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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

COMPLEX PROCESSING OF ALUNITE BASED ON THE PRINCIPLES OF GREEN CHEMISTRY

Speciality: 2303.01- Inorganic Chemistry

Field of Science: Chemistry

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The work was performed at the scientific research laboratory "Processing of mineral raw materials containing non-ferrous metals" at the Institute of Catalysis and Inorganic Chemistry named after Academician M. Nagiyev, Ministry of Science and Education of Azerbaijan.

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INTRODUCTION

Relevance of the topic and degree of development. Due to the use of aluminum alloys in machine building, electrical, automotive, chemical and metallurgical industries, construction sites, and household items, it is considered one of the strategically important metals.

In the production of aluminum, bauxite is used as the main source of raw materials around the world, and nepheline is used in Russia. Since there are no such ore raw materials in our country, its production had been carried out by processing another aluminumcontaining ore - alunite. According to estimates, the reserve of the Zaglik alunite ore deposit is more than 163 million tons. During the 31 years of operation of the Ganja Clay Plant, up to 18 million tons of alunite ore were processed, during which tons of necessary products such as Al₂O₃, H₂SO₄, K₂SO₄ were produced. The plant worked with ore containing 50% alunite mineral. Rocks containing less than 40% alunite minerals were not sent for processing and became production waste because they could not be enriched. Due to a number of reasons (transporting alunite ore to long distances, burning it together with loose rock at 600°C for several hours, consuming a large amount of fuel for combustion, not fully capturing and disposing of gases and dusts released into the atmosphere after combustion, purchasing reagents and materials used from outside (usually from foreign countries), reduction of rich ore reserves, loss of useful products, excess consumption of energy carriers) the operation of the plant was stopped. These shortcomings necessitate an innovative approach to the processing of Zaglik alunite.

In general, despite numerous studies,¹ the direct complex processing of poor alunite ore has not yet been solved. Therefore, the search for effective processing methods of alunite ore, an innovative approach to solving a number of environmental problems, and

¹ Taghiyev, E.I. Analysis of technological issues, related to processing of alunite at Ganja Alumina Plant (GAP), and ways of their solving // International Journal of Chemistry, – 2020. 12(1), – p. 69-76.

ensuring the principles of green chemistry are among the most important and urgent problems facing researchers.

Green chemistry is a new scientific direction, it is any improvement of any chemical processes that have a positive effect on the environment, the main strategy of which is to ensure the selection of alternative methods that are as harmless as possible to the environment in obtaining any substance². The principles of green chemistry are summarized as follows:

Finding chemical solutions to prevent environmental pollution (absence of burning stage in research, prevention of environmental pollution with sulfur gases and alunite dust); Using the minimum amount of chemicals during the process; Minimize the generation of hazardous waste; Get as little waste as possible (application of the obtained alunite slurry as a sorbent during the desilication stage, use in the construction field after the microcomponents in it are removed); Choose an alternative processing method as much as possible; Do not use hazardous solvents; The final product of the processing process must be clean and non-toxic (precipitation of aluminum hydroxide with hydrogen peroxide, a green reagent); Buying the substances used during the process from the process itself (buying the alkaline solution used during the processing from the process itself).

The determining direction for solving the mentioned problems is the development of new processes and methods based on environmentally friendly, waste-free production.

Currently, a new concept in the processing of alunite ore is the direct processing of the alunite mineral rock with an alkaline solution without burning. In this regard, it is possible to develop a new processing method of alunite as a result of studying the chemistry, kinetics, and physico-chemical bases of the processes occurring at each stage of alunite processing.

Thus, taking into account the raw material needs of Azerbaijan's aluminum industry and the requirements of the Strategic

² Sankar P.D, Sepa N.A textbook of green chemistry // First edition: September, India: 2021. 420 p.

Road Map put forward by the State, the creation of a new alunite technology is one of the urgent issues.

The object and subject of the research. The alunite ore taken from the Zaglik alunite deposit located in Dashkasan region of Azerbaijan has been used in the research work.

The purpose of the study and tasks: The aim of the research work is to study the chemical regularities and kinetics of the processes during the processing of alunite ore, and develop the scientific basis of a simple, environmentally friendly alunite processing technology that meets the principles of green chemistry. To achieve the chosen goal, the following tasks were set and solved :

- Conducting thermodynamic calculations to justify the method of direct dissolution of the main components of alunite ore in alkali;

- Finding the optimal conditions of processing stages, such as the complete transition of alunite mineral from ore to solution, desilication of aluminate solutions, precipitation of aluminum hydroxide from purified solutions with hydrogen peroxide, research of its chemistry and kinetics;

- Investigation of phase transformations occurring during the deposition of crystalline aluminum phase (boemite) from aluminate solutions by physico-chemical analysis methods;

- alkaline and acid solutions from potassium (sodium) sulfate salt solutions by electrodialysis using bipolar, anion and cation exchange membranes and increasing the concentration, researching the processes occurring in the membranes.

Research methods. Analysis methods such as X-ray phase (RFA) and X-ray fluorescence, infrared spectroscopy (IR), differential thermal analysis (DTA), flame photometric method, photocalorimetric method, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) were used during the research.

The main clauses that have been defended.

- Studying the dependence of the solubility of alunite mineral in alkali on factors such as temperature, time, alkali density;

- Preparation of the method of purification of silicate ions from aluminate solutions by sorption method, study of factors affecting adsorption; increasing of silicon module and desilication percentage; - Studying the kinetic regularities of the processing stages - rate constant of the reaction, composition of the reaction, calculation of activation energy;

- Finding the optimal conditions for precipitation of aluminum hydroxide with hydrogen peroxide solution, which is considered a green reagent, studying the chemistry and mechanism of precipitation, studying the phase transitions that occur during the crystallization of amorphous aluminum hydroxide depending on the ripening time;

- Study of the factors affecting the production of alkaline and acid solutions from diluted alkali metal sulfate salt solutions by electrodialysis method;

- Preparation of the principle technological scheme of the proposed alunite complex processing method based on the principles of green chemistry.

Scientific novelty of the research. Taking an innovative approach to the processing of Zaglik alunite ore, complex processing of raw alunite without burning was carried out, the thermodynamic evaluation of the reactions of the dissolution of the minerals that make up the alunite ore in the alkaline solution at low temperatures was calculated, the formal kinetics of the reactions occurring in the processing stages, the reaction mechanism and the chemistry of the process were studied.

To remove silicate ions from low-density aluminate solutions obtained from the processing of alunite ore, sulfated Friedel phase salt - $Ca_6Al_3(OH)_{18}(SO_4)_{15}(H_2O)_9$ was obtained, the individuality of the compound was confirmed by physicochemical analysis methods, its alunite and its mixture with sludge was used as an adsorbent and the method was patented in the Intellectual Property Agency. With this method, up to ~95% of silicon can be removed from the aluminate solution. Also, the kinetic parameters of the process were calculated.

The conditions for precipitation of aluminum hydroxide with hydrogen peroxide, a green reagent, from desilicated aluminate solutions were studied. The phase transformations occurring during the aging of aluminum hydroxide crystals at different times and temperatures were studied with the help of physicochemical analysis methods. It was found that increasing the time leads to the formation of the highly dispersed boehmite (AlOOH) phase, which is the final product.

The results obtained from the experiments were processed by the fuzzy logic theory.

The theoretical and practical significance of the research. Treatment of alunite ore with an alkaline solution, desilication of the obtained aluminate solutions, precipitation of aluminum hydroxide, obtaining the crystalline boehmite phase, and the methods of obtaining alkaline and acid solutions by electrodialysis are contributions to the method of obtaining aluminum oxide with the expectation of environmental cleanliness.

The practical significance of the work is that according to the principles of green chemistry, the processing stages of alunite are ecologically efficient and can be applied to the processing technology of alunite ore at the Clay-soil plant.

Approval and application. The materials of the dissertation were heard and discussed at the following scientific conferences: XII International Scientific and Practical Conference "Actual problems of chemistry" for doctoral students, undergraduates and young scientists dedicated to the 95th anniversary of the national leader Heydar Aliyev, BSU, Baku, 2018; The 2nd international scientific conference of students and young researchers dedicated to the 98th anniversary of the national leader of Azerbaijan Heydar Aliyev, BHOS, Baku, 2021: XIV International Scientific and Practical Conference "Actual Problems of Chemistry", BSU, Baku, 2021; Международной научной конференции "Молодые исследователи - регионам", Вологда, 2021; Научной конференции «Наука, Техника и Развитие Инновационных Технологий», Ашхабад, 2021; The 1st International Scientific and Practical Conference Scientific Paradigm in The Context of Technologies and Society Development, Geneva, Switzerland, 2021; IX Международной научно практической конференции "Challenges in science of nowadays" Вашингтон, CIIIA, 2021; VI International Scientific Conference of Young

Researchers, BEU, Baku, 2022; «Kimya və Kimya Texnologiyası» Respublika Elmi Konfransı, BDU, Bakı, 2022.

Personal contribution of the author. The executive candidate is responsible for solving the issues raised in the dissertation work, conducting analyzes based on the samples obtained from laboratory experiments, analyzing the results obtained by physico-chemical analysis methods, writing theses and articles, and the dissertation.

Published scientific works: 18 scientific works on the dissertation, including 8 articles (in scientific journals indexed in international databases 4 - WOS, 4 - SCOPUS), 1 patent and 9 conference materials were published.

The name of the organization where the dissertation work was performed . The dissertation work was carried out in accordance with the plan of scientific research conducted at the Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev (state registration No. 0115 Az 2099).

The structure and scope of the work: The dissertation consists of an introduction, 5 chapters, conclusions, and a list of references with 191 titles. The work consisted of 166 pages, 186395 signs (introduction 14883, chapter I 55403, chapter II 20334, chapter III 46134, chapter IV 24835, chapter V 21943, results 2863), 39 pictures, 19 tables and 23 graphs, abbreviations and conventional signs concludes with .

MAIN CONTENTS OF THE WORK

In the introduction , the relevance of the work is substantiated, provisions to be defended are given, information about the purpose, scientific innovation, practical importance, publication and approval of the work is explained.

The first chapter of the dissertation is devoted to the discussion of the literature review on complex processing of alunite ore. At the beginning of the chapter, materials on the past and present state of aluminum's natural compounds, acquisition, properties, application, and production are given. It is shown that despite the large number of proposed methods for the processing of alunite ore, none of them has been practically applied on an industrial scale. The

reason is that these methods are ineffective and environmentally unfriendly. In the last sections of the chapter, during the processing of alunite by the recovery-alkaline method at the Ganja clay-soil processing plant, its stages, their chemistry are highlighted and the defects in the processing stages are shown.

The second chapter is the methodical part, it is dedicated to the determination of the components of the alunite ore and a brief description of the physico-chemical research methods. As an analysis method, in the first stage, direct dissolution of alunite in alkaline solution, and in the second stage, dissolution of the residue obtained after processing with alkali in tsar vodka was taken.

The third chapter. Aluminum ore is distributed in the form of alunite (KAl₃(SO₄)₂(OH)₆) and dickite (Al₂Si₂O₅(OH)₄) minerals. X-ray analysis confirms the presence of alunite, dickite, hematite and quartz minerals in the ore. Since the components are unevenly distributed in the ore, most of the experiments were carried out with the average sample brought from the combine. The chemical composition is as follows, %: Al₂O_{3(alunite)} – 19.2, Al₂O_{3(dickite)} – 2.5, SO₃ –20.0, Na₂O – 1.38, K₂O – 3.72, SiO₂ – 41.4, Fe₂O₃ – 5.05, CaO – 0.2, P₂O₅ – 0.18, MgO – 0.12, TiO₂ – 0.53, H₂O – 6.5 (ω_{alunit} = 50.8%).

As can be seen from the results of SEM/EDS analysis of raw alunite ore sample, alunite ore consists of particles of different shapes (Fig. 1):

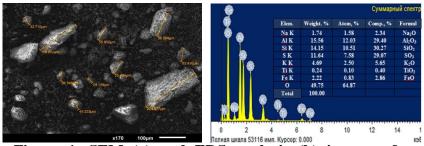


Figure 1. SEM (a) and EDS analysis (b) images of an alunite ore sample

Processing of alunite ore by hydrometallurgical method. The application of hydrometallurgical processes provides selective complex extraction of metals from poor and difficult-to-enrich ores. The main purpose of dissolution is to transfer the aluminum in the alunite ore to more solution, and to keep the quartz together with the hematite in the slurry.

First, a thermodynamic evaluation of the solubility of minerals in ore in alkali was carried out (table 1), the thermodynamic probability of reactions that may occur in the interval of 298-363K was calculated using the Ulix equation (1):

$$\Delta G_{\rm T}^{0} = \Delta H^{0}_{298} - T\Delta S^{0}_{298} + \Delta C_{\rm p,298} T[\ln(T/298) + (298/T) - 1]$$
(1)

where, ΔG_T^{0} - Gibbs energy, ΔH^{0}_{298} - enthalpy of formation, ΔS^{0}_{298} - entropy of formation, $\Delta C_{p, 298}$ - standard heat of formation, T - temperature.

The thermodynamic characteristics of the initial and obtained substances during the dissolution of ore in alkali were taken from the literature³ and calculated for the following reactions:

$$\begin{aligned} & \text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{KOH} = 2\text{K}_2\text{SO}_4 + 3\text{KAlO}_2 + 6\text{H}_2\text{O} \quad (2) \\ & \text{SiO}_2 + 2\text{KOH} = \text{K}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (3) \\ & \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{KOH} = 2\text{KAlO}_2 + 2\text{K}_2\text{SiO}_3 + 5\text{H}_2\text{O} \quad (4) \end{aligned}$$

Table 1.

Values of isobaric-isothermal potentials of dissolution reactions of alunite, quartz and dickite in alkali

		ΔH, k	J/mol		ΔG , kJ/mol					
Т	298K	323K	343K	363K	298K	323K	343K	363K		
Reac. 2	-888.2	-883.7	-880.1	-876.5	-958.7	-964.8	-969.9	-975.3		
Reac. 3	526.3	524.5	523.0	521.2	531.2	593.2	610.3	627.1		
Reac. 4	-118.3	-119.4	-120.2	-121.0	-150.0	-152.6	- 154.6	-150.0		

From the comparison of the Gibbs energy values, it can be seen that it is theoretically thermodynamically possible for both alunite and dickite to dissolve in alkali in this temperature range. However, the dissolution probability of dickite is 5.9 times smaller than that of

³ Rossini, FD Selected values of chemical thermodynamic properties / FD Rossini, DD Wagman, WH Evans [et al.] / Institute for Basic Standards National Bureau of Standards, – Washington: – 1960. – 270 p.

alunite. The dissolution of quartz and hematite is theoretically impossible.

The dissolution of alunite ore in an alkaline solution without burning was carried out by ball and tank dissolution methods, and the results showed that the alunite mineral in the ore can be dissolved in an alkaline solution (3 and 10% NaOH) even at room temperature. When a 3% alkali solution is poured into a heap of alunite ore, its mass decreases by 30.65% during 17 times washing, and by 47.82% during 14 times washing with 10% alkali. The final result shows that by increasing the hardness and the number of washing steps, the alunite mineral in the ore can be fully dissolved in the alkaline solution.

By mixing the solid:liquid phase mixture at room temperature with the "Roll bottle" method, it is possible to reduce the duration of the dissolution process and increase its speed. An increase in alkali concentration and temperature intensifies the decomposition of alunite mineral, accelerates the transition of sodium aluminate to solution. Experiments have shown that when the speed of the mixer is more than 700 period/min, the speed of aluminum entering the solution in the form of aluminate ion [Al(OH)₄]⁻ does not depend on the speed of mixing. Solid:liquid phase ratio (S:L) - 1:5, v_{mix} = 700 cycles/min, C_{alkali} = 110 g/l, t = 80°C, τ = 60 min., then ~ 96% of alunite mineral dissolves and goes into solution.

IR spectroscopy method was also used to monitor complete dissolution of alunite mineral from alunite ore in alkaline solution. For this purpose, infrared spectra of raw alunite ore and alunite mud samples obtained from its dissolution in 5% alkaline solution at different times were recorded. A broad absorption band with a maximum of 3481.02 (3480.03) cm⁻¹ in the region of 3000-3600 cm¹ in the initial alunite ore and the mud obtained after dissolution for 5 minutes indicates the presence of hydroxide groups in the alunite. Mud samples taken without dissolution for 15 and 30 min do not have these bands. On the other hand, the 1088 cm⁻¹, 1085 cm⁻¹ absorption band characteristic of the SO₄²⁻ group observed in the initial alunite sample and the mud obtained for 5 minutes. Intensities

characteristic of kaolin mineral (913.7 cm⁻¹) are observed in all samples.

Study of formal-kinetic laws of dissolution of alunite mineral in alkaline solution. Since alunite ore is multi-component, the study of its real kinetic parameters depending on the conditions of dissolution is complicated from an experimental point of view. Therefore, it is more appropriate to study the formal kinetics of dissolution. The study of kinetics is also important for explaining the mechanism of alunite mineral dissolution in alkali and choosing optimal conditions.

During the analysis of the kinetics, it is assumed that the alunite mineral in the ore goes into solution in the form of aluminate as a complete solution. The dissolution was carried out in a mixer equipped with a thermostat, the variable parameters were the concentration of KOH solution (C_{KOH}), temperature (t), mixing time (τ).

The kinetic parameters of the experimental results are calculated by the B.Verofiev equation.

$$1 - \alpha = e^{-k\tau^{n}} \quad \text{va ya } \alpha = 1 - e^{-k\tau^{n}}; \qquad \frac{d(1 - \alpha)}{d\tau} = -k(1 - \alpha) \tag{5}$$

Here, α and 1 - α is the mass fraction of alunite that passes into the solution and remains in the solid phase depending on time, *k* is the rate constant of the reaction, $\ln(1-\alpha)$ is determined experimentally as the tangent angle of the straight line in the τ coordinate, τ is the experimental period, n is the composition of the reaction. Figure 2 shows the kinetic dependences of the process of dissolution of alunite mineral from ore at 333K with KOH solutions of different concentrations.

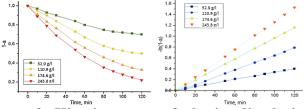


Figure 2. Kinetic curves of alunite dissolution process at 333K with KOH solutions of different concentrations

As can be seen from Figure 2, the amount of alunite that passes into the solution changes in direct proportion to the concentration of the alkali, and the increase in the concentration of KOH in the solution leads to the faster dissolution of the alunite mineral.

According to equation (5), the value of k determined by thickness is as follows: 0.0034; 0.0062; 0.0096; 0.0127. The dependence of the value of k on the concentration of the alkali is linear, which indicates that the solubility obeys the uniform reaction laws.

Temperature dependence of the logarithm of the rate constant (*k*) is described by the Arrhenius equation (Fig. 3).

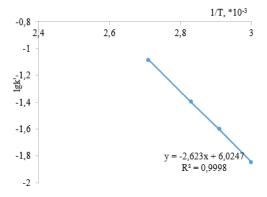


Figure 3. Temperature dependence of the logarithm of the rate constant of the dissolution of alunite mineral ($C_{KOH} = 110.9g/l$)

In this case, the activation energy is calculated by using the Arrhenius equation and knowing the value of the tangent of the straight line $E_a = 2.303 |tg \alpha| \xi$ can be determined by the formula

On the selected scale, $|tg \alpha|=1.91$, the ratio of scales along the abscissa and ordinate axes is $-\xi = (1:0.1\cdot 10^{-3}):(1:0.2)=2\cdot 10^{3}$. At this time: $E_a = 73.14 \text{ kJ/mol}$.

According to the found value of activation energy and reaction composition (n=1.1), it can be concluded that the reaction of alunite dissolution with alkali is caused by a homogeneous chemical reaction occurring on the surface in the range of 333-368 K.

Determining the conditions for desilication of aluminate solutions, studying the chemistry and kinetics of the process.

Siliceous compounds are considered harmful mixtures that negatively affect the quality of the product when clay-soil is produced by the alkaline method. Purification of aluminate solutions from silicon is determined by the silicon modulus $(\mu_{si} = m(Al_2O_3)/m(SiO_2))$, the higher the value, the purer the final solution.

It was determined by us that when the alunite mud obtained from the processing of alunite ore is treated with sulfuric acid, the dickite mineral in its content is decomposed, and a new phase containing $Ca_6Al_3(OH)_{18}(SO_4)_{1.5}(H_2O)_9$ is formed in the residue left after dissolution (picture 4).

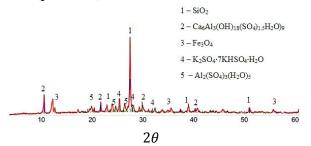


Figure 4. X-ray analysis result of the residue obtained from sulphation of alunite mud

The compound $Ca_6Al_3(OH)_{18}(SO_4)_{1.5}(H_2O)_9$ is a sulfated Friedel phase salt (FS) and has the ability to sorb silicate ions in solution.

Sorption experiments were first performed with sulfated alunite slurry, keeping the process conditions as in the initial stage and recirculating the aluminate solution repeatedly. After seven cycles, the concentration of aluminum oxide in the solution increases by approximately 1.7 times (69.2 g/l), and the concentration of silicon oxide decreases by 43 times (0.009 g/l).

In the next subchapters, the mechanism of desilication was clarified by studying the chemistry and kinetics of the process. Kinetics of desilicification was previously studied in model solutions - Al(OH)₃ and Na₂SiO₃·9H₂O reactants in an alkaline solution at a temperature of 90°C in solutions with a density of 1-4 g/l SiO₂.

The sulfated FS used in the experiments was synthesized using appropriate reagents. The compound with the chemical composition $Ca_6Al_3(OH)_{18}(SO_4)_{1.5}(H_2O)_9$ belongs to the family of layered double hydroxides and has the ability to separate anions due to the ion exchange reaction.

The chemical equation of silicate ion adsorption can be expressed as follows (6):

 $Ca_{4}Al_{2}(OH)_{12}SO_{4}(H_{2}O)_{6} + SiO_{2}(OH)_{2}^{2} = Ca_{3}Al_{2}(OH)_{12}SiO_{2} + SO_{4}^{2} + Ca(OH)_{2} + 6H_{2}O$ (6)

 SO_4^{2-} ion present in the solution again reacts with $Ca(OH)_2$ to form a $CaSO_4 \cdot 2H_2O$ (gypsum) precipitate, which has a high desilication ability and ensures the complete separation of silicon from the aluminate solution.

The results of SEM/EDS analyzes of the adsorbent before and after sorption show that the samples differ from each other both in terms of morphology and chemical composition (Fig. 5).

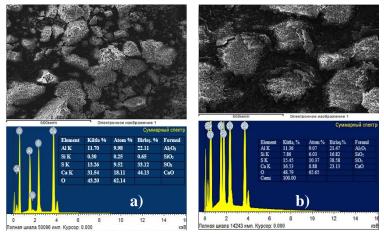


Figure 5. SEM/EDS analysis results of sulfated FS (a - before sorption and b - after sorption)

In alkaline aluminate solutions (pH=13), aluminum [Al(OH)₄]⁻, and silicon $H_3SiO_4^{-}(SiO(OH)_3^{-})$ or $H_2SiO_4^{2-}(SiO_2(OH)_2^{2-})$ exists in the form of ions. According to the results of SEM/EDS analysis, it

can be considered that the sorbed silicate ions are exchanged with sulfate ions in the intermediate layers of the adsorbent.

The rate of silicification, i.e. the amount of SiO_2 that passes into the adsorbent in a unit time amount of many factors: SiO_2 in solution depends on the initial density, time, temperature, mixing speed and adsorbent dosage. The rate of desilication reaction was calculated by the following formal kinetic equation (7):

$$-\frac{\mathrm{dC}}{\mathrm{d\tau}} = \mathbf{k} \cdot \mathbf{C}^{\mathrm{n}}; \qquad \ln \frac{\mathrm{C}_{0}}{\mathrm{C}_{\mathrm{SiO}}} = k \cdot \tau$$

where, C_0 – concentration of SiO₂ (g/l) during any time, C_{SiO_2} - initial density of SiO₂ in the solution (g/l), τ – time of desilication (minute), n – reaction order , *k* –reaction rate constant (min⁻¹).

Figure 6, a shows the linear dependence of the desilicification rate at different concentrations of SiO_2 in the solution.

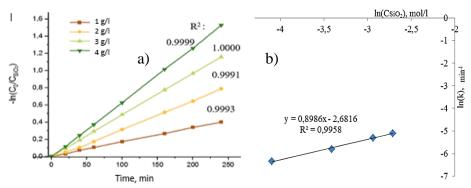


Figure 6. Kinetic curves of desilication process for silicon 4oxide solutions with different concentrations (a); dependence of $\ln k$ on $\ln C_{SiO_2}$ to determine the reaction order (b)

Tangens of these lines gives the numerical value of the coefficient *k* which is obtained from equation 7 gives the numerical value of the coefficient. The dependence of $\ln k$ on $\ln C_{sio_2}$ constructed according to these parameters, is straight-line, its inclination angle indicates that the composition of the reaction due to the density of SiO₂ is 0.99 (figure 6, b)

Further research is the calculation of the true rate of desilication as a function of solution temperature (Fig. 7).

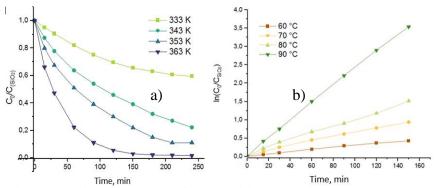


Figure 7. Kinetic curves of the desilication process in the range of 333-363K (m_{ads} – 40 g/l, v_{mix} – 300 cycles/min, C_{SiO_2} = 2 g/l)

It can be seen from the results of the experiments that the rate of silicification is directly proportional to the temperature.

The rate constants calculated according to the tangent of the angle of inclination of the straight line of the desilicification reaction occurring in the interval 333-363K are as follows, min⁻¹: 0.0021; 0.0057; 0.0097; 0.0238. The values of *k* are adequately written by the Arrhenius equation. From the value of the activation energy ($E_a = 74.36 \text{ kJ/mol}$), it can be concluded that the process of silicification of aluminate solutions in the range of 333-363K goes to the kinetic region as a result of anion exchange.

Considering these results, the adsorption of silicate ions was investigated in real aluminate solutions. Composition Al₂O₃ – 88 g/l; Na₂O – 110 g/l; SiO₂ – 0.327 g/l (μ_{si} =269) silicate ions were sorbed from the aluminate solution in the temperature range of 50-90°C for 2 hours (table 2).

According to the comparison of the results of the experiments, t= 50°C, $\tau = 2$ hours, alunite mud + FS mixture = 15 + 5g, $\upsilon_{mix} = 200$ cycles ⁻¹ were accepted as optimal conditions. The adsorbent mixture can remove up to 94.65% of silica from aluminate solutions.

Silica modulus of the final solution $\mu_{SiO_2} = 5034.2$, and the solution is considered suitable for obtaining pure aluminum oxide.

Table 2. Time, temperature, and adsorbent dosage on silica removal from solution

						пон	i solutioi
Exp.	t,°C	τ,	A.M. +		11		
N⁰	ι, υ	hour	sulfated-FS	Na ₂ O	Al_2O_3	SiO ₂	μ_{SiO_2}
	In	itial solu	tion	110	88	0.327	269.1
1	50	2	20 g	109.2	88	0.192	458.3
2	50	2	19+1	108.9	87.8	0.109	805.5
3	50	2	18+2	111	88.2	0.086	1029.2
4	50	2	17+3	110	88.1	0.043	2048.8
5	50	2	15+5	110	88.1	0.0175	5034.2
7	70	2	17+3	108.2	88.2	0.03	2940
8	80	2	17+3	109	88	0.028	3142.8
9	90	2	17+3	108.5	88.2	0.027	3266.6
11	50	3	17+3	109	87.8	0.039	2251
12	50	4	17+3	108.9	87.9	0.038	2313
13	50	5	17+3	130	88.1	0.04	2202.5

The fourth chapter. Investigation of conditions for the precipitation of aluminum hydroxide from aluminate solutions. The conditions of precipitation Al(OH)₃ from sodium aluminate solutions by hydrogen peroxide, which is an environmentally friendly reagent, and sending the recovered alkali to the dissolution of the next alunite rock have been studied. Also, in this chapter, the chemistry and mechanism of deposition were studied, the phase transformations occurring during the acquisition of the crystalline aluminum phase were studied by physico-chemical analysis methods. First, the factors affecting the precipitation of aluminum hydroxide hydrogen peroxide from poor aluminate with solutions: concentrations of H₂O₂ and alkali (Na₂O); Volume ratios of H₂O₂ and aluminate solution, temperature, time, alkali modulus (K_{α} = $m(Na_2O)/m(Al_2O_3)$ were investigated.

When the concentration of alkali in aluminate solutions is in the range of 1-6 mol/l, the aluminum monomer in the solution is in the form of ion $[Al(OH)_4]^-$. To precipitate $Al(OH)_3$, it is necessary to separate the hydroxide ion (OH⁻) from the monomer. This is done by the hydrogen (H⁺) ion obtained from the dissociation of H₂O₂. The formed proton decomposes the sodium aluminate solution and $Al(OH)_3$ precipitates (react. 8).

 $Na[Al(OH)_4] + H^+ \rightarrow Al(OH)_3 + H_2O + Na^+$ (8)

In the experiments, the aspect to pay attention to was the Al(OH)₃ precipitation percentage and the concentration of the alkali in the solution after the precipitation. The solidities of NaOH and Al(OH)₃ were calculated according to their oxides (respectively, Na₂O and Al₂O₃). By 10% H₂O₂ solution, the concentration of Al₂O₃ in the aluminate solution was decreased from 30.76 g/l to 8.21 g/l, and the concentration of Na₂O was from 20.47 g/l to 12.81 g/l. According to calculations, 73.26% of Al₂O₃ in the solution by 10% H₂O₂ is precipitated, and the increase of the concentration of H₂O₂ to 25% raises the concentration of Al₂O₃ leads to a decrease to 2.66 g/l. At this time, 91.34% of the aluminum oxide in the solution precipitates, and the initial density. Further experiments V_{H₂O₂ :V}

alum.sol. was carried out by changing their volumes (Fig. 8).

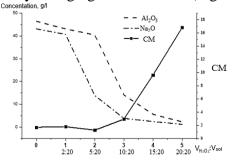


Figure 8. Concentration of Na₂O and Al₂O₃ in the aluminate solution on the volume ratios of H₂O₂ and sodium aluminate solution (t=25^oC, C_{Na₂O_{initial} -48.42g/l, C_{Al₂O_{3 initial} -46.42g/l, K_{α}-1.71, C_{H₂O₂ =30%; v_{mix} - 300 rpm)}}}

When the volume ratio of the solutions is 1:4, precipitation begins quickly, when this ratio is 1:2, the precipitation percentage of Al(OH) $_3$ is 69.58%, and when it is 1:1, it is 95%. Changing the ratios reduces the alkali density from 48.42 g/l to 23.675 g/l. Due to the sharp increase in alkali modulus, it is recommended to carry out precipitation in low volume ratios (1:2).

The effect of time and temperature on precipitation was investigated, and it was found that intensive precipitation occurs in the first minutes and reaches its maximum in 30 minutes. Comparison of temperature showed that further increase in temperature (60° C and 80° C) decreased the percentage of precipitation. The reason is the acceleration of the thermal decomposition of H₂O₂ as the temperature increases and the reaction of the obtained precipitate with alkali in aluminate solutions.

Since the production of $Al(OH)_3$ in the equation $[Al(OH)_4]^ \leftrightarrow Al(OH)_3 + OH^- + Q$ is an exothermic reaction, an increase in temperature shifts the direction of the reaction to the left endothermic reaction, and re-dissolution of $Al(OH)_3$ occurs.

Al(OH)₃ with H₂O₂ at different concentrations of alkali from low-density aluminate solutions (17.28-19.9 g/l) according to precipitation results, if the initial concentration of alkali (according to Na₂O) increases from 1.78% to 5.2%, the precipitation percentage of Al(OH)₃ (according to Al₂O₃) is from 84.72% to 95.22% increases to, the subsequent increase in alkali concentration (to 6.5%) reduces the precipitation percentage of the aluminum phase (84.92%). It should be noted that in all cases the consumption of alkali used for precipitation is very small. In this case, the solution after precipitation and filtration can be directed to dissolve a new batch of alunite rock.

As a result of the conducted studies, the optimal conditions for the precipitation of aluminum hydroxide from the solution it is defined as: C_{Na_2O} -42.33g/l (\approx 5%), $C_{H_2O_2}$ =10%, $V_{H_2O_2}$:V_{alum.sol.}=1:2; t=25°C.

The next part of the chapter is dedicated to obtaining crystalline aluminum hydroxide phase (boehmite - AlOOH) from

aluminate solutions and investigating the phase transformations that occur during this process.

 H_2O_2 is added to alkaline aluminate solutions, it first dissociates into hydroperoxide (HO₂⁻) and hydrogen (H⁺) ions (9):

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{9}$$

The hydroperoxide ion, in turn, breaks down into hydroxide ion (OH) and oxygen gas (10):

$$HO_{2}^{-} \rightarrow OH^{-} + \frac{1}{2}O_{2}$$
(10)

The ions formed from the decomposition affect the aluminate ion in the solution, forming there Al(OH) ₃ or AlOOH precipitates:

 $Na[Al(OH)_4] + H_2O_2 \longrightarrow AlOOH + NaOH + \frac{1}{2}O_2 + 2H_2O (11)$

Further experiments are focused on elucidating the formation mechanism of transformation of amorphous $Al(OH)_3$ to crystalline boehmite phase (AlOOH) precipitated by H_2O_2 .

The composition of the solid phase deposited in aluminate solutions at different times and temperatures was clarified by IR, X-ray and SEM/EDS analysis of the samples.

A X-ray analysis resul of a sediment sample aged for 30 days shows small peaks of bayerite with a low degree of crystallization and 2 distinct peaks of gibbsite (Fig. 9).

After two months of ripening, the gibbsite phase loses water, forming active sites for the formation of boehmite. In this case, small dispersed boehmite crystals are formed. The individuality of the crystals was confirmed according to the JCPDC database (№21-1307).

 H_2O_2 at room temperature and stored for one day is characterized by X-ray amorphism. In the IR spectrum of this sample, a broad absorption band corresponding to the maximum of 3419 cm⁻¹ is observed in the frequency interval of 3000-3800 cm⁻¹. At 1651 cm⁻¹, a single band corresponding to the deformation jump of the water molecule is observed. The scattering of absorption bands indicates the absence of a crystalline phase in this sample.

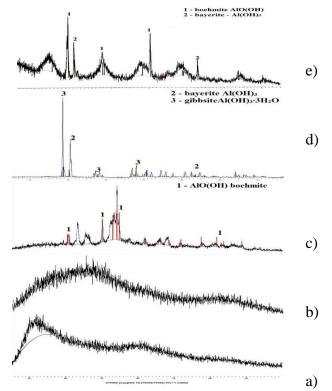


Figure 9. X-ray analysis of Al(OH)₃ deposited under different conditions: a) 1 day aging, b) after 13 days of aging, c) 48 hours of aging, d) 30 days aging, e) aging for 2 months

721 cm⁻¹ belongs to the asymmetric valence band of the $[Al(OH)_4]^-$ ion, the band observed at the wavelength of 665 cm⁻¹ belongs to the $[(OH)_3Al-O-Al(OH)_3]^{2-}$ ion and Al-O-Al can be attributed to the breakthrough of the group⁴. Amorphism is preserved in the X-ray image of the precipitate grown for 13 days, but no spikes corresponding to the polymer ion are observed in the IR spectrum, unlike the sample deposited for one day. It is assumed that the aluminous phase in the precipitate turns into a dimer. In the X-ray image of the precipitate dat pH=12-13 at 60°C for 48 hours,

⁴https://www.sciencedirect.com/science/article/abs/pii/S0959652617320802

irregular and scattered peaks are formed, which indicates the formation of crystallized centers in the obtained compound. The precipitate obtained initially consists of a mixture of boehmite and amorphous phases. The absorption band observed at 1670 cm⁻¹ frequency in the sample's IR spectrum confirms the presence of water of crystallization in its content. It can be concluded that the resulting gibbsite crystals act as a leavening modifier for the formation of boehmite. Electron microscope photos of the obtained sediments also confirm which phase the samples belong to (Fig. 10).

Thus, the morphology of the precipitate obtained during 2month ripening shows the formation of rhombic crystals. It is known from the literature that gibbsite crystallizes in the form of hexagonal particles and bemite in the form of tetragonal particles⁵.

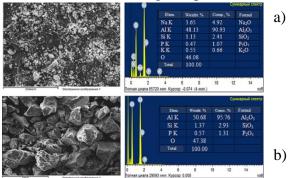


Figure 10. Electron microscope photographs of samples obtained after 30 days aging (a) and 2 months aging (b) (C_{Na_2O} -40.53 g/l, $K_a = 1.634$, t = 60⁰C)

Thus, the formation and precipitation mechanism of gibbsite and boehmite phases from aluminate solutions can be shown as follows:

 $[Al(OH)_4]^{-} \rightarrow [Al_n(OH)_{4n}]^{n-} \rightarrow [Al_6(OH)_{24}]^{6-} \rightarrow Al(OH)_3 \rightarrow AlOOH$

That is, the monomer form of aluminum in the solution $([Al(OH)_4]^-)$ is converted to the polymer form and then to the inorganic polymer form. The structure of $[Al_6(OH)_{24}]^{6-}$ polymer is

⁵https://www.sciencedirect.com/science/article/abs/pii/S1003632609601722

considered as the inner sphere of the crystal structure of gibbsite. When H_2O_2 is added to a weak alkaline solution, the latter forms hydrogen bonds with water molecules in the $[Al(OH)_4]^-$ sphere. The breaking of a water molecule leads to the formation of $Al(OH)_3$ precipitation in the solution, and with the passage of time, the release of a new water molecule leads to the formation of AlOOH.

Based on the conducted studies, it was concluded that when $Al(OH)_3$ is precipitated from aluminate solutions with H_2O_2 , first an amorphous phase is formed, depending on time and temperature, phase transformations occur. Hydrolytic decomposition of the amorphous phase during ripening leads to the formation of a bemite-containing precipitate.

Fuzzy logic theory was applied to the results of the experiments at the end of each chapter . Matlab - "fuzzy logic control" tool panel was used in order to specify the optimal conditions in the processes of dissolution of alunit mineral in alkali, desilication of aluminate solutions and precipitation of $Al(OH)_3$. Using fuzzy sets, it is possible to increase or decrease the results by changing the parameters affecting the processes according to the results obtained from the computer simulation. For example, using 11.5 ml of 10.2% H₂O₂ at 25^oC, 94.8% Al(OH)₃ is removed from the solution when applying the fuzzy sets corresponding to low, medium and high levels, based on the values of the experimental results in the precipitation stage. - is to collapse.

The surface function of the obtained results is shown in figure 11, b.

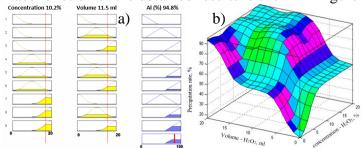


Figure 11. One of the possible results obtained during precipitation $Al(OH)_3$ from aluminate solution by H_2O_2 using fuzzy sets, (a); 3D model of the dependence of precipitation on the concentration and volume of H_2O_2 (b)

Applying the fuzzy logic approach to the processes allows to come to the conclusion that it is possible to achieve a high result by changing the parameters affecting the collapse according to the purpose.

The fifth chapter. Removal of alkali and acid from washing solutions by electrodialysis method. In Chapter V, the possibility of obtaining alkaline and acid solutions by electrodialysis from washing solutions obtained during alunite processing was investigated in order to prevent external extraction of the alkali used during dissolution.

The experiments were carried out in a custom-made flow diaphragm electrodialyzer and a PC Cell 64004 electrodialysis device made in Germany (Fig. 12).



Figure 12. Electrodialysis device (a) 1 – alkaline receiver, 2 – acid receiver, 3 and 4 – rotometer, 5 – voltmeter/ammeter, 6 – PC Cell 64004 electrodialyzer

Factors affecting energy consumption such as voltage, current intensity, temperature, solution flow rate were investigated in the research work. The sodium sulfate solution supplied to the device is released between the cation exchange (CEM) and anion exchange (AEM) membranes. Under the influence of the current, Na⁺ ions pass through the CEM and are directed to the cathode side of the device. The movement of Na⁺ ions is hindered by the positively charged layer of the bipolar membrane (BM). Equivalent amounts of H⁺ and OH⁻ ions are formed from water dissociation from BM due to constant current. The processed OH⁻ ions are separated from the BM on the left and combine with the Na⁺ ions that have passed through the CEM to form NaOH. At the same time, SO_4^{2-} ions released from the AEM on the right and combine with H⁺ ions released from the

anode zone to form sulfuric acid. OH^- ions and H_2 gas are formed due to the electrochemical reduction of water in the cathode part (12):

$$2H_2O + 2e \rightarrow 2OH^- + H_2 \tag{12}$$

Analogously, due to the electrochemical oxidation of water, H^+ ion and O_2 gas are formed (13):

$$2H_2O - 4e \rightarrow 4H^+ + O_2 \tag{13}$$

At the same time, as a result of the collection of Na^+ and $OH^$ ions in the solution, NaOH; H₂SO₄ is formed from the combination of H⁺ and SO₄²⁻ ions. The reaction during the electrolysis process is as follows (14):

 $2Na_2SO_4+6H_2O \xrightarrow{e-z} 4NaOH+2H_2(C)+2H_2SO_4+O_2(A) (14)$

Preliminary experiments were carried out with 500 ml of 1% sodium sulfate salt solution at different values of voltage (V) and current strength (A) by changing the flow rate of the solution from the chambers (1~10 ml/min). It is known that the longer the solution stays in the chamber, the greater the concentration of the alkali and acid obtained.

One of the most important factors affecting the concentration of acid in the anode chamber of the alkali in the cathode chamber is the current density. In experiments conducted in a three-chamber bipolar membrane device, the concentration of alkali increases with increasing current density. Figure 13, the change of the concentration of the alkali in the cathode chamber and the concentration of the acid in the anode chamber was monitored for 6 hours at the same time.

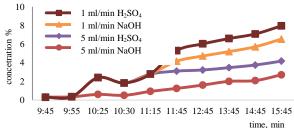


Figure 13. Time dependence of the change in the concentration of alkali in the cathode chamber and acid in the anode chamber ($C_{salt}=2.5\%$, I= 1-2A, respectively, $v_{flow} = 1$ and 5 ml/min, U=4-5V)

The concentration of sodium sulfate salt discharged from the chambers between the anion exchange and cation exchange membranes was 2.5%. In the first experiment, 1 ml/min, and 5 ml/min in the second series of experiments were taken with the speed of the solutions flowing from the chambers. During the experiment, the current intensity varied between 1-2A, and the voltage between 4-4.5V.

Experiments by periodically returning the solutions to the chambers resulted in obtaining alkali and acid up to 5% concentration ($v_{flow} = 1 \text{ ml/min}$). The obtained results showed that the concentration of the acid is 2 times higher than the concentration of the alkali.

Based on the principles of green chemistry, the theoretical and experimental aspects of aluminum oxide production during complex processing of alunite were systematically studied and effective parameters and regimes of aluminum extraction at all processing stages were determined.

As a conclusion of the research work, a laboratory mobile pilot plant of alunite ore processing technology is proposed (Fig. 14).



Figure 14. Laboratory mobile pilot plant of the proposed alunite ore processing technology

CONCLUSIONS

1. Kinetic studies of dissolution of Zaglik alunite ore with alkaline solution without burning were carried out. Increasing the concentration and temperature of the alkali in the solution intensifies the dissolution process. When the ratio of solid:liquid phases is 1:5, the mixing speed is 700 period/min, and the alkali density is 110.9g/l, at a temperature of 80° C, up to 96% of alunite mineral is dissolved and goes into solution in 60 minutes [3].

2. The value of the activation energy calculated at the temperature of 333-368K for the dissolution of the alunite mineral in the ore by crump dissolution method is 73.14 kJ/mol. This shows that the solubility is limited by the homogeneous chemical reaction on the surface [2].

3. New scientific results have been obtained on the desilication of aluminate solutions. For the first time, the sorption capacity of a sulfated Friedel phase salt mixture with an activated alunite mud and the kinetics of its separation from the solution were studied. It has been shown that the rate constant of the desilication reaction, the calculated value of the activation energy (74.36 kJ/mol) and the order of the reaction is 0.99 are regulated by the desilication process proceeding in the kinetic region [4, 5].

4. $Ca_6Al(OH)_{18}(SO_4)_{1.5}(H_2O)_9$ was detected in activated alunite mud using physico-chemical analysis methods, and its silicate ions $(SiO_2(OH)_2^{2^-})$ were removed from the solution. It is proven to be a deep cleansing sorbent. It was determined that sorbed silicate ions are exchanged with sulfate ions located in the intermediate layers of the adsorbent and become $Ca_3Al_2(OH)_{12}SiO_2$ compound. By the proposed method, the percentage of desilication of the solution is 94.65% [10, 12].

5. Optimum conditions for precipitation of aluminum hydroxide from aluminate solutions with hydrogen peroxide, which is a green reagent ($C_{H_2O_2} = 10\%$, t=25°C, $V_{H_2O_2}$: $V_{volume} = 10:20$ ml, $C_{Na_2O} =$ 42.33 g/l) were found. Under these conditions, up to $\approx 95\%$ Al(OH)₃ from the aluminate solution it becomes possible to precipitate [15]. The results obtained from the experiments were processed by applying fuzzy logic theory [6, 7, 14].

6. The chemistry and mechanism of aluminum hydroxide precipitation by hydrogen peroxide was studied, it was shown that H⁺ ions formed from the dissociation of hydrogen peroxide combine with the OH⁻ ion that has entered into the coordination in the [Al(OH)₄]⁻ ion and first form Al(OH)₃, then AlOOH compound. Precipitated amorphous Al(OH)₃ crystallization in the solution and the phase transformations occurring during this time were studied. It was found that the maturation of crystals varies depending on time and temperature. During the study of physico-chemical analysis methods, it became known that the monomer Al[(OH)₄]⁻ ion of aluminum turns into [Al₆(OH)₂₄]⁶⁻ polymer, which is an element of the crystal structure of gibbsite, and it turns into bayerite and boehmite [1, 16].

7. By using a three-chamber, bipolar membrane electrodialysis device, conditions for increasing the concentration of alkaline solutions in the cathode chamber and acid solutions in the anode chamber up to $\approx 5\%$ have been studied [13, 18].

8. As a result of the conducted research, a basic technological scheme and a mobile pilot unit were developed, which allows to obtain aluminum compounds, alkali metal sulfate salts, alkaline and acid solutions as finished products from alunite ore in anticipation of the principles of green chemistry [8, 9].

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The defense will be held on <u>21 December 2023</u> at <u>10:00</u> at the meeting of the Dissertation Council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev, Ministry of Science and Education of Azerbaijan.

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