | 27.05            | 20.18                          | 0.12              | 2.69             | 5.93  | 1.72 |  |
| roasting at 950 °C  | 86.3      | 46.66                          | 27.54            | 19.92                          | 0.09              | 2.68             | 3.11  | 1.69 |  |
| roasting at 1000 °C | 87.3      | 46.09                          | 26.30            | 20.07                          | 0.11              | 2.67             | 4.76  | 1.75 |  |

Table 1. Chemical composition of the FKF after sintering.

Sample No. 1—FKF after sintering at a temperature of 900 °C. Sample No. 2—FKF after sintering at a temperature of 950 °C. Sample No. 3—FKF after sintering at a temperature of 1000 °C.

The X-Ray phase composition of the FKF depending on the sintering temperature is given in Table 2 and Figures 6–8.

Table 2. X-Ray phase composition of the FKF as a function of the sintering temperature.

|                     | Initial    | <b>Roasting Temperature</b> , °C |      |      |  |  |  |  |
|---------------------|------------|----------------------------------|------|------|--|--|--|--|
| Description         | IIIItiai   | 900                              | 950  | 1000 |  |  |  |  |
| -                   | Content, % |                                  |      |      |  |  |  |  |
| Gibbsite            | 48.8       |                                  |      |      |  |  |  |  |
| Kaolinite—1 A       | 15.9       |                                  |      |      |  |  |  |  |
| Iron titanium oxide | 14.7       |                                  |      |      |  |  |  |  |
| Goethite            | 10.8       |                                  |      |      |  |  |  |  |
| Halloysite          | 9.8        |                                  |      |      |  |  |  |  |
| Haematite           | -          | 68.4                             | 82.1 | 87.0 |  |  |  |  |
| Quartz              | -          | 18.0                             | 17.9 | 13.0 |  |  |  |  |
| Anatase             | -          | 13.7                             | -    | -    |  |  |  |  |



**Figure 6.** X-Ray image of the FKF after sintering at 900  $^{\circ}$ C.



Figure 7. X-Ray image of the FKF after sintering at 950 °C.





As a result of sintering, the crystalline part of the samples was destroyed. The content of the X-Ray amorphous fraction at 900 °C was 34.3%, that at 950 °C was 40.0%, and that at 1000 °C was 45.5%. The contents of other phases could not be determined using an X-Ray phase analysis.

To clarify the phase composition of the samples, an IR analysis was performed after sintering (Figures 9–11).

The infrared spectrum of the FKF sample after preliminary sintering at 900 °C showed intense absorption in a range of 900–500 cm<sup>-1</sup>, with a maximum at 573 cm<sup>-1</sup>, which is characteristic of amorphous aluminum oxide (Al<sub>2</sub>O<sub>3)</sub> and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase. The peaks at 1094, 800, and 478 cm<sup>-1</sup> are characteristic of SiO<sub>2</sub>. In addition to the intense absorption of the oxides Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, vibration modes at 590, 540, 478, 377, and 328 cm<sup>-1</sup> were recorded, which are characteristic of the iron oxide  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase. The peak at 1402 cm<sup>-1</sup> is characteristic of the [CO<sub>3</sub>]<sup>2–</sup> group, and those at 635 and 573 cm<sup>-1</sup> are characteristic of corundum Al<sub>2</sub>O<sub>3</sub>. The absorption band at 492 cm<sup>-1</sup> falls into the region where AlO<sub>6</sub> polyhedra appear.

The infrared spectrum of the sample after sintering at 950 °C revealed intense absorption in a range of 900–500 cm<sup>-1</sup>, with a maximum at 576 cm<sup>-1</sup>, which is characteristic of amorphous aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase. The vibration modes at 1095, 793, and 478 cm<sup>-1</sup> are characteristic of SiO<sub>2</sub>. In addition to the intense absorption caused by the oxides Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, vibration modes at 591, 542, 478, and 372 cm<sup>-1</sup>,

which are characteristic of the presence of the iron oxide  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase, were recorded. The peak at 1402 cm<sup>-1</sup> is characteristic of the [CO<sub>3</sub>]<sup>2–</sup> group; the peaks at 641, 634, 576, and 398 cm<sup>-1</sup> are characteristic of corundum and Al<sub>2</sub>O<sub>3</sub>; the peaks at 641, 605, and 576 cm<sup>-1</sup> are characteristic of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> corundum; and the peaks at 576 and 343 cm<sup>-1</sup> are characteristic of anatase and TiO<sub>2</sub>. The vibrations at 398 and 372 cm<sup>-1</sup> indicate the presence of quartz  $\alpha$ -SiO<sub>2</sub>, and the vibrations at 576, 398, and 343 cm<sup>-1</sup> indicate the presence of rutile and TiO<sub>2</sub>.



Figure 9. Infrared spectrum of the FKF after sintering at 900 °C.



Figure 10. Infrared spectrum of the FKF after sintering at 950 °C.



Figure 11. Infrared spectrum of the FKF after sintering at 1000 °C.

The weak band at 3617 cm<sup>-1</sup> corresponds to the hydroxyl groups of kaolinite  $Al_4[(OH)_8 | Si_4O_{10}]$ , which are directed toward octahedral vacancies. The spectrum does not contain a band of stretching vibrations associated with interlayered hydroxyl groups in kaolinite, with a maximum near 3698 cm<sup>-1</sup> [5]. The absorption band at 492 cm<sup>-1</sup> corresponds to  $AlO_6$  polyhedra.

The infrared spectrum of the sample after preliminary sintering at a temperature of 1000 °C showed intense absorption in a range of 900–500 cm<sup>-1</sup>, with a maximum at 579 cm<sup>-1</sup>, which is characteristic of the amorphous aluminum oxide Al<sub>2</sub>O<sub>3</sub> and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase. The peaks at 1090, 792, and 473 cm<sup>-1</sup> are characteristic of SiO<sub>2</sub>. In addition to the peaks of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, fixed vibration modes at 591 and 473 cm<sup>-1</sup> were observed and are characteristic of the presence of the oxide  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The peak at 1400 cm<sup>-1</sup> is characteristic of the [CO<sub>3</sub>]<sub>2</sub> group. The peaks at 642, 603, and 579 cm<sup>-1</sup> are characteristic of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The peaks at 579 and 340 cm<sup>-1</sup> are characteristic of anatase and TiO<sub>2</sub>.

The band at 491 cm<sup>-1</sup> occurs in region V, indicating the presence of AlO<sub>6</sub> polyhedra. The stripe takeovers at wavenumbers 356 and 349 cm<sup>-1</sup> in region V indicate FeO<sub>6</sub>, Fe<sub>3+</sub>O<sub>6</sub>, and MgO<sub>6</sub> polyhedra.

Physical and chemical studies of the FKF revealed that after sintering, the crystal structure of the samples was destroyed, and the required chemically resistant corundum phase was obtained at temperatures of 950 and 1000 °C.

#### 3.3. Chemical Enrichment

Chemical enrichment of FKF after sintering was carried out using treatment with an alkaline solution; in this case, due to the dissolution of a part of the  $SiO_2$ , there is a decrease in the mass of the sample, and as a result, the percentage of the  $Al_2O_3$  content increases. The chemically resistant corundum phase obtained during firing reduces the transition of  $Al_2O_3$  into solution during alkaline treatment. Chemical enrichment was carried out on the FKF sample after sintering using treatment with an alkaline solution (Table 3).

| Description   | sring Temperature, °C<br>Weight, g |                             |   | Content, %                      |                              |                             |                               |   | Al2O3 Extraction, %         | SiO <sub>2</sub> Extraction, % |
|---|------------------------------------|-----------------------------|---|---------------------------------|------------------------------|-----------------------------|-------------------------------|---|-----------------------------|--------------------------------|
|   | Sinter                             |                             | Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub>  | Na <sub>2</sub> O            | TiO <sub>2</sub>            | Other                         |   |                             |                                |
| With no sintering<br>Sample No. 1<br>Sample No. 2<br>Sample No. 3 | 900<br>950<br>1000                 | 100<br>90.2<br>87.0<br>86.4 | 42.2615.2550.9814.7152.9513.0353.3212.84        | 21.4<br>22.46<br>23.16<br>23.16 | 5.5<br>4.54<br>3.657<br>3.41 | 2.6<br>2.96<br>3.07<br>3.09 | 14.99<br>4.34<br>4.14<br>4.19 | $\begin{array}{c} 2.77 \\ 3.47 \\ 4.06 \\ 4.15 \end{array}$ | 5.7<br>0.28<br>0.24<br>0.24 | 47.1<br>51.0<br>58.8<br>58.5   |

Table 3. Results of the chemical enrichment of the FKF after sintering.

The results of the chemical enrichment of Samples 2 and 3, which contained a chemically resistant corundum phase, confirmed a decrease in the amount of  $Al_2O_3$  extracted into the solution and an increase in the amount of  $SiO_2$  extracted, which resulted in an increase in the silicon modulus of the FKF.

# 3.4. Autoclave Leaching

After chemical enrichment, the FKF was leached in an autoclave using the circulating PAS solution.

The results of autoclave leaching are shown in Tables 4 and 5.

An analysis of the results of autoclave leaching of the sintering FKF in the recycling solution revealed that the optimum conditions were a sintering temperature of 950 °C and

Table 4. Composition of the liquid phase of the sludge.

| Description  |           | Cor                              | μsi          | $\alpha_{\mathbf{V}}$ . Units   |                  |      |      |  |
|--------------|-----------|----------------------------------|--------------|---------------------------------|------------------|------|------|--|
| Description  | $Al_2O_3$ | Na <sub>2</sub> O <sub>tot</sub> | $Na_2O_{ca}$ | Na <sub>2</sub> O <sub>cu</sub> | SiO <sub>2</sub> | 1 51 |      |  |
| Sample No. 1 | 176.9     | 201.7                            | 20.26        | 181.5                           | 1.200            | 147  | 1.69 |  |
| Sample No. 2 | 177.3     | 203.2                            | 23.27        | 180.0                           | 1.190            | 149  | 1.67 |  |
| Sample No. 3 | 177.0     | 203.2                            | 24.77        | 178.5                           | 1.200            | 148  | 1.66 |  |

**Table 5.** Composition of the solid phase of the sludge.

| NT           | Loss From Initial<br>Weight, % | Content, % |                  |                                |                   |                  |        |     | Extract. Al <sub>2</sub> O <sub>3</sub> |
|--------------|--------------------------------|------------|------------------|--------------------------------|-------------------|------------------|--------|-----|---|
| Name         |                                | $Al_2O_3$  | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | TiO <sub>2</sub> | Others | μSi | into Solution, %                        |
| Sample No. 1 | 37.5                           | 23.0       | 21.9             | 30.5                           | 16.1              | 4.2              | 4.3    | 1.0 | 64.2                                    |
| Sample No. 2 | 38.3                           | 24.9       | 20.6             | 31.1                           | 14.8              | 4.5              | 4.2    | 1.2 | 70.4                                    |
| Sample No. 3 | 39.1                           | 29.0       | 18.7             | 29.9                           | 13.8              | 4.3              | 4.2    | 1.6 | 59.8                                    |

## 3.5. Low-Temperature Desiliconization

To obtain an aluminate solution suitable for aluminum extraction via the decomposition method with an  $Na_2O_{cu}$  content of  $\approx 120 \text{ g/dm}^3$ , the autoclave leaching sludge was diluted with water, and the material was then subjected to low-temperature desiliconization.

The compositions of the aluminate solutions and solid phases (red mud) from autoclave leaching after sludge dilution and desiliconization are presented in Tables 6 and 7.

Table 6. Composition of the liquid-phase aluminate solutions after dilution and desiliconization.

| Norma        |           | Co                              | alt Inite    | lle          |                  |           |       |  |
|--------------|-----------|---------------------------------|--------------|--------------|------------------|-----------|-------|--|
| Iname        | $Al_2O_3$ | Na <sub>2</sub> O <sub>ta</sub> | $Na_2O_{ca}$ | $Na_2O_{cu}$ | SiO <sub>2</sub> | ak, Units | μSi   |  |
| Sample No. 1 | 113.2     | 138.5                           | 21.5         | 117.0        | 0.70             | 1.70      | 167.0 |  |
| Sample No. 2 | 113.1     | 129.5                           | 14           | 115.5        | 0.68             | 1.68      | 169.0 |  |
| Sample No. 3 | 117.6     | 131                             | 11           | 118.0        | 0.70             | 1.65      | 168.5 |  |

Table 7. Composition of the solid phase (red mud).

| Name         | Loss From Initial Solid Phase Content, % |                                |                  |                                |                   | olid Phase Content, % |        |      | Extract. Al <sub>2</sub> O <sub>3</sub> into Solution, % |
|--------------|--|--------------------------------|------------------|--------------------------------|-------------------|-----------------------|--------|------|--|
|              | weight, 70                               | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | TiO <sub>2</sub>      | Others |      |  |
| Sample No. 1 | 37.5                                     | 21.4                           | 21.9             | 31.0                           | 16.9              | 3.6                   | 5.2    | 0.98 | 67.6   |
| Sample No. 2 | 34.8                                     | 27.7                           | 21.5             | 25.8                           | 15.8              | 3.5                   | 5.6    | 1.29 | 77,4   |
| Sample No. 3 | 30.1                                     | 33.1                           | 17.5             | 27.9                           | 12.4              | 4.0                   | 5.1    | 1.89 | 61.15  |

Analysis of the results of autoclave leaching of the FKF sintering in the recycling solution revealed that the optimum conditions were a sintering temperature of 950 °C and extraction of 77.4% of the alumina in the solution. Aluminate solutions with caustic moduli ranging from 1.69 to 1.66 suitable for the extraction of aluminum hydroxide via the decomposition method were obtained.

# 4. Conclusions

The technology for the selective processing of the finely dispersed kaolinite fraction isolated from gibbsite–kaolinite bauxite from the Krasnogorsk deposit through gravitational

enrichment was performed. This will solve the problem of storage by utilizing efficient recycling and additional aluminum recovery. It increases the economic feasibility of processing low-quality high-siliceous bauxite. The developed method includes preliminary thermal transformation, chemical enrichment, autoclave leaching in a circulating aluminate solution, and low-temperature desiliconization to obtain a solution for decomposition.

Based on an X-Ray phase analysis, infrared spectroscopy, and thermal analysis, physicochemical studies of samples after sintering at temperatures ranging from 900 to 1000 °C were carried out. As a result of the thermal transformation of the phase composition of the kaolinite fraction at temperatures ranging from 950 to 1000 °C, a chemically stable corundum phase formed. The optimum sintering temperature is 950 °C, at which a chemically resistant corundum phase is formed.

During chemical enrichment, a maximum recovery of 58.8% of the SiO<sub>2</sub> solution was obtained after sintering at a temperature of 950  $^{\circ}$ C.

As a result of autoclave leaching of the enriched kaolinite fraction in a circulating aluminate solution and low-temperature desiliconization, an aluminate solution with a caustic modulus of 1.65–1.7 was obtained. This solution is suitable for decomposition. The alumina recovery was 77.4%. After the leaching sludge was diluted, the degree of desiliconization of the solutions averaged 13.6%.

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