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Research and development of a comprehensive technology for processing kaolinite clays in Kazakhstan

Abstract: In the Republic of Kazakhstan, the most promising are kaolinite clays of the Alekseevsky deposit. For effective processing of clays, it is necessary to develop special methods of processing, since satisfactory results were not achieved when using standard methods of gravity processing. The article provides the results of studies of the effect of preliminary chemical activation on the yield of the kaolinite fraction during gravitational processing. 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 is determined that as a result of preliminary chemical activation, changes in the phase composition occurred. The dependence of the yield of the kaolinite fraction on the temperature of chemical activation, duration, and the ratio of W:T and the concentration of the sodium bicarbonate solution. Based on the results obtained, a technology for the complex processing of kaolinite clays has been developed, which provides for the preliminary chemical activation of the feedstock at the beginning of the process, which will effectively isolate high-quality kaolinite and quartz products, which will significantly reduce the flow of materials entering for sintering. As a result of activation, the phase composition of the kaolinite fraction has changed: the percentage of the kaolinite fraction has decreased; new phases of muscovite and sodium aluminosilicate appeared; the amount of quartz increased.

Keywords: kaolinite, quartz, silicon module, chemical activation, chemical processing, technology.

Introduction

The Pavlodar Aluminum Smelter (PAZ), the only alumina producer in the Republic of Kazakhstan, uses low-quality bauxites from the Krasnooktyabrsk deposit located in the Kostanay region, with a low flint modulus and high iron and carbonate contents [1, 2]. Existing bauxite reserves can be enough to operate PAZ at existing capacities for not more than 15 years, therefore, it is relevant to the search for alternative raw materials sources of alumina, one of which can be kaolinite ores; the world reserves are estimated at 16 billion tons [3]. 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 [4].

The characteristics of the raw materials are of paramount importance when selecting the optimal technological process for processing kaolinite clays, which determine the theoretical yield of alumina, the consumption of reagents in key technological operations and the amount of sludge to be further processed, which should maximally meet the capabilities and interests of the respective region [5].

By now, a significant number of methods for processing kaolins and kaolinite clays are known and continue to be improved, among which acid technologies are historically significant. Their disadvantages are the formation of hard-to-filter finely dispersed sediments and the use of expensive acid-resistant materials and equipment [6-9].

The technology of autoclave opening in the medium of high-modulus aluminate solutions with the precipitation of silica in the form of ferrous hydro-garnets or sodium-calcium hydrosilicate ($Na_2O \cdot 2CaO \cdot 2SiO_2 \cdot H_2O$) is of considerable interest for the processing of kaolinite clays [5]. The undoubted advantage of this method is its versatility and the possibility of using the hydrometallurgical process for processing high-silicon raw materials of various nature. Additionally, it is distinguished by the significant complexity of the technological scheme and its hardware design, which has ruled out the industrial implementation of this method until now.

The most industrially developed method is the technology of sintering kaolin raw materials with soda and limestone added in a ratio based on the following stoichiometry [10]:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 4CaCO_3 + Na_2CO_3 = 2NaAlO_2 + 2(2CaO \cdot SiO_2) + 2H_2O + 5CO_2 \qquad (1)$$
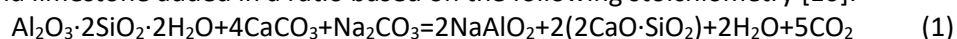
This stoichiometry makes it possible to determine the mass of the charge, as well as to estimate the consumption of reagents and the yield of sludge, which corresponds to the composition of calcium orthosilicate with high accuracy.

Methods

X-ray fluorescence analysis was performed on a wave dispersion spectrometer Venus 200 (PANalyical B.V., Holland).

Chemical analysis of the samples was carried out on an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (Perkin Elmer, USA).

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 of the provided sample was carried out using a simultaneous thermal analysis instrument STA 449 F3 Jupiter.

Chemical activation of kaolinite clays was carried out in a solution containing from 40 to 120 g/dm^3 $NaHCO_3$ at the ratio L:T = 2 - 10.0 and temperatures of 90 - 230 °C using a thermostated installation with 6 autoclaves rotating through the head with a working volume of 250 cm^3, duration of activation ranged from 30 to 300 minutes. The maximum content of sodium hydrocarbonate in the solution was 120 g/dm^3, taking into account its solubility limit.

Results and discussion

The raw product was a representative sample of kaolinite clay from the Alekseevskiy deposit provided by company Arai pro LLP.

The chemical composition of the clay sample, wt. %: Al_2O_3 - 26.9; SiO_2 - 56.6; Fe_2O_3 - 0.537; Na_2O - 0.07; SO_3 - 0.028; K_2O - 1.31; LOI 14.555, silicon module (μ_{si}) - 0.47. Appearance: free-flowing whitish sand, density 2.06 g/cm^3, bulk density 1.36 kg/cm^3, average grain size 2 mm.

X-ray phase analysis of a clay sample is presented as, %: kaolinite 31.4, muscovite 1.1, and quartz 67.5.

According to thermal analysis, the kaolinite phase appears with endothermic effects (-) 167.8 °C, (-) 566.6 °C, and exothermic effects (+) 993.8 °C. The endothermic effect with an extremum at 575 °C on the DTA curve, as well as endothermic effects with extrema at 539.8 °C, 555.9 °C on the dDTA curve, are associated with the manifestation of dehydration of aluminum hydroxides - boehmite, diaspora with varying degrees of grinding. The combination of the endothermic effect with an extremum at 167.8 °C and an exothermic effect with a peak at 993.8 °C on the DTA curve is associated with the manifestation of the clay mineral allophan - $mAl_2O_3nSiO_2pH_2O$. The combination of an endothermic effect with an extremum at 167.8 °C and an exothermic effect with a peak at 647.2 °C is a manifestation of the SiO_2nH_2O opal phase.

A finely dispersed kaolinite fraction was isolated with the composition by washing with running water for further research, wt%: Al_2O_3 - 31.2; SiO_2 - 51.6; Fe_2O_3 - 0.53; CaO - 0.43; Na_2O - 0.095; MgO - 0.2;

SO_3 - 0.02; K_2O - 1.5; TiO_2 1.05; Cl - 0.02; LOI 13,355; μ_{si} - 0.6. The phase composition of the kaolinite fraction: kaolinite - 63.2%, quartz - 21.6%, muscovite - 15.3%. The fraction yield was 41.4%.

The chemical composition of the separated coarse quartz fraction, wt%: Al_2O_3 - 7.65; SiO_2 - 65.5; Fe_2O_3 - 0.68; CaO - 0.29; Na_2O - 0.031; MgO - 0.08; SO_3 - 0.05; K_2O - 0.39; TiO_2 - 0.9; Cl - 0.016; LOI 24.413; μ_{si} - 0.12.

The optimal conditions for carrying out the preliminary chemical activation of kaolinite clay were determined for studies of the dependence of the yield of the kaolinite fraction on temperature, duration, S:L ratio, and concentration of sodium hydro carbonate solution.

When studying the dependence of the yield of the kaolinite fraction on the temperature of chemical activation, the maximum yield of 79.36% was obtained at a temperature of 150 °C (Figure 1).
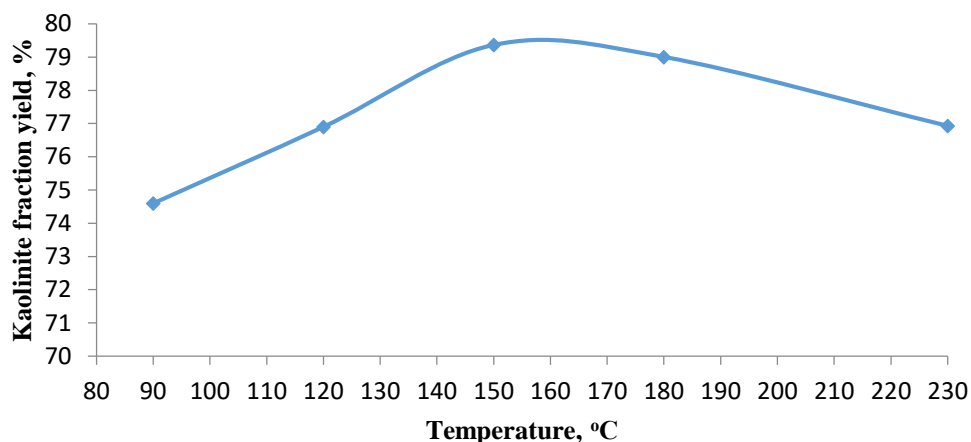
Figure 1. Dependence of the kaolinite fraction yield on the temperature of chemical activation

During chemical activation, changes in the phase composition took place, the content of muscovite decreased almost twofold, and a sodium aluminosilicate phase was formed.

The phase composition of the kaolinite fraction samples depending on the temperature of chemical activation is presented in Table 1.

Table 1. The phase composition of kaolinite fraction samples depending on the temperature of chemical activation

Name	Content, %					
	Activation temperature, °C					
	Ref.	90	120	150	180	230
Kaolinite-1A $Al_2Si_2O_5(OH)_4$	63.2	52.9	52.1	57.0	56.3	54.8
Quartz SiO_2	21.6	29.9	31.0	25.4	26.7	28.0
Muscovite – 1M $KMgAlSi_4O_{10}(OH)_2$	15.3	8.0	8.0	8.9	8.1	8.0
Sodium aluminosilicate $Na_2Al_{1.1}Si_{94.9}O_{192}$	-	5.8	5.2	4.9	5.2	5.5
Magnetite $Fe((Fe_{1.538}Ti_{0.462})O_4)$	-	3.5	3.7	3.7	3.6	3.7

When the dependence of the yield of kaolinite fraction on the duration of chemical activation is studied, it was found that the optimal duration is 120 minutes (Figure 2). A further increase in the duration of activation causes a slight increase in the yield of the kaolinite fraction.
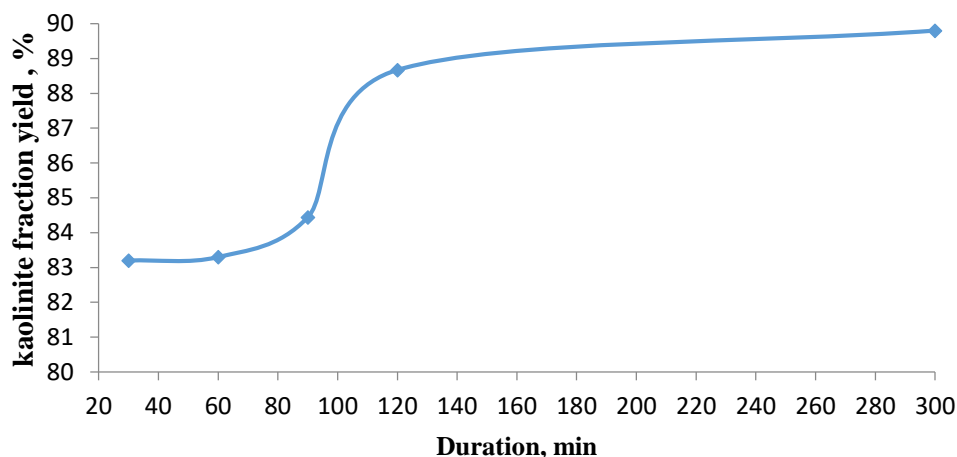
Figure 2. Dependence of the kaolinite fraction yield on the duration of chemical activation

The phase composition of the kaolinite fraction samples depending on the duration of chemical activation is presented in Table 2.

Table 2. The phase composition of kaolinite fraction samples depending on the duration of chemical activation

Name	Content, %					
	Duration, min					
	Ref.	30	60	90	120	300
Kaolinite-1A $Al_2Si_2O_5(OH)_4$	63.2	62.8	62.1	61.3	63.0	64.9
Quartz SiO_2	21.6	24.3	28.5	28.3	28.0	26.3
Muscovite – 1M $KMgAlSi_4O_{10}(OH)_2$	15.3	5.5	5.1	4.4	3.8	3.7
Sodium aluminosilicate $Na_2Al_{1.1}Si_{94.9}O_{192}$	-	4.2	4.0	3.8	3.3	3.1
Magnetite $Fe((Fe_{1.538}Ti_{0.462})O_4)$	-	3.1	2.4	2.2	1.9	2.0

In the studies, it was determined that the yield of the kaolinite fraction practically does not depend on the S:L ratio during chemical activation, therefore, it must be selected taking into account the performance of the equipment (Figure 3).
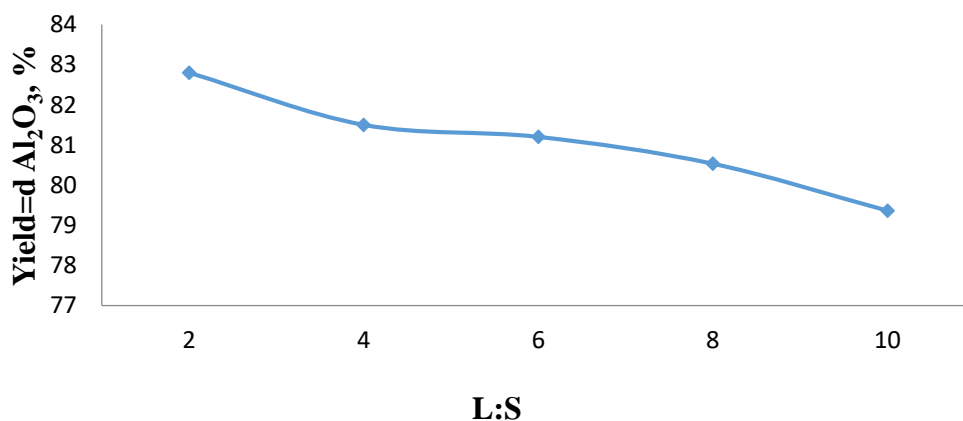

Figure 3. Dependence of the Al_2O_3 yield in the kaolinite fraction on the S:L ratio of chemical activation

The phase composition of the kaolinite fraction samples depending on the S:L ratio of chemical activation is presented in Table 3.

Table 3. The phase composition of kaolinite fraction samples depending on the S:L ratio of chemical activation

Name	Content, %					
	S:L ratio					
	No ref.	2:1	4:1	6:1	8:1	10:1
Kaolinite-1A $AL_2Si_2O_5(OH)_4$	63.2	63.1	62.6	62.5	60.4	60.1
Quartz SiO_2	21.6	29.5	27.3	25.7	27.2	26.9
Muscovite – 1M $KMgAlSi_4O_{10}(OH)_2$	15.3	3.8	4.2	5.6	5.5	5.4
Sodium aluminosilicate $Na_2Al_{1.1}Si_{94.9}O_{192}$	-	2.3	3.7	3.8	4.3	4.9
Magnetite $Fe((Fe_{1.538}Ti_{0.462})O_4)$	-	1.3	2.3	2.5	2.6	2.7

Studies of the dependence of the yield of the kaolinite fraction of clay on the concentration of sodium hydro carbonate solution during chemical activation were carried out at a temperature of 150 °C at a duration of 120 minutes and a S:L ratio = 10:1 (Figure 4).

As a result of research, it was found that the yield of the kaolinite fraction increases with an increase in the concentration of sodium hydro carbonate solution.
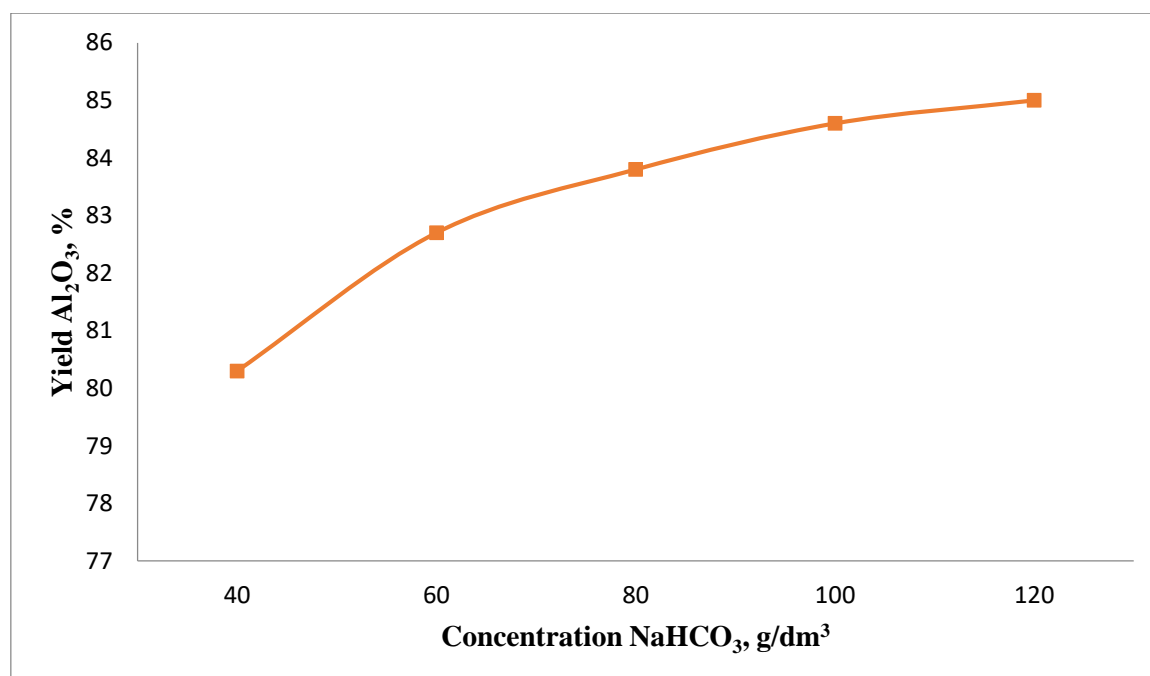

Figure 4. Dependence of the Al_2O_3 yield into the kaolinite fraction on the concentration of sodium hydro carbonate solution during chemical activation

The phase composition of the kaolinite fraction samples depending on the concentration of sodium hydro carbonate solution during chemical activation is presented in Table 4.

Table 4. The phase composition of kaolinite fraction samples depending on the concentration of sodium hydro carbonate solution during chemical activation

Name	Content, %					
	NaHCO₃, g/dm³					
	No ref.	40	60	80	100	120
Kaolinite-1A AL₂Si₂O₅(OH)₄	63.2	62.2	63.6	62.1	65.7	65.0
Quartz SiO₂	21.6	28.9	26.1	26.2	24.8	24.6
Muscovite – 1M KMgAlSi₄O₁₀(OH)₂	15.3	3.8	4.1	5.4	4.1	4.0
Sodium aluminosilicate Na₂Al₁.₁Si₉₄.₉O₁₉₂	-	3.2	3.7	3.9	3.4	3.5
Magnetite Fe((Fe₁.₅₃₈Ti₀.₄₆₂)O₄)	-	2.0	2.2	2.5	2.0	2.2

Based on the results obtained, a technology for the complex processing of kaolinite clays has been developed, which provides for the preliminary chemical activation of the feedstock at the beginning of the process, which will effectively isolate high-quality kaolinite and quartz products, which will significantly reduce the flow of materials entering for sintering (Figure 5).
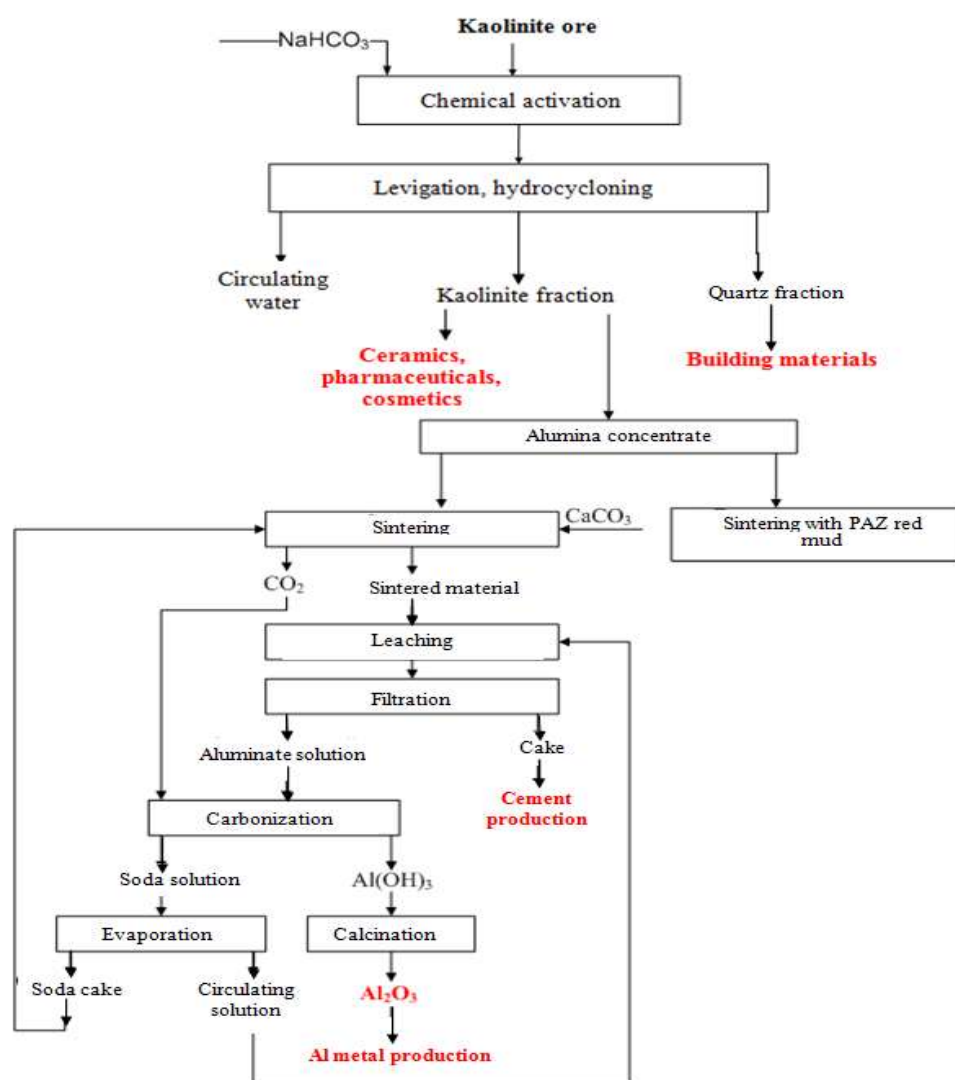

Figure 5. Process flow scheme of complex processing of kaolinite ore

Conclusions. Research has been carried out on the effect of preliminary chemical activation of kaolinite clays of the Alekseevskiy deposit in a sodium hydro carbonate solution on the separation of kaolinite and quartz fractions. The optimal mode of activation should be considered a temperature of 150 °C, a duration of 120 minutes, and a concentration of sodium hydro carbonate solution of 120 g/dm^3.

As a result of activation, the phase composition of the kaolinite fraction has changed: the percentage of the kaolinite fraction has decreased; new phases of muscovite and sodium aluminosilicate appeared; the amount of quartz increased.

The process flow scheme of the complex processing of kaolinite ore has been developed.

Acknowledgments

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