

ISSN 2518-170X (Online)

ISSN 2224-5278 (Print)



ҚАЙЫРЫМДЫЛЫҚ ҚОРЫ

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«ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
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«ХАЛЫҚ» ЖҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

РОО «НАЦИОНАЛЬНОЙ
АКАДЕМИИ НАУК РЕСПУБЛИКИ
КАЗАХСТАН»
ЧФ «Халық»

N E W S

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF
KAZAKHSTAN
«Halyk» Private Foundation

SERIES
OF GEOLOGY AND TECHNICAL SCIENCES

3 (465)
MAY – JUNE 2024

THE JOURNAL WAS FOUNDED IN 1940

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАНПК сообщает, что научный журнал «Известия НАНПК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАНПК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.



ЧФ «ХАЛЫҚ»

В 2016 году для развития и улучшения качества жизни казахстанцев был создан частный Благотворительный фонд «Халык». За годы своей деятельности на реализацию благотворительных проектов в областях образования и науки, социальной защиты, культуры, здравоохранения и спорта, Фонд выделил более 45 миллиардов тенге.

Особое внимание Благотворительный фонд «Халык» уделяет образовательным программам, считая это направление одним из ключевых в своей деятельности. Оказывая поддержку отечественному образованию, Фонд вносит свой посильный вклад в развитие качественного образования в Казахстане. Тем самым способствуя росту числа людей, способных менять жизнь в стране к лучшему – профессионалов в различных сферах, потенциальных лидеров и «великих умов». Одной из значимых инициатив фонда «Халык» в образовательной сфере стал проект *Ozgeris powered by Halyk Fund* – первый в стране бизнес-инкубатор для учащихся 9-11 классов, который помогает развивать необходимые в современном мире предпринимательские навыки. Так, на содействие малому бизнесу школьников было выделено более 200 грантов. Для поддержки талантливых и мотивированных детей Фонд неоднократно выделял гранты на обучение в Международной школе «Мирас» и в Astana IT University, а также помог казахстанским школьникам принять участие в престижном конкурсе «USTEM Robotics» в США. Авторские работы в рамках проекта «Тәлімгер», которому Фонд оказал поддержку, легли в основу учебной программы, учебников и учебно-методических книг по предмету «Основы предпринимательства и бизнеса», преподаваемого в 10-11 классах казахстанских школ и колледжей.

Помимо помощи школьникам, учащимся колледжей и студентам Фонд считает важным внести свой вклад в повышение квалификации педагогов, совершенствование их знаний и навыков, поскольку именно они являются проводниками знаний будущих поколений казахстанцев. При поддержке Фонда «Халык» в южной столице был организован ежегодный городской конкурс педагогов «Almaty Digital Ustaz».

Важной инициативой стал реализуемый проект по обучению основам финансовой грамотности преподавателей из восьми областей Казахстана, что должно оказать существенное влияние на воспитание финансовой грамотности и предпринимательского мышления у нового поколения граждан страны.

Необходимую помощь Фонд «Халык» оказывает и тем, кто особенно остро в ней нуждается. В рамках социальной защиты населения активно проводится

работа по поддержке детей, оставшихся без родителей, детей и взрослых из социально уязвимых слоев населения, людей с ограниченными возможностями, а также обеспечению нуждающихся социальным жильем, строительству социально важных объектов, таких как детские сады, детские площадки и физкультурно-оздоровительные комплексы.

В копилку добрых дел Фонда «Халык» можно добавить оказание помощи детскому спорту, куда относится поддержка в развитии детского футбола и карате в нашей стране. Жизненно важную помощь Благотворительный фонд «Халык» оказал нашим соотечественникам во время недавней пандемии COVID-19. Тогда, в разгар тяжелой борьбы с коронавирусной инфекцией Фонд выделил свыше 11 миллиардов тенге на приобретение необходимого медицинского оборудования и дорогостоящих медицинских препаратов, автомобилей скорой медицинской помощи и средств защиты, адресную материальную помощь социально уязвимым слоям населения и денежные выплаты медицинским работникам.

В 2023 году наряду с другими проектами, нацеленными на повышение благосостояния казахстанских граждан Фонд решил уделить особое внимание науке, поскольку она является частью общественной культуры, а уровень ее развития определяет уровень развития государства.

Поддержка Фондом выпуска журналов Национальной Академии наук Республики Казахстан, которые входят в международные фонды Scopus и Wos и в которых публикуются статьи отечественных ученых, докторантов и магистрантов, а также научных сотрудников высших учебных заведений и научно-исследовательских институтов нашей страны является не менее значимым вкладом Фонда в развитие казахстанского общества.

**С уважением,
Благотворительный Фонд «Халык»!**

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«ҚР ҰҒА» РҚБ Хабарлары. Геология және техникалық ғылымдар сериясы».

ISSN 2518-170X (Online),

ISSN 2224-5278 (Print)

Меншіктеуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» РҚБ (Алматы қ.).

Қазақстан Республикасының Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 29.07.2020 ж. берілген № **KZ39VPU00025420** мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Тақырыптық бағыты: *геология, мұнай және газды өңдеудің химиялық технологиялары, мұнай химиясы, металдарды алу және олардың қосындыларының технологиясы.*

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

Редакцияның мекен-жайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., тел.: 272-13-19

<http://www.geolog-technical.kz/index.php/en/>

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«Известия РОО «НАН РК». Серия геологии и технических наук».

ISSN 2518-170X (Online),

ISSN 2224-5278 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы).

Свидетельство о постановке на учет периодического печатного издания в Комитете информации Министерства информации и общественного развития Республики Казахстан № **KZ39VPY00025420**, выданное 29.07.2020 г.

Тематическая направленность: *геология, химические технологии переработки нефти и газа, нефтехимия, технологии извлечения металлов и их соединений.*

Периодичность: 6 раз в год.

Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, оф. 219, тел.: 272-13-19

<http://www.geolog-technical.kz/index.php/en/>

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News of the National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technology sciences.

ISSN 2518-170X (Online),

ISSN 2224-5278 (Print)

Owner: RPA «National Academy of Sciences of the Republic of Kazakhstan» (Almaty).

The certificate of registration of a periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan **No. KZ39VPY00025420**, issued 29.07.2020.

Thematic scope: *geology, chemical technologies for oil and gas processing, petrochemistry, technologies for extracting metals and their connections.*

Periodicity: 6 times a year.

Circulation: 300 copies.

Editorial address: 28, Shevchenko str., of. 219, Almaty, 050010, tel. 272-13-19

<http://www.geolog-technical.kz/index.php/en/>

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NEWS of the National Academy of Sciences of the Republic of Kazakhstan
SERIES OF GEOLOGY AND TECHNICAL SCIENCES
ISSN 2224–5278
Volume 3. Number 465 (2024), 35–57
<https://doi.org/10.32014/2024.2518-170X.408>

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SELECTING AND IMPROVEMENT OF A METHOD FOR PROCESSING KAOLINITE FRACTION OF BAUXITE

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Abstract. The methods of separate processing of fine kaolinite fractions of gibbsite-kaolinite bauxites have been studied, including: preliminary thermochemical transformation, combined processing by Bayer hydrochemistry and hydrochemical processing with preliminary chemical activation. The preliminary thermal transformation was carried out by pre-firing. When using recycled aluminate solutions of the Bayer branch for leaching, solutions suitable for the extraction of $\text{Al}(\text{OH})_3$ by decomposition were obtained. The extraction of Al_2O_3 into the leaching solution was 70 %. For the hydrochemical processing of leaching sludge in the Bayer branch, a method for obtaining the active form of a calcium additive has been developed. The extraction of $\text{Al}(\text{OH})_3$ in the Bayer branch was obtained by 38.0 % and by 87.2 % in the branch of hydrochemical sludge processing. The total recovery was 92.06 %. As a result of preliminary chemical activation in a solution of sodium bicarbonate, a complete transformation of the phase composition occurred: the phases of gibbsite, kaolinite, quartz disappeared and the phases of sodalite, dawsonite and boehmite were formed. After hydrochemical leaching in a high-modulus solution with the addition of an active calcium additive, a dump sludge and

a medium-modulus solution were obtained, while the extraction of Al_2O_3 into the solution was 89.5 %. According to the research results, the choice of technology for processing fine fractions by various hydrochemical methods depends on the specific production conditions – the availability of existing equipment and the amount of modernization.

Keywords: gibbsite–kaolinite bauxite, kaolinite, fraction, processing, thermochemical transformation, hydrochemistry, chemical activation, leaching, decomposition, sludge, calcium additive, dawsonite

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БОКСИТТЕРДІҢ КАОЛИНИТ ФРАКЦИЯСЫН ӨНДЕУ ӘДІСІН ТАҢДАУ ЖӘНЕ ЖЕТІЛДІРУ

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Аннотация. Гиббсит-каолинит бокситтерінің ұсақ дисперсті каолинит фракцияларын жеке өндеу әдістері: алдын ала термохимиялық трансформация, Байер – гидрохимия бойынша аралас өндеу және алдын ала химиялық активациямен гидрохимиялық өндеу жұмыстарына зерттеулер жүргізілді. Термохимиялық трансформацияны алдын ала күйдіру арқылы жүзеге асырылды. Шаймалау үшін қайта өңделген алюминий ерітінділерін пайдаланған кезде Байер тармақтарында ыдырау әдісімен $Al(OH)_3$ алуға жарамды ерітінділер алынады. Шаймалау ерітіндісіне Al_2O_3 алу 70 % құрады. Байер тармағындағы сілтілеу шламын гидрохимиялық өндеу үшін кальций қоспасының белсенді түрін алу әдісі жасалды. $Al(OH)_3$ Байер тармағында 38,0 % - ға және шламды гидрохимиялық өндеу тармағында 87,2 % - ға алынды. Жалпы алу 92,06

% құрады. Алдын ала химиялық белсендіру нәтижесінде натрий гидрокарбонатының ерітіндісінде фазалық құрамның толық трансформациясы болды: гиббсит, каолинит, кварц фазалары жоғалып, содалит, даусонит және бемит фазалары пайда болды. Белсенді кальций қоспасын қосып, жоғары модульді ерітіндіде гидрохимиялық шаймалаудан кейін шлам мен орташа модульді ерітінді алынды, ал ерітіндіге Al_2O_3 алу 89,5 % құрады. Әр түрлі гидрохимиялық әдістермен ұсақ фракцияны қайта өңдеу технологиясын таңдаудың зерттеу нәтижелері өндірістің нақты жағдайларына – қолданыстағы жабдықтың болуына және модернизация көлеміне байланысты.

Түйін сөздер: гиббсит-каолинит бокситтері, каолинит, фракция, қайта өңдеу, термохимиялық трансформация, гидрохимия, химиялық белсендіру, сілтілеу, ыдырау, шлам, кальций қоспасы, даусонит

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ВЫБОР И СОВЕРШЕНСТВОВАНИЕ СПОСОБА ПЕРЕРАБОТКИ КАОЛИНИТОВОЙ ФРАКЦИИ БОКСИТОВ

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Аннотация. Проведены исследования способов отдельной переработки мелкодисперсной каолиновой фракций гиббсит-каолиновых бокситов, включающих: предварительную термохимическую трансформацию, комбинированную переработку по Байер – гидрохимии и гидрохимическую переработку с предварительной

химической активацией. Предварительную термическую трансформацию проводили путем предварительного обжига. При использовании для выщелачивания оборотных алюминатных растворов ветви Байера получены растворы, пригодные для извлечения $\text{Al}(\text{OH})_3$ методом декомпозиции. Извлечение Al_2O_3 в раствор выщелачивания составило 70 %. Для гидрохимической переработки шлама выщелачивания в ветви Байера разработан способ получения активной формы кальциевой добавки. Получено извлечение $\text{Al}(\text{OH})_3$ в ветви Байера на 38,0 % и на 87,2 % в ветви гидрохимической переработки шлама. Общее извлечение составило 92,06 %. В результате предварительной химической активации в растворе гидрокарбоната натрия произошла полная трансформация фазового состава: исчезли фазы гиббсита, каолинита, кварца и образовались фазы содалита, даусонита и бемита. После гидрохимического выщелачивания в высокомолекулярном растворе с добавлением активной кальциевой добавки получили отвалный шлам и среднемолекулярный раствор, при этом извлечение Al_2O_3 в раствор составило 89,5 %. По результатам исследований выбор технологии переработки мелкодисперсной фракции различными гидрохимическими способами зависит от конкретных условий производства – наличия существующего оборудования и объема модернизации.

Ключевые слова: гиббсит – каолиновые бокситы, каолинит, фракция, переработка, термохимическая трансформация, гидрохимия, химическая активация, выщелачивание, декомпозиция, шлам, кальциевая добавка, даусонит

Introduction

The most simple and cost-effective method of processing bauxites is the Bayer process grounding in leaching the bauxite based on binding silicon dioxide SiO_2 into sodium hydroalumosilicate (SHAS), which constitutes the major portion of the insoluble residue known as red mud, which is then disposed in a mud field (Medvedev, Akhmedov, 2014; Ibragimov, Budon, 2010). However, this method requires bauxites with a high silica modulus (determined by the ratio of aluminum oxide to silicon dioxide) >7 . During the processing of low-grade, high-silica bauxites with a silica modulus 3–4, alkali and alumina oxide losses become significant. Therefore, they are initially subjected to mechanical and chemical enrichment through several stages to elevate them to a category suitable for Bayer process treatment. Alternatively, sintering methods or alkali processes combined with sintering are applied (Ibragimov, Budon, 2010; Dubovikov, Yaskelyainen, 2016; Danczuk, Belousova, 2019; Dubovikov, 2012).

Preliminary chemical enrichment of bauxites with separation of excess silica (desilicization) is carried out by leaching in a low-concentrated alkaline solution containing Na_2O – 100–150 g/dm³ (Ibragimov, Budon, 2010; Dubovikov, Yaskelyainen, 2016).

Gravity enrichment of bauxites is achieved by separating the kaolinite fraction through water washing simultaneously with grinding, dividing the resulting slurry on hydrocyclones in multiple stages, leaching the sands after separation in the Bayer branches, extracting sands from the overflow, and subsequently sending the sands for sintering (Synkova et al., 2004). In this process, the slurry separation is carried out in at least three stages, directing the sands from the last stage to sintering, and subjecting the sands from all previous stages to leaching. The overflow from the last stage is removed from the process. The slurry separation at all stages is carried out in battery hydrocyclones, with a decreasing diameter at each successive stage. The number of stages is determined by the total content of kaolinite and goethite in the

overflow of the last stage, which is no less than 40 %. The method allows for the enrichment of bauxite by removing the most finely dispersed fraction, primarily kaolinite and goethite, from the process. This leads to a reduction in losses of aluminum hydroxide and alkali, as well as a decrease in flocculant consumption and loading of sintering furnaces. The isolated sands are leached into the Bayer branches. However, the method does not involve the processing of the fine-dispersed clay kaolinite fraction.

The sintering process involves sintering of bauxite with limestone and soda in rotating furnaces at the temperature of 1100–1200 °C, during which silicon dioxide binds into insoluble calcium orthosilicate $2\text{CaO}\cdot\text{SiO}_2$. This process requires significant fuel and electrical energy expenditures, it is carried out with substantial labor and operational costs, and accompanied by a notable environmental impact on the air basin. The sintered material is subjected to leaching by a combination of water with the mother or circulating soda-alkaline solution. The solid residue is environmentally harmful and unsuitable for disposal (Dubovikov et al., 2018).

According to the combined Bayer and sintering process, the bauxite raw material is initially entirely fed into the Bayer branch for leaching. The resulting red mud is separated from the aluminate solution and then sintered with limestone and soda at the temperature of 900–1100 °C (Ibragimov, Budon, 2010). The sintered material undergoes leaching, resulting in the extraction of aluminate solution and the generation of waste mud unsuitable for disposal. This method is ineffective, time-consuming and environmentally harmful.

During the processing of kaolinite ores using the alkaline method, a preliminary operation is conducted to enhance the reactivity of kaolinite. This involves transforming the phase composition through heat treatment, resulting in the conversion of kaolin into metakaolin. Metakaolin can then be easily leached to extract alumina oxide (ElDeeb, 2019). The disadvantage of the thermal transformation of kaolinite ores is also the high energy intensity of the process.

There is a hydrochemical process known as the Ponomarev-Sazhin process (Ibragimov, Budon, 2010), in which the sintering process of red mud is replaced by the hydrochemical leaching of the mud in autoclaves at temperatures of 280–300 °C. This method utilizes a concentrated high-modulus aluminate solution ($\text{Na}_2\text{O}_{\text{caust}} > 450 \text{ g/dm}^3$, $\alpha_{\text{caust}} 30$) with the addition of lime to produce calcium monosilicate $\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$. The method was not implemented due to the lack of corrosion-resistant high-pressure equipment and high thermal energy consumption.

Unlike the Ponomarev-Sazhin process, for hydrochemical-hydrogarnet technology, high-modulus aluminate solutions of medium concentration are used for the processing of high-iron bauxite for the leaching of red mud - not higher than $200 \text{ g/dm}^3 \text{ Na}_2\text{O}_{\text{ca}}$ with the addition of lime to form hydrogarnets ($3 \text{ CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ и $3 \text{ CaO}\cdot\text{Fe}_2\text{O}_3\cdot 6\text{H}_2\text{O}$) at temperatures of 230–235 °C. The successful implementation of the process requires the presence of a sufficient amount of calcium hydroxide in the reaction medium, the presence of a solution with an adequate mass of free silicon ions, and an active iron-containing phase (Bekturganov et al., 2015).

The basis for the conducted research was the absence of high-quality bauxites in Kazakhstan, making the Pavlodar Aluminum Plant (PAP) of JSC «Aluminium of Kazakhstan» to use gibbsite-kaolinite bauxites from the Krasnogorsk deposit in the production for the sequential Bayer and sintering process. These bauxites are characterized by a low silicon modulus. Bauxites are processed using the combined alkali Bayer and sintering process without prior enrichment, involving the separation of the fine-dispersed clay kaolinite fraction

refractory in the Bayer branch. This makes the production marginally profitable. The paper explores potential methods and ways to improve the technologies for the separate processing of the fine-dispersed kaolinite fraction (FDKF) of bauxite after its preliminary separation, allowing for a significant reduction in the amount of material sent to sintering.

Materials and reserch methods

Materials and reserch methods

X-ray fluorescence analysis was performed on Venus 200 PANalytical B.V. spectrometer with wave dispersion (PANalytical B.V., the Netherlands).

The chemical analysis of samples was performed on Optima 2000 DV ICP optical emission spectrometer (USA, PerkinElmer).

X-ray experimental data were obtained on BRUKERD8 ADVANCE using copper radiation at an accelerating voltage of 36 kW, current of 25 mA.

The IRS-analysis was obtained using the Avatar 370 IR-Fourier spectrometer.

The micrographs were taken on a scanning low-vacuum electron microscope with a thermionic cathode (LaB6) JSM-6610LV manufactured by JEOL.

The thermal transformation of FDKF was carried out by calcination at the temperature of 900–1000 °C for 2 hours in a tubular rotary furnace.

The chemical enrichment of FDKF was carried out in a reactor, while stirring in the solution with 100 g/dm³ Na₂O_{ca} at the temperature of 100 °C, L:S =6:1 and duration of 2 hours.

The leaching of FDKF in the Bayer branch was carried out in an autoclave at the temperature of 105-110 °C, duration of 4 hours, and L:S ratio = 4:1 in the circulating alkaline-aluminate solution of the PAP with the following composition, g/dm³: Al₂O₃ 118,3; Na₂O_t 256,7; Na₂O_{carb} 30,7; Na₂O_{caust} 226,0; α_{caust} =3,14 units.

To desilicate the liquid phase, the leaching slurry in the Bayer branch was diluted with distilled water to Na₂O_{caust} of 120 g/dm³ and subjected to agitated holding at the temperature of 105 °C for two hours.

Hydrochemical leaching of the mud in the Bayer branch and the FDKF after thermochemical transformation was carried out with the addition of the active form of calcium oxide in the high-modulus solution (HMS) of the composition, g/dm³: Na₂O_{caust} 245.0; Na₂O_{carb} 11.4; Al₂O₃ 13.43; SO₃ 4.23; SiO₂ 0.024; α_{caust} = 30.0. At the temperature of 240 °C, duration of 4 hours and L:S ratio = 4:1 and CaO/SiO₂ ratio = 1.5.

The active form of calcium oxide was obtained in the solution containing 20 g/dm³ Na₂SO₄ at the temperature of 200 °C and duration of 2 hours.

The particle size analysis of slaked lime was carried out using Laser Particle Size Analyzer Winner 2000 of Photocor series. The measurement principle of this analyzer is based on the method of static and dynamic light scattering.

The decomposition of tricalcium hydroaluminate (TCHA) was conducted according to the technology (Gladyshev et al., 2012) with the concentration of Na₂O_{carb} ranging from 140 to 160 g/dm³, temperature of 180 °C, leaching duration of 90 minutes in an autoclave, and L:S ratio = 4:1.

The calculation of the extraction of Al₂O₃ and SiO₂ into solution was carried out according to the formula:

Accepted designations:

$$\left(100 - \frac{P_s \cdot C_s}{P_f \cdot C_f}\right) \cdot \% \quad (1)$$

α_{caust} is a caustic module;

μ_{Si} is a silicon module;

μ_{caust} is a caustic alkali;

μ_{carb} – carbonate alkali;

μ_{total} is the total alkali.

The caustic modulus was determined from the ratio of $1,645 \cdot \text{Na}_2\text{O}/\text{Al}_2\text{O}_3$.

The silicon modulus (μ_{Si}) of samples was determined from the ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$.

Discussion of the results

Gibbsite-kaolinite bauxites of the Krasnogorsk deposit of the Republic of Kazakhstan served as the raw material for the research.

Chemical composition of bauxite, % wt: Al_2O_3 42,0; SiO_2 11,5; Fe_2O_3 19,5; CaO 1,08; Na_2O 0,22; MgO 0,18; K_2O 0,03; TiO_2 2,05; SO_3 0,24; Cl^- 0,04; μ_{Si} 3,65.

The phase composition of bauxite is represented by, %: gibbsite 54.95; kaolinite 15.19; siderite 60.9; quartz 5.1; calcite 5.07; hematite 4.89; titanium oxide 4.88 and dolomite 3.82.

The separation of the finely dispersed kaolinite fraction (FDKF) was carried out using the gravity enrichment method through water elutriation, separating the light clay fraction from the heavy sandy fraction. As a result of water elutriation, a coarse-crystalline sandy fraction and the fine-dispersed kaolinite fraction (FDKF) were obtained, with yield of 62%.

The chemical composition of the sand fraction, % wt: Al_2O_3 42,0; SiO_2 9,65; Fe_2O_3 19,9; CaO 1,1; Na_2O 1,06; MgO 0,19; K_2O 0,02; TiO_2 2,3; other products (o.p.) 23,38; μ_{Si} 4,35.

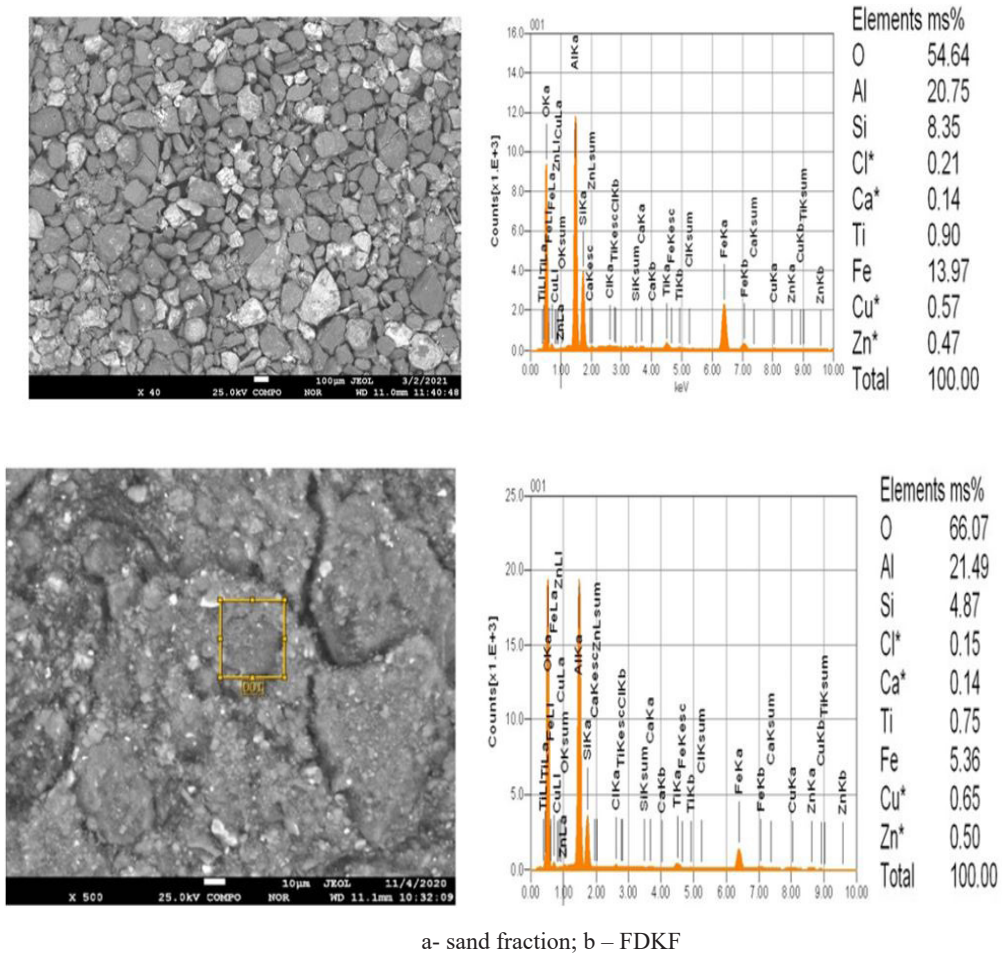
The chemical composition of the FDKF, % wt: Al_2O_3 38,8; SiO_2 19,6; Fe_2O_3 16,96; CaO 1,45; Na_2O 0,187; MgO 0,26; K_2O 0,06; TiO_2 3,2; pp 19,24; μ_{Si} 1,98.

The X-ray phase composition of the sand and FDKF bauxite is presented in the Table 1.

Table 1. X-ray phase composition of bauxite fractions

Name	Formula	Content, %	
		Sand fraction	FDKF
Gibbsite	$\text{Al}(\text{OH})_3$	47.5	39.5
Kaolinite-1A	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	6.2	28.6
Siderite	FeCO_3	7.7	
Quartz	SiO_2	5.1	6.0
Hematite	Fe_2O_3	10.6	18.2
Titanium Oxide	TiO_2	7.5	7.7
Dolomite	$\text{CaCO}_3 \cdot \text{MgCO}_3$	10.2	
Calcite	CaCO_3	5.2	

Microphotographs and electron microscopic analysis of the gravity enrichment fractions of the original bauxite are shown in Figure 1.



a- sand fraction; b – FDKF

Figure 1. Micrographs and electron microscopic analyses of bauxite fractions

The separated sandy fraction of bauxite obtained through gravity enrichment, after undergoing the chemical enrichment to increase the silicon modulus, is processed in the Bayer branch (Dyussenova et al., 2022).

For choosing a technology of processing the FDKF, research was conducted on the feasibility and improvement of alternative methods, including:

- preliminary thermochemical transformation, chemical enrichment, leaching in the circulating solution in the Bayer branch, desilication, and decomposition;
- combined processing under the Bayer process - hydrochemistry;
- hydrochemical processing with preliminary chemical activation.

The processing of the FDKF according to the method involving preliminary thermochemical transformation and chemical enrichment was carried out following the technological scheme presented in Figure 2.

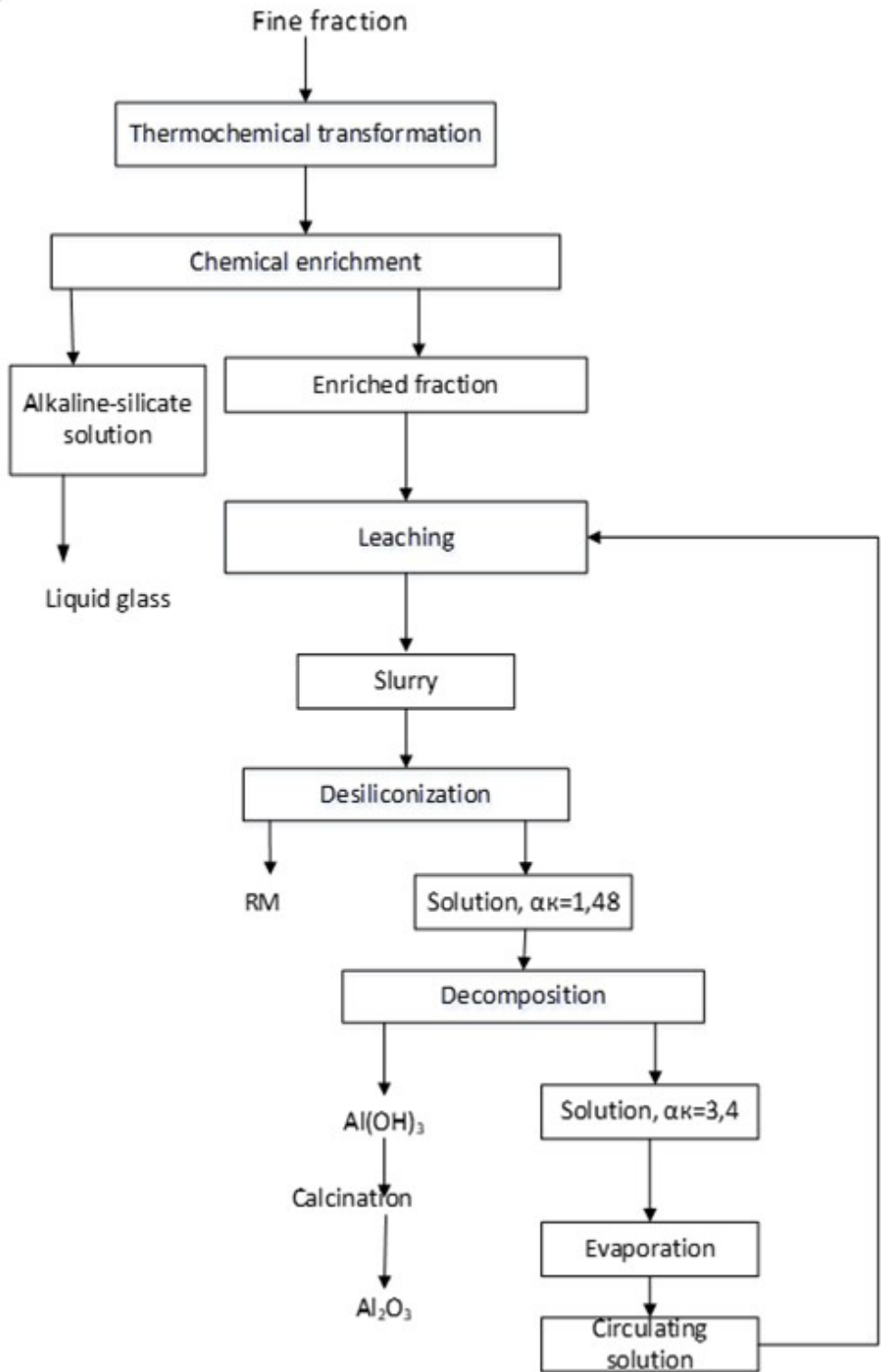
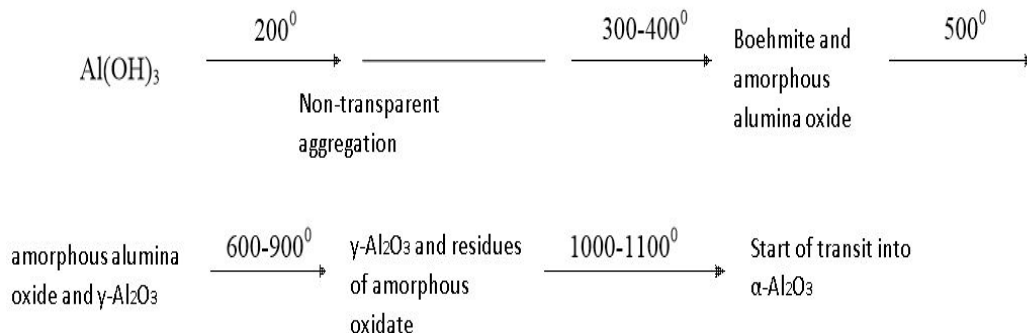


Figure 2. Technological scheme of processing the FDKF with preliminary thermochemical transformation and chemical enrichment.

This technology includes the thermal transformation of FDKF by pre-calcination at temperatures of 900–1000 °C. The aim of which was to obtain a chemically stable aluminum-containing corundum phase, preventing the transition of Al_2O_3 into the alkaline solution and ensuring the maximum dissolution of amorphous SiO_2 .

Reactions of thermal transformation of aluminum hydroxide:



The X-ray phase composition of the FDKF, depending on the calcination temperature, is shown in Table 2.

Table 2. Phase composition of the FDKF depending on the calcination temperature

Name	Int.	900	950	1000
	Content, %			
Gibbsite $Al(OH)_3$	29.5	-	-	-
Hematite Fe_2O_3	13.1	48.3	34.6	34.4
Siderite $FeCO_3$	3.3	-	-	-
Dolomite $CaMg(CO_3)_2$	8.6	-	-	-
Titanium Oxide TiO_2	7.7	10.2	10.4	7.7
Kaolinite-1A $Al_2Si_2O_5(OH)_4$	28.6	-	-	-
Calcite $CaCO_3$	3.2	-	-	-
Quartz SiO_2	6.0	8.9	11.8	12.7
Corundum	-	17.9	24.3	26.6

The results of the phase analysis showed that after calcination, the corundum phase appeared, and the phases of gibbsite, kaolinite, siderite, calcite and dolomite disappeared. There was a disruption in the crystalline structure of the samples. The content of the X-ray amorphous part in the FDKF at calcination temperatures was as follows: 900 °C – 34.3 %; 950 °C – 40.0 %; and 1000 °C – 45.5 %.

The results of chemical enrichment of the FDKF after thermal transformation are presented in Table 3.

Table 3. Results of chemical enrichment of the FDKF after thermal transformation

FDKF after calcination at the temperature, °C	Solid phase content, %					M _{SiO₂}	Extraction into solution, %	
	Na ₂ O	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	o.p.		SiO ₂	Al ₂ O ₃
900	4.54	50.98	14.71	22.46	7.31	3.47	51.0	0.28
950	3.657	52.95	13.03	23.16	7.2	4.06	58.8	0.24
1000	3.41	53.32	12.84	23.16	7.27	4.15	58.5	0.24

The preliminary thermal transformation of the FDKF allowed for an extraction of silica in the solution of over 50.0 % during the chemical enrichment. The alkaline silicate solution can be used to produce silicate products (Pyagai et al., 2023).

After the chemical enrichment, the FDKF was leached in the Bayer branch in the circulating aluminate solution. The compositions of the solid and liquid phases of the leaching slurry are shown in Tables 4 and 5.

Table 4. Composition of the solid phase of the FDKF leaching slurry in the circulating solution

FDKF after calcination at the temperature, °C	Solid phase content, %					Extr. Al ₂ O ₃ into solution, %
	Na ₂ O	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	o.p.	
900	16.95	21.403	21.869	30.986	8.7	67.6
950	15.82	27.731	21.483	25.778	9.2	77, 4
1000	12.44	33.053	17.486	27.875	9.1	61.15

Table 5. Composition of the liquid phase of the FDKF leaching slurry in the circulating solution

FDKF after calcination at the temperature, °C	Content, g/dm ³					α _{caust} [?] units
	Al ₂ O ₃	Na ₂ O _t	Na ₂ O _{carb}	Na ₂ O _{caust}	SiO ₂	
900	176.9	201.76	20.26	181.5	1.200	1.69
950	177.3	203.27	23.27	180.0	1.190	1.67
1000	177.07	203.27	24.77	178.5	1.200	1.66

After dilution and agitative holding of the leaching slurry, aluminate solutions and the solid phase, the red mud (as indicated in Tables 6 and 7), were obtained.

Table 6. Composition of aluminate solutions after agitation holding of the leaching slurry of the FDKF

FDKF after calcination at the temperature, °C	Content, g/dm ³					α _{caust} [?] units
	Al ₂ O ₃	Na ₂ O _t	Na ₂ O _{carb}	Na ₂ O _{caust}	SiO ₂	
900	113.2	138.52	21.52	117.0	0.70	1.70
950	113.1	129.49	13.99	115.5	0.76	1.68
1000	117.64	130.99	10.99	118.0	0.700	1.65

Table 7. Composition of the red mud

FDKF after calcination at the temperature, °C	Content, %					Extr. Al ₂ O ₃ into solution, %
	Na ₂ O	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	o.p.	
900	16.28	22.057	22.44	30.31	8.9	63.8
950	15.35	22.947	21.19	31.50	9.01	70.0
1000	13.48	30.286	18.70	29.19	8.34	52.7

The X-ray phase analysis of the red mud is shown in Figure 3.

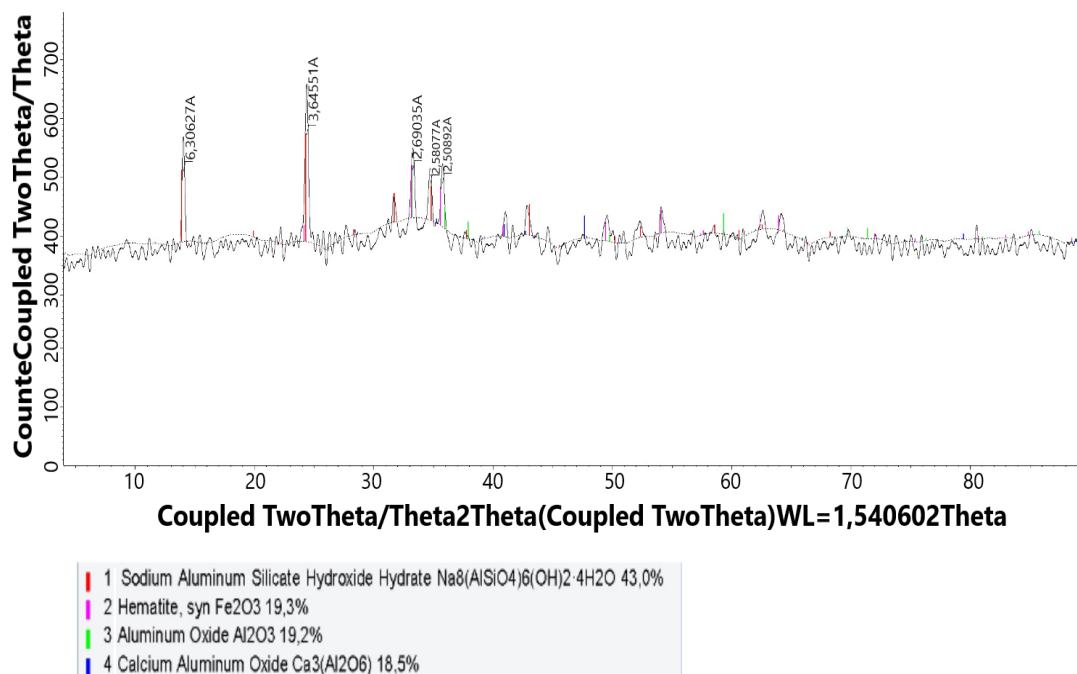


Figure 3. X-ray diagram of the red mud of the diluted slurry of the FDKF after the agitation holding

The analysis of the results of processing the FDKF using a technology that includes thermal transformation, chemical enrichment and autoclave leaching in a circulating alumina-alkali solution showed that the optimal processing conditions involve pre-calcination at the temperature of 950 °C. Under these conditions, the extraction of Al₂O₃ in the leaching solution reached 70 %, and aluminate solutions with $\alpha_{\text{caust}} = 1.65\text{--}1.7$ were obtained, suitable for extracting Al(OH)₃ through the decomposition method (Savchenko, Savchenko, 1999). The low extraction of Al₂O₃ in the solution during leaching can be explained by the presence of the chemically stable corundum phase obtained during calcination.

At the next stage, the possibility of applying a combined Bayer and hydrochemistry process for processing the FDKF was investigated (Figure 4). The novelty of the technology lies in the use of an active calcium additive for the hydrochemical processing of the Bayer branch's mud, which has enabled the reduction in a required concentration of the high-modulus alkaline leaching solution to 240 g/dm³ Na₂O.

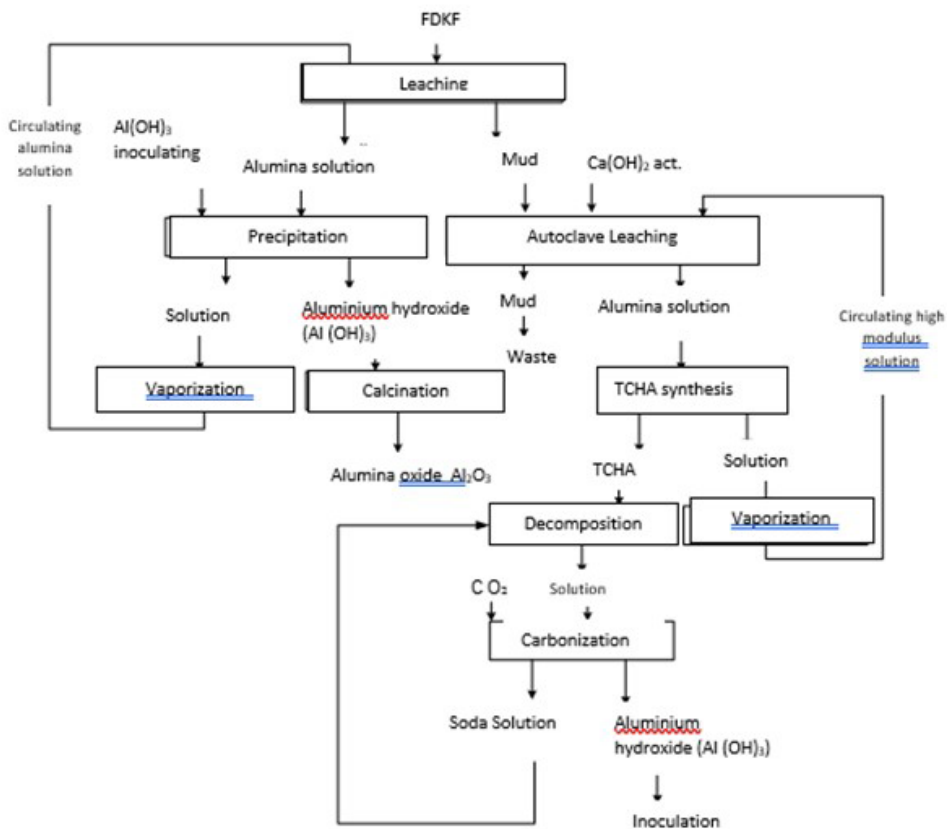


Figure 4. Processing of the FDKF using the combined Bayer and hydrochemistry process with an active calcium additive

As a result of leaching the FDKF in the Bayer branch and desilication, an aluminate solution suitable for extracting $\text{Al}(\text{OH})_3$ through the decomposition method was obtained with the following composition, % wt: Al_2O_3 105,09; Na_2O_t 130,5; $\text{Na}_2\text{O}_{\text{carb}}$ 15,0; $\text{Na}_2\text{O}_{\text{caust}}$ 115,0; $\alpha_{\text{caust}}=1,8$ units. The extraction of Al_2O_3 reached 38.0%.

The chemical composition of the red mud of the Bayer branch leaching is presented by, % wt: Al_2O_3 22,3; SiO_2 23,5; Fe_2O_3 30,4; Na_2O 16,1; o.p. 7,7.

The red mud of the Bayer branch was processed by hydrochemical autoclave leaching in the high-modulus aluminate solution with addition of the active form of calcium oxide. In contrast to the known hydrochemical method for processing high-iron bauxites, where the required amount of calcium oxide is determined based on $\text{CaO}/\text{Fe}_2\text{O}_3$ ratio (Ibragimov, Budon, 2010), in the conducted studies for processing the high-silica FDKF, a fine-dispersed active form of calcium oxide in the form of slaked lime powder was used in quantity necessary to achieve CaO/SiO_2 ratio =1.5 in the slurry.

The activity of slaked lime powder depends on its surface area, the extent of which determines its dispersity. The production of fine-dispersed active calcium additive was carried

out by slaking CaO under elevated pressure at the temperature of 200 °C for duration of 2 hours. When slaking CaO in water, the number of powder particles less than 1 μm was about 80 %. As a result of slaking CaO in the solution containing 20 % Na₂SO₄, the proportion of lime powder particles with size of less than 1 μm reached 94.7 % (see Table 8 and Figure 5). Increasing the slaking temperature above 200 °C did not result in increase in the number of particles of lime powder less than 1 μm. When slaking CaO at the temperature of 20 °C, the particle size of slaked lime powder finer than 1 μm amounted to only 40–50 %.

Table 8. Structure of the slaked lime powder obtained at the temperature of 200 °C, in 20 % Na₂SO₄ solution

Temperature, °C	Duration, hour	Particle sizes, nm	%	∑particles less than 1000 nm
200	2	0.506	0.4	94.7
		4.82	5.1	
		153.6	89.2	
		2.6*10 ⁶	5.3	

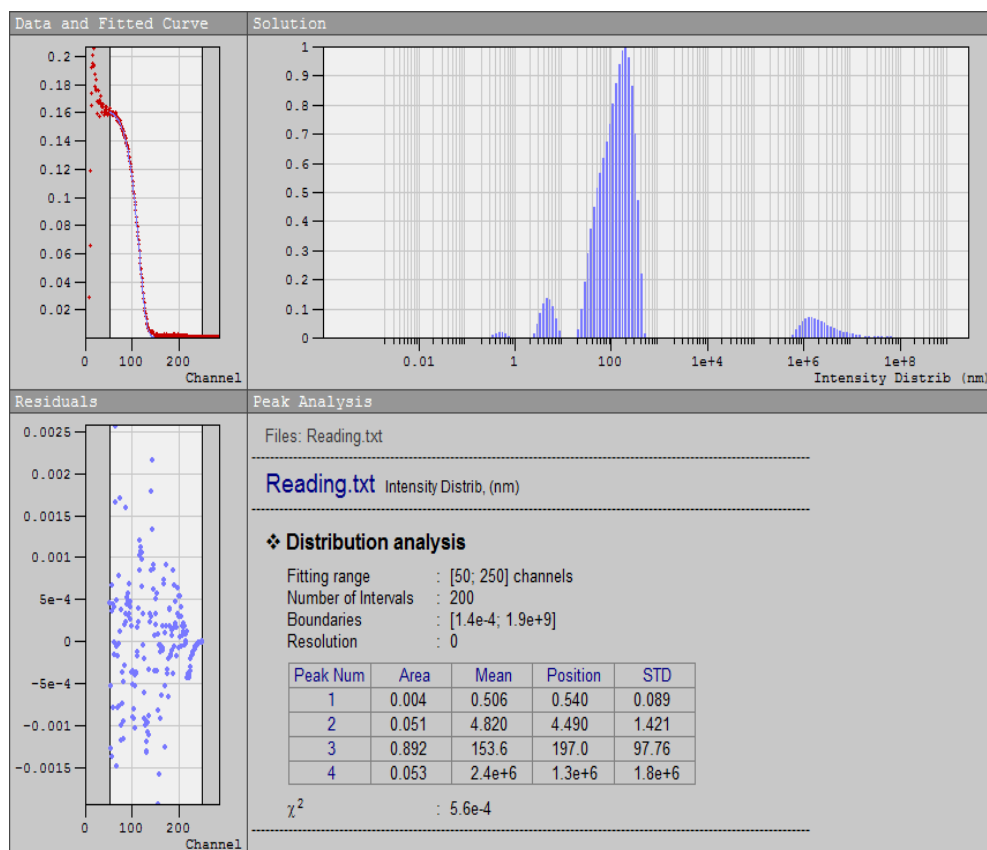


Figure 5. Structure of the slaked lime powder obtained at the temperature of 200 °C, in 20 % Na₂SO₄ solution

The achievement of a more fine-dispersed structure of slaked lime powder when using Na_2SO_4 solution can be explained by the presence of CaSO_4 , which hinders the agglomeration of calcium hydroxide powder.

Under normal conditions and atmospheric pressure, calcium oxide does not interact with sodium sulfate. However, under the specified conditions and increased pressure, the presence of calcium sulfate in the slaked lime was detected through X-ray phase analysis and infrared spectroscopy, amounting to 3.5 % (see Figure 6).

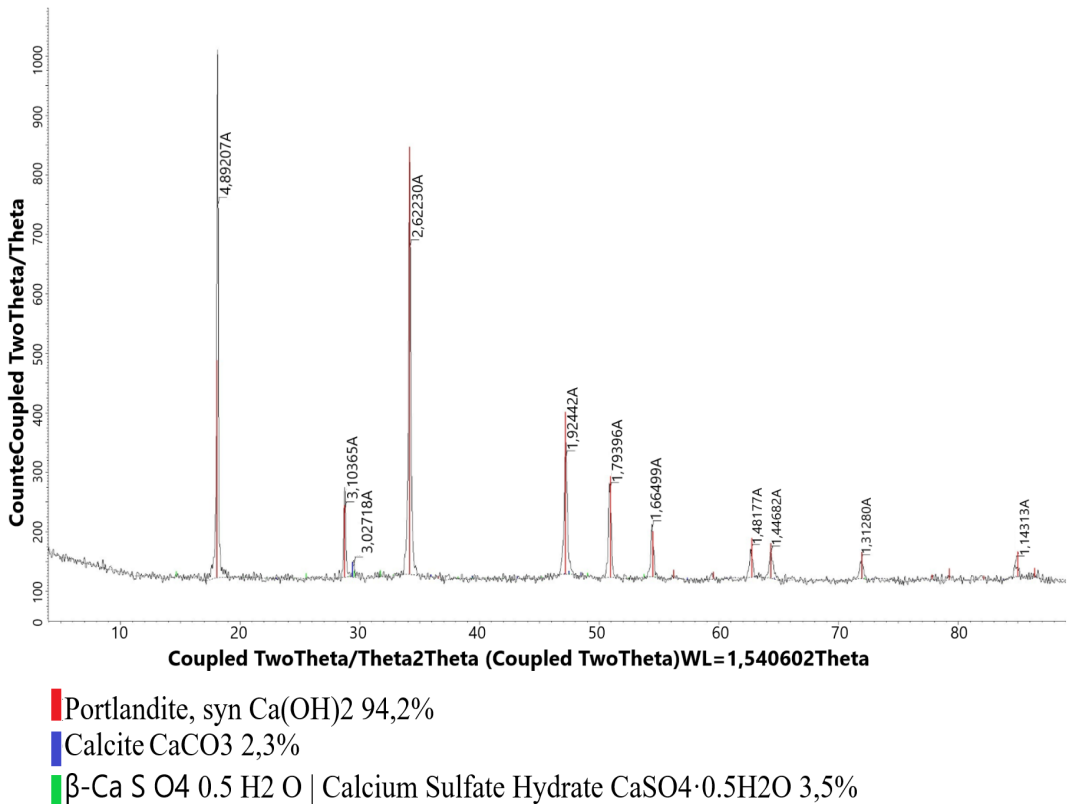


Figure 6. X-ray diagram of lime milk with calcium sulfate content

The analysis of lime powder - the slaked lime by infrared spectroscopy (Figure 7) showed the presence of the following phases:

$\text{Ca}(\text{OH})_2$ - 3643 cm^{-1} (Ni, Khalyapina, 1978; Yurchenko et al., 1981).

Monohydrocalcite $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ - $3422, 1794, 1477, 1431, 1084, 875, 859, 714, 700 \text{ cm}^{-1}$ (Yurchenko et al., 1981).

Group $[\text{SO}_4]^{2-}$ - 1139 cm^{-1} (Yurchenko et al., 1981; Pakhomov et al., 2017).

Gypsum $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ - $3500, 1139, 999, 670 \text{ cm}^{-1}$ (Yurchenko et al., 1981);

Calcoxite CaO - $542, 420 \text{ cm}^{-1}$ (Amayri et al., 2004).

Valence vibrations $\nu_{\text{Ca-O}}$ - 319 cm^{-1} (Little, 1969).

Valence vibrations $\nu_{\text{Mg-O}}$ - $542, 388 \text{ cm}^{-1}$ (Little, 1969).

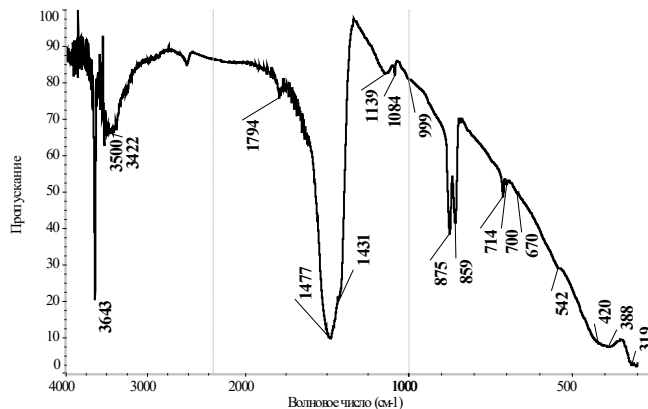


Figure 7. Infrared spectrum of the active form of lime milk with calcium sulfate content

As a result of leaching, the medium-modulus aluminat solution (MAS) and the mud were obtained with the following composition, % wt: Na₂O 2,9; Al₂O₃ 13,67; SiO₂ 20,35; CaO 28,49; Fe₂O₃ 24,37; TiO₂ 4,1; o.p. 6,12.

The phase composition of the FDKF leaching mud is shown in Figure 8.

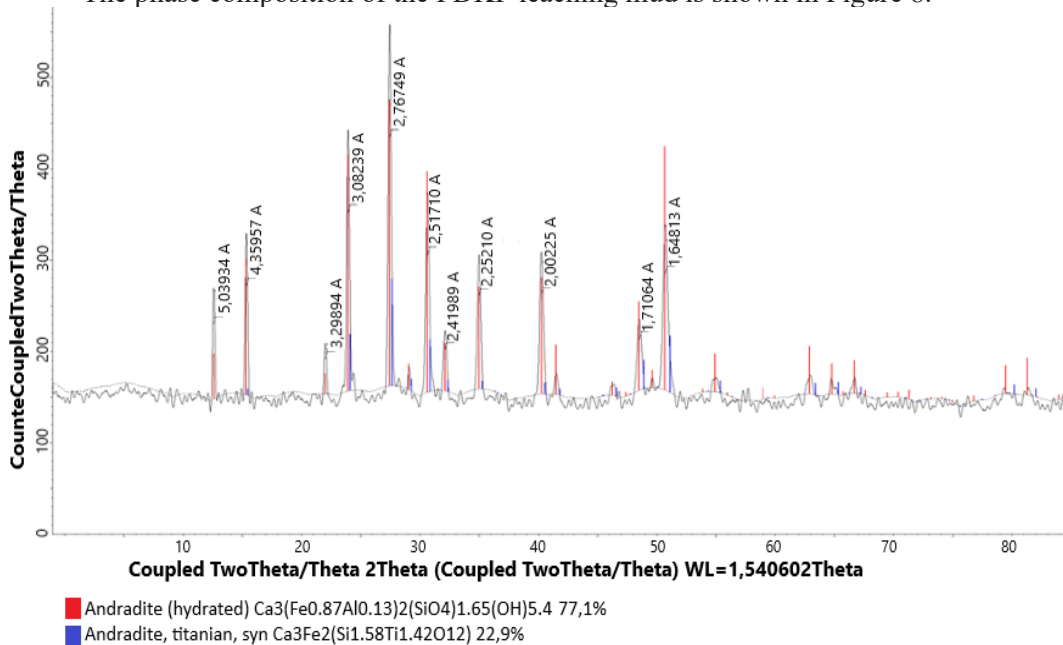


Figure 8. X-ray diagram of the leaching mud

The chemical composition of the medium-modulus solution (MMS), g/dm³: Na₂O_{caust} 248,1; Na₂O_{carb} 12,9; Al₂O₃ – 38,87; SiO₂ 0,1; α_{caust} = 10,5.

Autoclave leaching of the FDKD in the high-modulus solution (HMS) using a fine-dispersed active calcium additive made it possible to extract Al₂O₃ into the solution of 87.2 %.

The regeneration of the MMS solution was carried out by the synthesis of tricalcium hydroaluminat (TCHA) using Ca(OH)₂ according to the reaction:



The synthesis of TCHA was carried out at the temperature of 100 °C for 4 hours, with the addition of CaO from the stoichiometric amount of 100–120 %. The extraction of Al_2O_3 in TCHA was 70.5 %. At the same time, α_k of the resulting solution was 29.5 %. After evaporation, the resulting HMS can be used as the circulating solution for leaching a new portion of mud (Figure 4).

The chemical composition of TCHA, % wt: Al_2O_3 24,5; CaO 50,3, o.p. 25,2.

The phase composition of TCHA is shown in Figure 9.

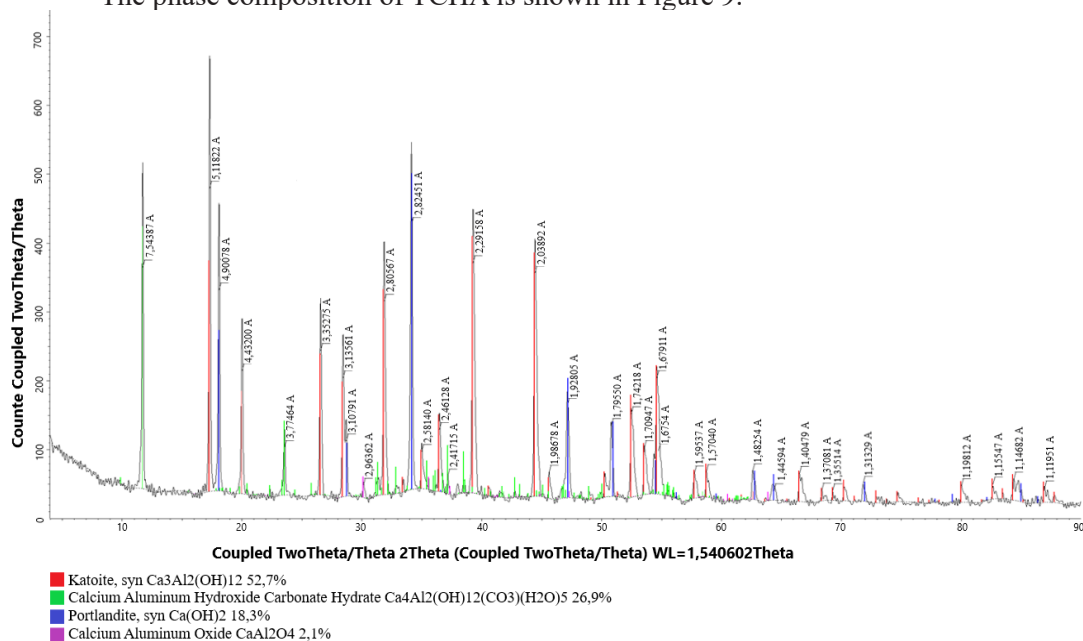
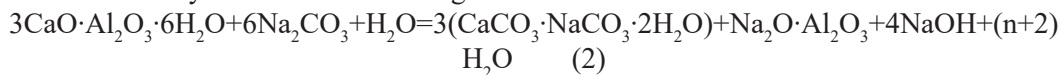


Figure 9. X-ray diagram of TCHA

To regenerate calcium oxide in form of CaCO_3 or $\text{Ca}(\text{OH})_2$, as well as to extract Al_2O_3 into the aluminum-alkaline solution, TCHA was decomposed in soda solution. Decomposition of TCHA in the system occurs according to the reaction:



As a result of the decomposition of TCHA, the extraction of Al_2O_3 was 95.8 %.

The chemical composition of the decomposition solution of TCHA, g/dm^3 : $\text{Na}_2\text{O}_{\text{caust}}$ 100,6, $\text{Na}_2\text{O}_{\text{carb}}$ 39,1, Al_2O_3 25,41, $\alpha_{\text{caust}} = 6,5$.

The phase composition of the sediment from TCHA leaching is represented by, %: calcite 88.5; hydrate 5.0 and hydrocarbonate 6.5.

The technology (figure for FDKF processing using the combined Bayer and hydrochemistry process with the application of active calcium additive) involves extracting $\text{Al}(\text{OH})_3$ from the solution through the decomposition of TCHA using the carbonization method (Brichkin, Sizyakov, 2004).

Thus, the FDKF processing using the combined Bayer and hydrochemistry process

with the application of active calcium additive made it possible to extract $\text{Al}(\text{OH})_3$ in the Bayer branch by 38.0 % and in the branch of hydrochemical mud processing - by 87.2 %. The total extraction was 92.06 %.

The possibility of applying the technology of hydrochemical processing of the FDKF in the HMS, including preliminary chemical activation, has been investigated (Figure 10).

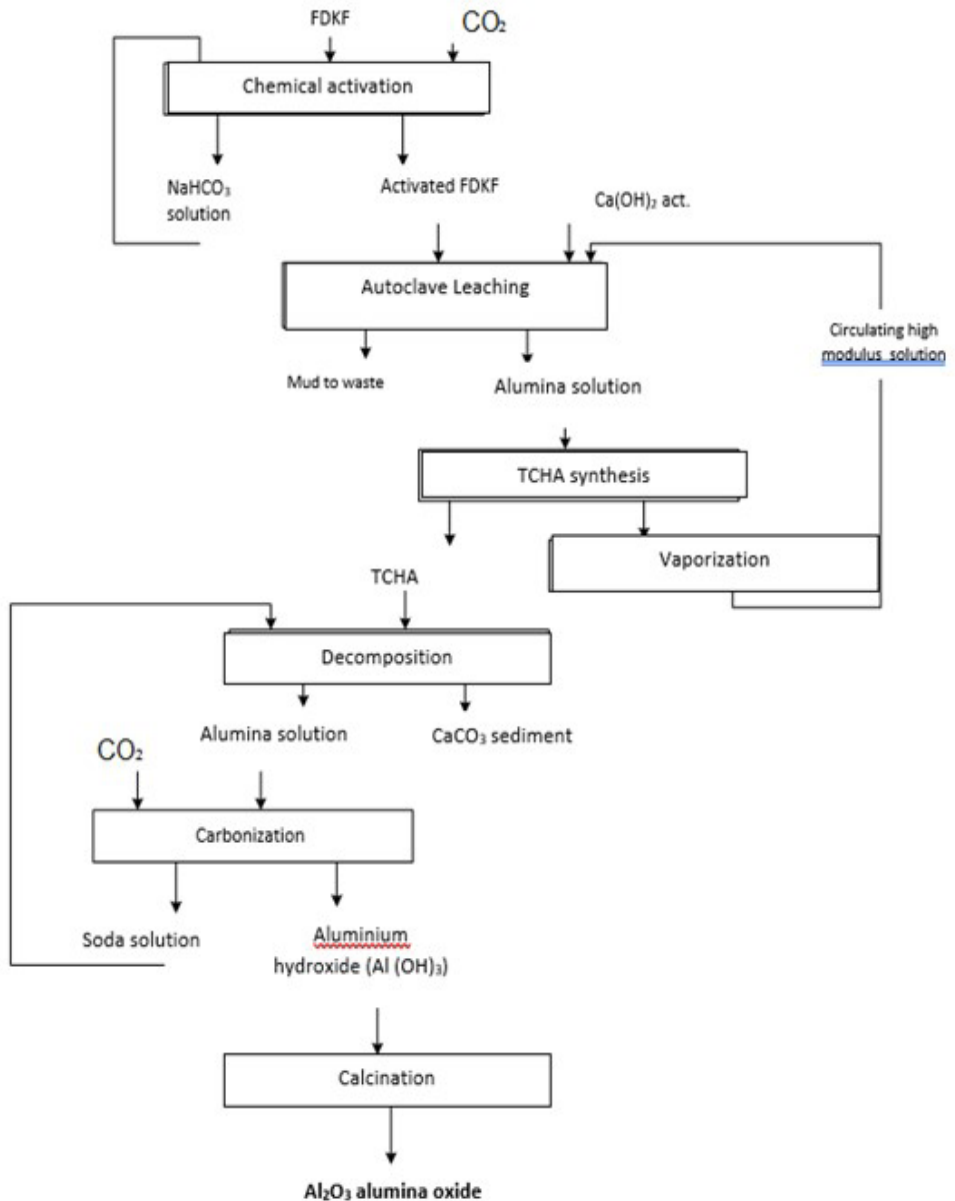


Figure 10. Processing of the FDKF according to a method including the preliminary chemical activation

The novelty of the hydrochemical processing technology for the refractory aluminosilicate material FDKF lies in the chemical activation and subsequent leaching in HMS using an active calcium additive, allowing for a single-stage leaching.

The chemical activation of the FDKF was conducted according to the method (patent for the ash 32333), involving thermochemical treatment in an autoclave, in NaHCO_3 solution, at the temperature of 120 °C, for duration of 180 minutes. Under these conditions, there is a complete transformation of the phase composition of the FDKF. Increasing the activation temperature up to 200 °C resulted in the completion of phase transformation processes within 60 minutes. However, conducting the process under these conditions would require higher energy consumption and the use of equipment operating at elevated temperature and pressure.

As a result of processing the FDKF, the phases of gibbsite, kaolinite and quartz disappeared, and new phases such as sodalite, dawsonite, and boehmite were formed (Figure 11).

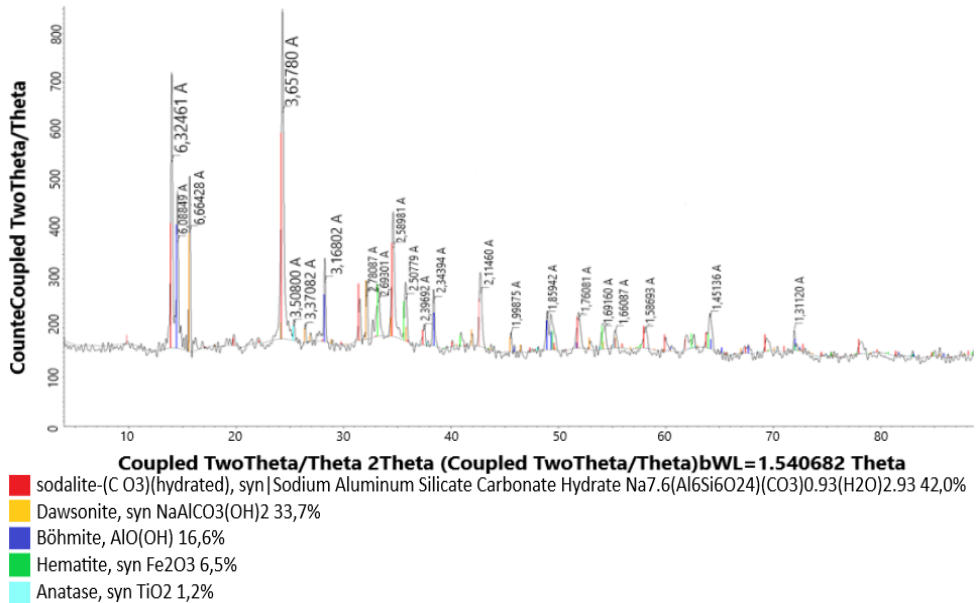


Figure 11. X-ray diagram of the FDKF after chemical activation

After preliminary chemical activation, hydrochemical leaching of the FDKF was carried out with the addition of the active form of calcium oxide to the HMS.

As a result of leaching, the waste mud and MMS were obtained. The extraction of Al_2O_3 into the solution was 89.5 %.

The chemical composition of MMS, g/dm^3 : $\text{Na}_2\text{O}_{\text{caust}}$ 250,1; $\text{Na}_2\text{O}_{\text{carb}}$ 11,2; Al_2O_3 – 38,09; SiO_2 0,1; $\alpha_{\text{caust}} = 10,8$.

The chemical composition of the dump sludge, wt. %: Al_2O_3 5,74; SiO_2 18,9; Fe_2O_3 10,3; CaO 28,35; Na_2O 1,1; TiO_2 4,0 and o.p. 31,61.

The phase composition of the waste mud is shown in Figure 12.

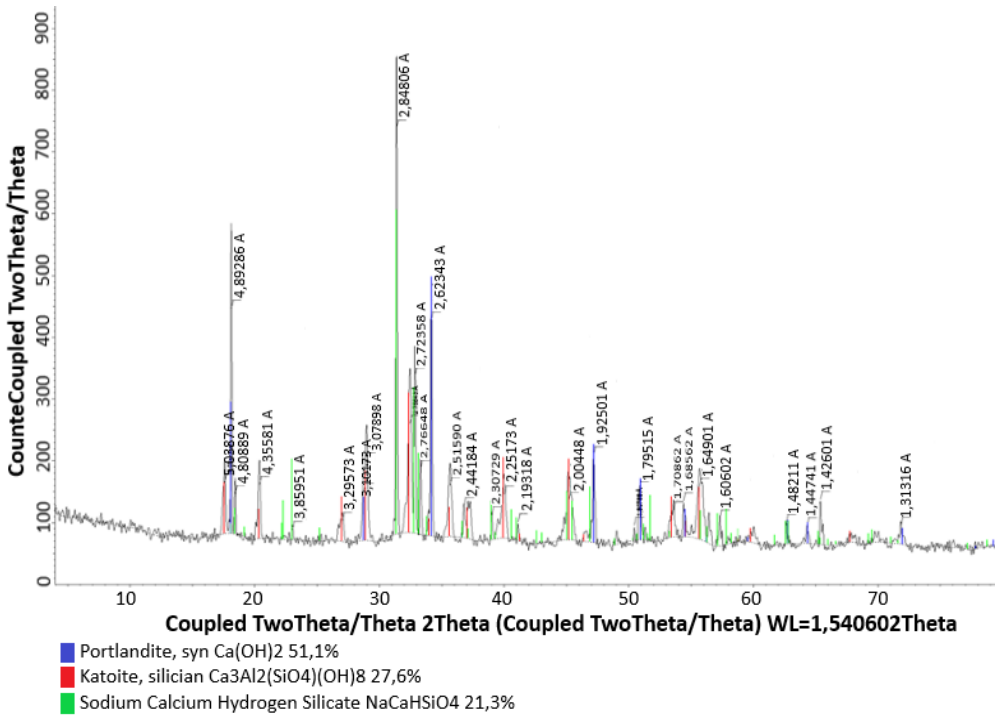


Figure 12. X-ray diagram of the waste mud

The MMS was processed using a similar method of synthesis and decomposition of TCHA in soda solution and carbonation (Figure 10).

The results of studies on the possibility of using and improving alternative methods of processing the FDKF bauxite are shown in Table 9.

Table 9. Characteristics of the FDKF processing methods

Name of the FDKF processing method	Technological operations			Extraction of Al_2O_3 into solution, %	Disadvantages	Advantages
	Calcination	Chemical activation	Use of an active calcium supplement			
Preliminary thermochemical transformation	+	-	-	70	Energy-consuming calcination, low extraction of Al_2O_3	Obtaining a silicate product

Combined processing under the Bayer process - hydrochemistry	-	+	+	92.06	Two-stage leaching; necessary modernization of the existing Bayer and sintering production	Possible use of existing equipment for the Bayer and sintering process; Reduction of material flow directed to autoclave leaching
Hydrochemical processing with preliminary chemical activation	-	-	+	89.5	Necessary modernization of the existing Bayer and sintering production	Single-stage leaching

Conclusions

The studies have been conducted on methods for separate processing of the FDKF gibbsite-kaolinite bauxites, including: preliminary thermochemical transformation, combined processing using the Bayer and hydrochemistry process, and hydrochemical processing with the preliminary chemical activation.

The optimal conditions for the preliminary thermochemical transformation of the FDKF is pre-calcination at the temperature of 950 °C. When using it for leaching the circulating aluminate solutions of the Bayer branch, solutions with $\alpha_{\text{caust}} = 1.65-1.7$ were obtained, suitable for extracting $\text{Al}(\text{OH})_3$ by the decomposition method. The extraction of Al_2O_3 into the leaching solution was 70 %.

For the hydrochemical processing of the FDKF leaching mud in the Bayer branch, a method has been developed for obtaining the active form of a calcium additive as a result of slaking CaO in the solution containing 20 % Na_2SO_4 , the number of lime powder particles less than 1 μm was 94.7 %. The extraction of $\text{Al}(\text{OH})_3$ in the Bayer branch was obtained by 38.0 % and in the branch of hydrochemical mud processing by 87.2 %. The total extraction was 92.06 %.

As a result of the preliminary chemical activation of the FDKF in sodium hydrocarbonate solution at the temperature of 120 °C for 180 minutes, the complete transformation of the phase composition occurred. Gibbsite, kaolinite, and quartz phases disappeared, while new phases such as sodalite, dausonite and bemitite were formed. When the activation temperature increases up to 200 °C, the phase transformation processes end within 60 minutes, however, this leads to an increase in energy consumption and the need for appropriate equipment.

After the chemical activation of the FDKF, as a result of hydrochemical leaching in the HMS with the addition of an active calcium additive, the waste mud and the MMS were obtained, while the extraction of Al_2O_3 into the solution was 89.5 %.

Thus, the possibilities of processing the FDKF through various hydrochemical methods, including transformation techniques, chemical activation and use of active calcium additives, have been investigated. The choice of technology depends on the specific production conditions – the availability of existing equipment and the amount of modernization.

The work was carried out with the financial support of the Committee of the Ministry of Education and Science of the Republic of Kazakhstan upon the grant financing No. AR14869208.

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ISSN 2518-1483 (Online), ISSN 2224-5227 (Print)

<http://geolog-technical.kz/en/archive/>

Подписано в печать 15.06.2024.

Формат 60x88¹/₈. Бумага офсетная. Печать - ризограф.

15,0 п.л. Тираж 300. Заказ 3.