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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEVELOPMENT OF GALLIUM EXTRACTION TECHNOLOGY FROM INDUSTRIAL WASTE

Specialty: 3303.01 - Chemical technology and engineering

Field of science: Technical science

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The work was performed at the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev of the Azerbaijan National Academy of Sciences at the laboratory "Processing of non-ferrous metal mineral raw materials".

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GENERAL DESCRIPTION OF WORK

Relevance and development of the topic. Late XX - beginning XXI century development of science, modern technologies and innovations, especially information and communication technologies, caused both positive and negative changes in society and the world. Among the negative consequences, one should especially note the pollution of the environment and ecology. Industrial waste is one of the factors influencing environmental pollution.

Recently, preference has been given to the creation of energy efficient and environmentally friendly technologies for processing industrial waste. Over a long period of time, during the development and processing of ore deposits, a large amount of industrial waste is generated. At present, the content of rare metals in a number of industrial waste is many times higher than in primary raw materials. These metals are used in aircraft construction, the production of heat-resistant and cold-resistant steels and alloys, semiconductors, catalysts, electrical engineering, radio engineering, electrovacuum equipment, etc. are used in such areas as. Therefore, their acquisition is one of the pressing problems.

Dispersed rare earth metals (REM) are commonly found in various minerals, such as isomorphic mixtures. Extraction of SNM from non-ferrous metallurgy and energy waste is considered more profitable. Ga is one of these rare metals. At present, about 90% of gallium is obtained from the production of aluminum, the rest - from dust and semi-finished products of the zinc plant (cake, raymovka), ash from the combustion of coal and fuel oil. The expansion of the scope of gallium application, its high selling price makes it necessary to look for new types of raw materials.

More than 97% of the gallium produced is used in the manufacture of semiconductor materials and solar cells (GaAs). However, gallium is used in the production of integrated circuits, laser diodes, Blu-ray drives, in the treatment and diagnosis of cancer in medicine (isotopes of gallium-67 and 68), in the treatment of certain bacterial infections, in dentistry, when installing photocells

3

on space satellites and all-terrain vehicles. Anylight solar panels are also based on gallium arsenide. These batteries are specially designed for drones, and the new battery is said to allow drones to stay aloft for many years.

Along with this, on December 6, 2016, regarding the development of heavy industry and mechanical engineering in the Republic of Azerbaijan, in paragraph 7.2.3 of the strategic roadmap in Article 2.3, Priority the widespread use of local raw materials, primarily ores and waste from their processing.[1]

The presented dissertation is also aimed at solving the problems mentioned in this article, and in priority order.

Taking into account the above information, the research work can be considered relevant.

The object and subject of the research - these are wastes of ore deposits rich in non-ferrous metals located on the territory of our republic (Zeylik alunite ore, Filizchay polymetallic sulfide ore) and ash residues from heating boilers.

The purpose and objectives of the study. By studying the physicochemical foundations of the extraction of gallium from various industrial wastes, a technological scheme has been developed that provides a high percentage of its extraction. To achieve this goal, it is necessary to solve the following issues:

- Clarify the chemical, mineralogical and granulometric composition of individual waste:

- Determination of places of thickening at the stages of its processing by studying the mineral form of gallium in various wastes or the production of minerals that carry it;

- Study the mechanism of gallium dissolution depending on the mineralogical and chemical composition of the waste and find the type of solvent;

- The search for conditions that ensure the maximum penetration of gallium into the solution, and the study of the optimal conditions for the extraction of gallium from the solution;

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[1] Strategic roadmap for the development of heavy industry and mechanical engineering in the Republic of Azerbaijan // Decree of the President of the Republic of Azerbaijan No. 1138. - Baku: - December 6, 2016 - 50 p.

- Creation of a basic technological scheme for the production of gallium for each type of waste;

Research methods. When studying the chemical and mineralogical composition and properties of raw materials and products of its processing, modern research methods are widely used: X-ray phase (XRD), IR spectroscopy, differential thermal analysis (DTA), atomic emission spectrometry (ICP-AES).), flame photometric method, photocalorimetric (FEC), SEM / EDS, etc.

Basic provisions for defense. Determination of economically profitable metals removed from the enrichment wastes of the Dashkasan iron ore; study of efficient parameters and modes of removal of Co, Cu, Zn, Mn from wastes; obtaining selective concentrates using from arsenic and iron purification, hydrolytic sedimentation and sorption methods of precious metals (Co, Cu, Zn, Mn) that have passed into the solution; development of technology for the extraction of a number of precious metals from the wastes by means of a solution and the creation of a mobile technological complex.

The scientific novelty of the research. As a result of the research, new scientific results were obtained on the extraction of gallium from other metals from individual waste (sludge, cake, ash samples).

- For the first time, conditions were found for the separation of minerals from sludge by sulfation of gallium, vanadium and aluminum by sulfation-combustion-dissolution of minerals in the sludge.

- Studied the kinetic laws of the extraction of gallium, vanadium and aluminum ions from solutions of di- (2-ethylhexyl) phosphate acid in kerosene, studied the chemical composition of the resulting complex in the organic phase. Depending on the equilibrium pH of the solution, the conditions for the separation and thickening of gallium from aluminum were studied by the distribution coefficients.

- For the first time, the conditions of thermal oxidation of ash from burning fuel oil with soda and dissolution of galvanic and vanadium as a result of dissolving the baked mass in water and

separating gallium from other elements by hydrolytic precipitation have been investigated.

- A more efficient method of thickening and separating gallium has been proposed by studying the kinetic regularities of the separation of gallium from iron and non-ferrous metals (copper, zinc and lead) during an autoclave solution of a pyrotinized product in the presence of sulfur (IV) oxide.

Theoretical and practical significance of the research.

As a result of the study of the distribution of gallium and other valuable components (vanadium, aluminum) in the products of processing in the process of complex processing of the listed industrial wastes, a principle technological scheme for determining the places of thickening was proposed.

As a result of the introduction of the proposed technologies, our country can partially meet the demand for gallium and vanadium. Application of the process will significantly expand the raw material base of gallium and vanadium, save mineral resources, improve environmental conditions in the waste disposal area, and prevent air pollution with dust and the release of toxic detergents into the soil.

Approval and application. Approbation and application of the work. The materials of the dissertation were heard and discussed at the following scientific conferences:

II International scientific-practical conference "Modern resource-saving technologies. Problems and prospects" Odessa National University named after II Mechnikova, (Odessa, October 1-5, 2012); 1st International chemistry and chemical engineering conference. Dedicated to the 90th Anniversary of the National Leader of Azerbaijan, Heydar Aliyev (Baku, 17-21 April, 2013); Republican scientific conference dedicated to the 90th anniversary of academician TN Shakhtakhtinsky. (Baku, October 22, 2015); International symposium «Environmental and engineering aspects for Sustainable living» euro, Hannover (Germany, 2 December, 2017); XII International Scientific Conference of Doctoral Students, Masters and Young Researchers "Actual Problems of Chemistry", dedicated to the 95th anniversary of national leader Heydar Aliyev (Baku, May 03-04, 2018); XIII International Scientific Conference of

Doctoral Students, Masters and Young Researchers "Actual Problems of Chemistry", dedicated to the 96th anniversary of national leader Heydar Aliyev (Baku, May 15-16, 2019); Materials of the I International scientific-practical conference "Universities of Azerbaijan and Turkey: education, science and technology", part III, (Baku, December 18-20, 2019); Proceeding of the 9th International Scientific and Practical Conference- «Challenges in Science of Nowadays», (Washington, USA, 16-18.07.2021); XII International Scientific-Practical Conference "World science: Problems, prospects and innovations" (Toronto, Canada, 11-13.08.2021); II International scientific-practical conference "Science, innovations and education: problems and prospects", (Japan, Tokyo, 15-17.09.2021).

Name of the organization where the dissertation is performed. The dissertation research was carried out in accordance with the scientific program of the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev of ANAS (State Registration № 0115 Az 2099).

Structure and scope of work. The dissertation consists of an introduction, 5 chapters, results, and a list of 189 references. The work consists of 180420 (introduction 12854, Chapter I 58971, Chapter II 10572, Chapter III 53511, Chapter IV 25336, Chapter V 16510, results 2666) and covers 33 tables, 42 pictures.

The introduction substantiates the relevance of the work, the purpose of the work, the defended provisions, the scientific novelty of the work, its practical significance, information about publications and approbation.

The first chapter of the thesis is devoted to a discussion of a review of the literature on modern methods and technologies for the extraction of gallium from ores and waste. First, materials on the geochemical properties, applications, production and consumption of gallium were discussed.

Analysis of the literature showed that there are many methods and technologies for the extraction of gallium and other valuable components from red mud during the processing of aluminum-containing raw materials, solids during the processing of fuel oil and fuel oil, as well as semi-finished products. products of processing of

polymetallic ores. It can be concluded that the production of gallium as a result of the processing of these wastes can be considered very promising. However, the industrial production of gallium from the studied wastes is not organized at any enterprise. The reason is the lack of economically viable and environmentally friendly technology that allows the production of valuable components in waste, including gallium, poor understanding of the physical and chemical foundations of the process and, finally, lack of investor interest in this area.

The second chapter is methodical, which provides information on the methods of physicochemical analysis used to study the distribution of gallium in waste. Due to the very complex mineralogical and chemical composition of the studied objects, attention was paid to the choice of effective, practically simple and inexpensive methods for extracting precious metals.

As an effective treatment method, acid and soda cooking methods can be used to break the waste into components and ensure that the gallium compound contained in it is completely absorbed into the solution.

This chapter also provides information on the ionic form of a solution in the extraction of gallium from process solutions, depending on the pH of the solution, analytical methods used in the determination of gallium and aluminum in processed products.

The third chapter of the dissertation is devoted to the study of the conditions for the extraction of gallium and vanadium by sulfation-combustion-dissolution of sludge obtained from an alkaline solution of the Zeylik alunite ore. In this chapter, the conditions for the extraction of gallium and vanadium with di- (2-ethylhexyl) phosphoric acid, an organic compound of phosphorus, were studied, the optimal process parameters were determined, and the chemical composition was explained.

As a result of the research, a conceptual and apparatus-technological scheme for sludge processing was proposed. At the end of the chapter, an assessment of the economic efficiency of the proposed method for processing alunite sludge is given.

The fourth chapter of the dissertation is devoted to the

extraction of gallium, nickel and vanadium from ash residues formed during combustion in boilers of thermal power plants operating on fuel oil.

Studies have shown that gallium and vanadium are converted to water-soluble gallates and vanadates during processing. At the end of the research, a new environmentally friendly technology was proposed that provides a high yield of Ga, V, Ni from the ash residue.

The fifth chapter of the dissertation is devoted to clarifying the places of concentration of gallium during the complex processing of Filizchay ore and studying the conditions for extracting gallium without changing the technological scheme for the main components.

It was found that gallium and other precious metals (In, Ag and Au) are added to the pyrhotinized product 1.3 times during the pyrotechnic combustion of the ore. At the next stage of processing, when pyrotrinized ore (Fe_7S_8) is dissolved in an autoclave in the presence of sulfur (IV) oxide, sulfides of non-ferrous metals (ZnS, CuS, PbS) remain inert, while gallium, indium and iron compounds remain inert. sulfated into solution. The gallium concentration in the resulting rare metal cake increases to 0.16%.

In conclusion, a technological scheme was presented, reflecting the concentration of gallium and indium in the complex processing of ore.
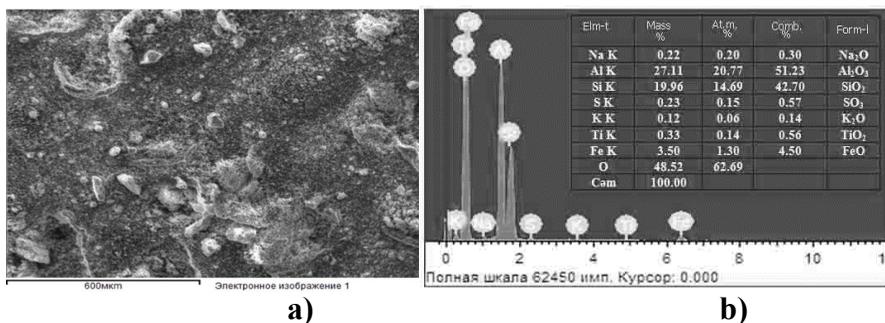
MAIN CONTENT OF WORK

At the Ganja clay-soil plant, the remainder of the processing of bauxite was called "red silt", and the remainder of the processing of alunite was simply called "silt", so alunite silt was used as waste.

Based on the results of X-ray phase analysis, the mineralogical composition of alunite slimes was determined: quartz (SiO_2) -78%, dikkit ($Al_2Si_2O_5(OH)_4$) -10%, hematite- (Fe_2O_3) -8.6%, others minerals 3.4%. When processing alunite ore, the alunite mineral easily dissolves in an alkaline solution and goes into solution, therefore, other minerals (quartz, dikite, hematite, gibbsite) accumulate in the unallocated residue - alunite fragments. The chemical composition of alunite sludge is as follows,%: Na_2O-0.23; MgO-0.17; Al_2O_3-4.53; SiO_2-82.21; P_2O_5-0.24; SO_3-0.15; K_2O-0.07; CaO-0.28; TiO_2-1.15; MnO-0.01; Fe_2O_3-8.60, V-0.099; Ga-0.005; Rb-0.0012, H_2O_{wet}-2.17.

As seen from the chemical composition, gallium and vanadium are rare elements that can be recovered from alunite sludge.
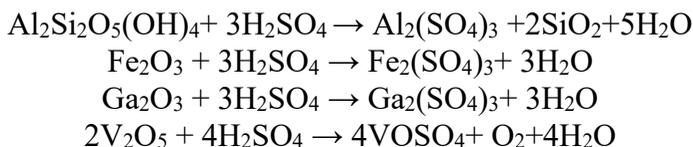
SEM analysis was used to study the morphology of alunite slimes (Fig.1 a). As can be seen from the figure, alunite slimes consist of particles of various shapes. The results of the SEM / EDS analysis showed that the intensities inherent in gallium and vanadium on the scale were not determined in the sludge due to the small amount of these elements in the sample. Although there are 0.3% Na, 0.14% K and 0.56% Ti on the scale (Fig.1 b).

Elm-t	Mass %	At.m. %	Comb. %	Form-I
Na K	0.22	0.20	0.30	Na_2O
Al K	27.11	20.77	51.23	Al_2O_3
Si K	19.96	14.69	42.70	SiO_2
S K	0.23	0.15	0.57	SO_3
K K	0.12	0.06	0.14	K_2O
Ti K	0.33	0.14	0.56	TiO_2
Fe K	3.50	1.30	4.50	FeO
O	48.52	62.69		
Сэм	100.00			

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a)   b)

Fig. 1. Micrograph of the mass of alunite cuttings.

The main criterion in sulfate combustion experiments is that aluminum, gallium and vanadium are converted to a more water-soluble sulfate salt and that iron is burned as much as possible in the form of an oxide with quartz. The technological scheme of the process consists of 3 main stages: at the first stage, the moistened sludge is mixed with sulfuric acid of various concentrations, at the second stage, the sulfated mass is boiled (burned), and the sulfated mass is dissolved in water at the third stage.

Waste mixed with a solution of sulfuric acid of various concentrations (density 1.06-1.84 g/cm^3) is first heated for 1-12 hours at a temperature of 130°C in a drying oven until water evaporates. In this case, sludge compounds containing dickite, hematite, gallium and vanadium interact with sulfuric acid and turn into sulfur salts of nonferrous, rare metals and iron.

$$Al_2Si_2O_5(OH)_4 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2SiO_2 + 5H_2O$$
$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$
$$Ga_2O_3 + 3H_2SO_4 \rightarrow Ga_2(SO_4)_3 + 3H_2O$$
$$2V_2O_5 + 4H_2SO_4 \rightarrow 4VOSO_4 + O_2 + 4H_2O$$

To elucidate the phase changes that occur during the sulfation of minerals in waste depending on temperature, differential thermal analysis of individual sulfate salts was carried out, and it was determined that the most rapidly decomposing iron (III) sulfate. Thermal decomposition starts at 500°C and ends at 650°C. At 650°C, the decomposition of Al, Ga and V sulfates is negligible. These studies helped to determine the temperature of sulfation of alunite sludge.

After obtaining these data, a thermogravimetric analysis of the sample was carried out after the alunite slurry was mixed with solid sulfuric acid in a 1: 1 weight ratio and dried at 130°C (Figure 2). The derivatogram shows that the interaction of sulfuric acid with force is accompanied by a number of effects and weight loss. Initial weight loss occurs below 300°C (8%). This is due to the separation of physically adsorbed and chemically bound water from the mass. A sharp weight loss in the range of 680-820°C leads to the active

11

decomposition of aluminum, gallium and vanadium sulfates. By the end of the experiment, the weight loss was 51.98% (at 898.4°C). The results of X-ray phase analysis in a sample of sulfated sludge at 450°C revealed the following phases: SiO_2, $H_3OAl(SO_4)_2$, $Al_2(SO_4)_3(H_2O)_5$, $Ca_6Al_3(OH)_{18}(SO_4)_{15}(H_2O)_9$, $K_2SO_4 \cdot 7KHSO_4 \cdot H_2O$, $(H_3O)Fe(SO_4)_2$.

RFA analysis of a sample taken at 620°C showed that it did not contain iron salts. When the sulfated mass dissolves in water at 650°C, the solubility of gallium, vanadium and aluminum sulfate salts increases, and in the insoluble residue, quartz and hematite phases are clearly visible.
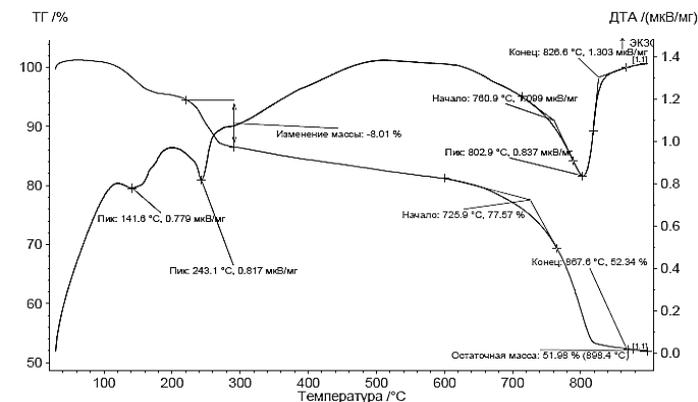
Fig. 2. Curve of TG and DTA of sulfated mass of alunite sludge sample (mass ratio of sludge + H_2SO_4 1:1)

As already mentioned, the main criterion in experiments on the combustion of sulfates is the conversion of aluminum, gallium and vanadium into a more sulfated salt form and the retention of iron in the oxide form with quartz in the residue (cake). These judgments are also confirmed by experience. As can be seen from Figure 3, the transformation of Fe, Al, Ga and V into the original sulfated salt is still observed when the waste sample is treated with sulfuric acid (density 1.84 g / cm^3) in the temperature range 100-120°C (Fe-80%, Ga-40%, Al 95% and V 45%). An increase in the sulfation temperature to 350-450°C increases the sulfation rate of all elements.

Due to the dissolution of the sulfate salt of iron at a temperature of 450°C, 95.5% of iron passes into solution, and a further increase in temperature (620°C) reduces the rate of sulfation of iron to 14%. At 720°C, traces of soluble iron salts are visible. At 620°C, the rate of sulfation of Al, Ga, and V reaches its maximum value. Pic. 2. Curve of TG and DTA of sulfated mass of alunite sludge sample (mass ratio of sludge + H_2SO_4 1: 1).

As already mentioned, the main criterion in experiments on the combustion of sulfates is the conversion of aluminum, gallium and vanadium into a more sulfated salt form and the retention of iron in the oxide form with quartz in the residue (cake). These judgments are also confirmed by experience. As can be seen from Figure 3, the transformation of Fe, Al, Ga and V into the original sulfated salt is still observed when the waste sample is treated with sulfuric acid (density 1.84 g/cm^3) in the temperature range 100-120°C (Fe-80%, Ga-40%, Al 45% and V 45%). An increase in the sulfation temperature to 350-450°C increases the sulfation rate of all elements. Due to the dissolution of the sulfate salt of iron at a temperature of 450°C, 95.5% of iron passes into solution, and a further increase in temperature (620°C) reduces the rate of sulfation of iron to 14%. At 720°C, traces of soluble iron salts are visible. At 620°C, the rate of sulfation of Al, Ga, and V reaches its maximum value.
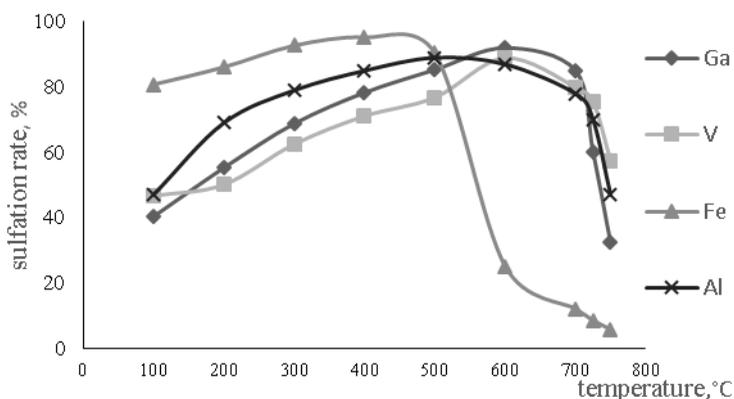
Fig. 3. Influence of combustion temperature on the degree of sulfation of iron, aluminum, gallium and vanadium.

13

A further increase in temperature adversely affects the solubility of the sulfated mass in water. An increase in temperature from 650°C to 800°C reduces the yield of gallium and vanadium in solution from 93.26% to 60%.

The similarity of the curves of sulfation of gallium and vanadium with aluminum shows that the solubility of these metals depends on the soluble form of aluminum. Based on the experimental data obtained, it can be concluded that the phase of aluminum compounds containing gallium and vanadium in the slime is up to 620°C. This property is associated with the closeness of the radii of the ions of gallium, vanadium and aluminum (0.62; 0.74 and 0.57 nm) and the similarity of their chemical properties.

Subsequent studies focused on the effect of the dissolution time of the sulfated mass on the yield of the main elements (Na, Al, Fe) and trace elements (V, Ga) in the sludge. The results are shown in Pic. 4. At 650°C, the S:L weight ratio was dissolved in a 1:1, 1:50 solution with burnt water obtained within 1 hour after sulfation. As you can see, these are sulfates of Na, Ga and V, soluble in water in the first minutes. Approximately 92% Na sulfates, 49% Ga and 60% V dissolve in 1 hour. The output of aluminum in solution is 30%, and iron - 12%. The subsequent increase in time brings the Ga and V solution closer to 90-93.26%.
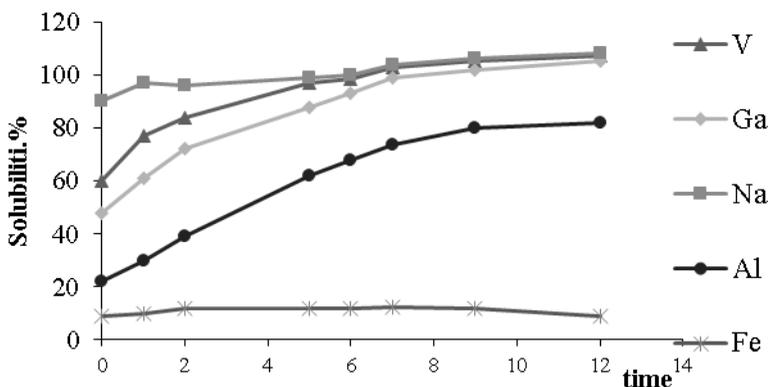
Fig. 4. Influence of the dissolution time on the solution yield of macro (Na, Al, Fe) and microelements (Ga, V).

The obtained experimental data allow us to conclude that under the conditions chosen by the operation "sulfation-combustion-dissolution", gallium and vanadium in alunite sludge can be converted into a water-soluble sulfate salt together with aluminum. In this case, the sulfation of iron is minimal and is separated from the iron upon dissolution.

When the sulfated mass of alunite chips is dissolved in hot water, the chemical composition of the resulting solution changes depending on the ratio of the phases S:L. 100 g of shavings are mixed with 500 ml of 10% H_2SO_4 and dried at 80°C for 7 hours. The mass of the resulting sulfated mass is 179 g. The sulfated mass is boiled at 620°C, cooled and 500 g of water is added to it, dissolved with stirring and filtered through a sieve. The weight of the resulting residue is 72.8 g and consists mainly of SiO_2, Fe_2O_3 and TiO_2 (Fig. 5 a, b).
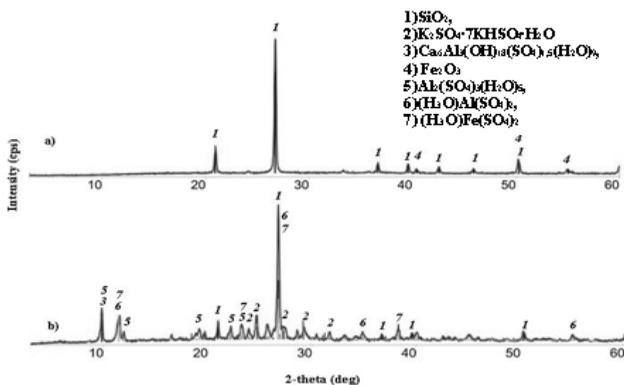
Fig. 5. Diffractogram of the sulfated mass (b) at 450 °C and the residue obtained from its solubility in water (a).

Complete decomposition of the mineral kaolinite (dikkite) during sulfate treatment of alunite sludge is also evident from the SEM analysis. In this case, the particle size decreases, and the surface area of the quartz mineral increases. A decrease in the amount of aluminum in full (1.41% Al_2O_3) and up to 96.03% silicon dioxide indicates a complete transition of macro- and microelements

from the sulfated mass to the solution. Concentration of valuable components in solution: 8.174 g/1 Al^{3+}; 2.24g/1 Fe^{3+}; 0.495 g/1 Na; 12.3 mg/l Ga^{3+}; 182 mg/l V^{2+} is precipitated by adding a 10% excess of an alkaline solution to the solution. By returning the resulting solution to the circuit, the concentration of Ga^{3+}, VO^{2+} and Al^{3+} ions can be increased several times.

Subsequent research focused on the separation and thickening of gallium and vanadium from aluminum. The extraction and thickening of gallium and vanadium from sulfate solutions obtained from water-soluble sulfate sludge was carried out using di (2-ethylhexyl) phosphate acid (D2EHPA), a phosphorus extractant. Extraction was carried out in both synthetic and technological solutions. The dependence of the yield of these metal ions (Ga^{3+}, VO^{2+} and Al^{3+}) on acidic sulfate solutions, the distribution coefficient depends on the pH of the solution, the concentration of the acid and extractant, the volumetric ratio of the phases, the contact time of the aqueous and organic phases, and the concentration of metal ions. The biggest factor affecting the extraction of gallium with D2EHPA is the acidity of the aqueous phase. It was found that the optimal pH of gallium extraction is 1.42-2, when the concentration of the organic reagent in kerosene is 0.3-0.6 mol/l increasing the acidity of the aqueous phase decreases the percentage of gallium in the organic phase. The lgD_{Ga}-lgC_{D2EHPA} dependence is linear in different intervals of the extractant thickness, the tangential angle is close to 3. The chemical formula of the extract obtained in the organic phase corresponds to the formula $GaR_3 \cdot 3HR$.

$$Ga^{3+}_{(su)} + 3(RH)_{2(uzvi)} \rightleftharpoons GaR_3 \cdot 3HR_{(uzvi)} + 3H^+_{(su)}$$

Experiments have shown that the extraction of D2EHPA Ga (III), V (IV), and Al (III) ions from sulfate solutions occurs via the cation exchange mechanism. Subsequent studies were carried out to separate, thicken and obtain pure selective compounds from aluminate solutions by extraction of Ga, V and Al. The percentage (ε,%), distribution (D) and separation factors (β) of metals from technogenic solutions into the organic phase were studied.

The influence of the equilibrium pH of the solution on the yield of Ga, V and Al was investigated under the following conditions: time - 15 minutes; O:W.=1:1; the initial concentration of the organic reagent is a 0.3 M solution of D2EHPA in kerosene. The results of the study are shown in Figure 6. It was found that 97.58% gallium, 95.1% vanadium and 3% aluminum pass into the organic phase at pH-2.
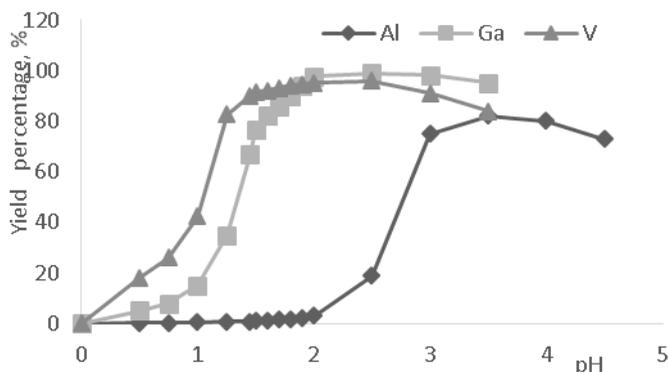
Fig. 6. Dependence of the percentage of the organic phase Ga (III), V (IV) and Al (III) on the equilibrium pH of the solution - the ratio organic: aqueous phase 1:1, t = 20ºC, Т = 15 min, C_{D2EHFT} = 0.3M kerosene solution C_{Ga} = 0.007 mol/l, C_V= 0.04 mol/l, C_{Al} = 0.193 mol/l.

The results showed that as the pH increased, the percentage of all three cations entering the organic phase increased. The process is cationic. Figure 6 shows that although D2EHPA selectively separates gallium and vanadium in the pH range 1.4–1.8, aluminum extraction occurs after pH>2. Further increases in pH also increase the recovery of gallium and vanadium. If the equilibrium pH of the solution rises from 0.5 to 2.5, the yield of vanadium increases from 18.1 to 95.8%, while this yield of gallium (~ 98.2%) occurs when the equilibrium pH of the solution is in the range 1.0-2.0. The low equilibrium pH (pH 1.8) allows the simultaneous separation of V and Ga from aluminum. The extraction of aluminum begins at pH = 2. The maximum extraction of aluminum (82%) occurs at an equilibrium pH of the solution = 4. An increase in pH to 4.5 reduces the extraction of Al (III) from 82% to 71%. At pH> 4, the aluminum solution becomes

17

cloudy, and a third phase is formed during the extraction process. X-ray phase analysis of the third phase confirmed the presence of the phases $Al(OH)_3$, $CaSO_4 \cdot 2H_2O$ and $CaPO_3(OH)_2 \cdot H_2O$. Therefore, it is not recommended to increase the pH above 4.0 when extracting gallium and vanadium from a sulfate solution, since both $Al(OH)_3$ precipitates and the gallium-vanadium extract is contaminated with aluminum.

Table 1

Influence of equilibrium solution pH and distribution (D) and separation factor (β) of aluminum. $C_{Al}=0.193$ mol/l (5.211 q/l), $C_{Ga}=6.7 \cdot 10^{-3}$ mol/l (0.474 q/l), $C_V=0.04$ mol/l (2.06 q/l)

| Equilibrium pH	D_{Ga}	D_{Al}	D_V	$\beta=\dfrac{D_{Ga}}{D_{Al}}$	$\beta=\dfrac{D_V}{D_{Al}}$
0.5	0.05	0.0101	0.208	4.95	20.59
0.75	0.07	0.011	0.369	6.36	33.54
1.0	0.11	0.012	0.736	9.16	61.33
1.25	0.6	0.038	4.75	15.78	125
1.50	2.8	0.060	9.50	46.6	158.3
1.70	5.09	0.090	14.0	56.55	188
1.80	6.35	0.10	16.0	63.5	160
1.90	16.13	0.22	18.0	73.32	81.81
2.00	40.21	0.32	19.34	125.6	60
2.2	173	0.56	24.62	308.9	43.96

Table 1 shows the distribution coefficients of gallium, vanadium and aluminum depending on the equilibrium pH of the solution, as well as the results of the coefficients of separation of gallium and vanadium from aluminum. As can be seen from the table, the distribution and separation coefficients of these elements differ depending on the value of the equilibrium pH. When the extractant density is 0.3 M, the equilibrium pH rises to 2.2, indicating that gallium is 308.9 times more than aluminum and vanadium is 43.96 times more than aluminum.

As shown in Figure 6 and Table 1, while the extraction of Ga^{3+}, VO^{2+} and Al^{3+} ions occurs in a weakly acidic environment, the extraction of these ions can be carried out in strongly acidic

solutions. Studies have shown that the transition of complex compounds from the organic phase to the aqueous phase depends on the initial concentration of sulfuric acid, the duration of repeated extraction, and the volume ratio of the organic and aqueous phases.

Gallium was removed from the organic phase with 1 M H_2SO_4. O:W= 4:1; at a temperature of 21°C and a time of 30 minutes, 79% gallium, 95.4% vanadium and 21.2% aluminum enter the aqueous phase. From the aqueous phase, vanadium can be precipitated as ammonium vanadate salt at 90°C in 97.6% yield using a 10% NH_4OH solution.

On the basis of research and practice of sludge processing, a technology for processing alunite sludge was developed. As a result of the research, a basic technological scheme for sludge processing was proposed (Fig.7).
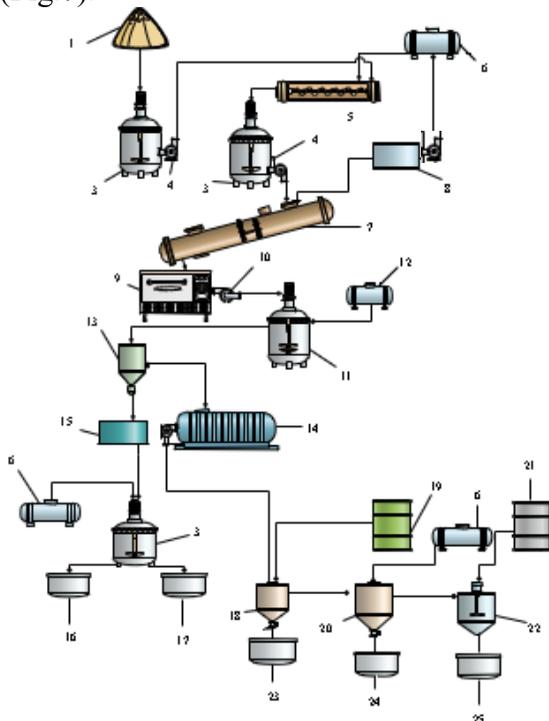
Fig. 7. Hardware-technological scheme for processing alunite sludge.

19

Finally, the cost-effectiveness of sulphation-incineration-dissolution treatment of alunite sludge was evaluated. It was concluded that the cost of processing income per day is $ 2757.5 (Table 2).

Table 2
Estimated income from processing 20 tons of sludge

Consumed weight, kg / day		Price in US dollars / t	Price USD / day
Fe_2O_3	1634	6.5 x 102	1062.1
Al_2O_3	770.1	0.7 x 103	539
TiO_2	195.5	1.86 x 103	363.63
K_2O	14.36	13.054 x 103	187.45
Na_2O	46	5 x 102	23
Ga	0.92	2.81 x 105	258.52
Va_2O_5	18.22	5.50 x 104	100.188
Rb	0.2	11.18 x 106	223.6
Total			2757.5

* $ 2757.5 at the national exchange rate is 4687.61 azn.

The chapter ends with information on the mass of acid and water used to treat 20 tonnes of sludge, annual electricity consumption, cost of equipment used, income statement and annual income.

The gains and losses from processing are presented in Table 3.

Table 3.
Gains and losses report

Benefit and loss of reagents		Annual (dollar)	Daily (dollar)
1		2	3
1. Income, *total*		**661797.12**	**2757.5**
a)	Fe_2O_3	254904	1062.1
b)	Al_2O_3	129360	539
c)	TiO_2	87271.2	363.63
d)	K_2O	44988	187.45
e)	Na_2O	5520	23
f)	Ga	62044.8	258.52
g)	V_2O_5	24045.12	100.188
h)	Rb	53664	223.6

2. Expenses, *total*	574129.6	2392.206
a) Used sulfuric acid	-296553.6	-1235.64
b) Electricity used	-126673	-527.804
c) Water consumption	-77467	-322.779
d) The cost of the purchased equipment	-22760	
e) Remuneration of labor of workers involved in production	-50676	-211.15
f) Depreciation of equipment	-2958.8	
3. Profit (loss) before tax	87670.4	365.29
4. Income taxes	-1753.4	-7.30
5. Net profit (loss)	85917	357.99

*First year income is slightly lower due to equipment purchases. In other years, after deducting equipment income and taxes ($ 2,208,608 per year), the profit will be $ 1082 21,792 per year ($ 450,924 per day).

Chapter 4 of the thesis is devoted to the extraction of gallium and vanadium from the ash of fuel oil combustion.

In this section, studies were carried out to study the chemical laws governing the extraction of vanadium, nickel and gallium from ash, which is a combustion product of the heavy oil fraction, and to develop an effective technological scheme.

The chemical composition of the investigated sample of ash in oxide is as follows, (wt.%): V_2O_5 -22.65; SiO_2-14.54; Al_2O_3-9.9; Fe_2O_3-16.4; CaO-5.9; MgO-3.92; K_2O-3.8; Na_2O-2.5; N_2O-3ş4; Ga_2O_3-0.01; SO_2-7.85; $H_2O_{wet.}$-5.72; NiO-3.4%.

The main ash minerals are $Ɣ$-Al_2O_3; anhydrous $CaSO_4$; hematite - Fe_2O_3; galena - $Ca_2Al[(SiO)_2O_7]$, anorthite - $Ca[Al_2Si_2O_8]$, kaolinite $H_4Al_2Si_2O_9$, vanadium oxides (V_2O_3, V_2O_5). The samples also contain spinel compounds V and Ni ($RO \cdot R_2O_3$).

As can be seen, the ash sample is based on complex composition aluminosilicates. The study of the yield of vanadium, nickel and gallium in solution was tested by the solubility of the material in hot water, and it was found that the yield of elements in solution fluctuated within the range of 0.7-2.24%. The bulk of these elements remains in the insoluble residue (cake). The treatment of raw ash with water and solutions of various concentrations of H_2SO_4 (1.5-25%) and alkali (NaOH) (5-20%) does not ensure the complete

release of these elements into solution. With 30% acid H_2SO_4 at 90° C for 2 hours, when the S:L phase ratio is 1:10, 72.1% V, 67.8% Ni and 62% Ga goes into solution. 4% goes into solution. When processing an ash sample with a 20% alkaline solution, the vanadium yield into the solution is 43.6%. Alkaline processing of the ash sample is considered effective, since the transition of iron into solution (22-29%) during acid processing is undesirable in technological operations. In this case, the compounds $R(OH)_2$ and $R(OH)_3$ (R = Fe, Ni, Ca, Mg, etc.) in the ash can be separated from vanadium and gallium as the main mass at the beginning of the process.

However, the yield of Ga and V during alkaline treatment does not exceed 43.6%. It can be concluded that the ash residues contained spinel-like vanadium compounds $[(V,Fe)O \bullet (V \bullet Fe)_2O_3]$, and gallium and nickel were distributed in the crystal lattice of these compounds. To convert these elements into soluble compounds, we thermooxidized the ash using alkaline substitutes (Na_2CO_3). In this case, the ferrous spinel vanadium compounds in the ash are converted to vanadium hematite.

$$2[(V,Fe)O \cdot (V,Fe)_2O_3] + 0,5O_2 = 3(V,Fe)_2O_3$$
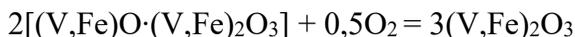
Continued oxidation converts the vanadium phase to $V_2O_5.$

$$(V,Fe)_2O_3 + 2,5O_2 = V_2O_5 + Fe_2O_3$$

The material was calcined with soda to form vanadium and gallium phases in ash to form a water-soluble compound.

$$V_2O_5 + Na_2CO_3 \rightarrow 2NaVO_3 + CO_2 \uparrow$$
$$Ga_2O_3 + Na_2CO_3 \rightarrow 2NaGaO_2 + CO_2 \uparrow$$
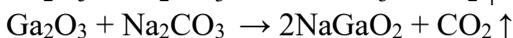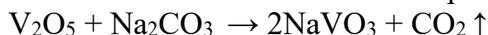
The specification of the optimum temperature and the mechanism of the process was carried out by the thermogravimetric method (Figure 8 (b)). A series of endo- and exothermic effects is observed on the curve of the DTA in the figure. Three endothermic effects in the temperature range of 50-200°C indicate a gradual decomposition. The first endo effect at 90°C is related to the dehydration of moisture in water in the sample, and the endo effect at 136.3°C and 200°C is related to the dehydration of crystalline water in the sample. Two different endothermic effects observed at weight loss at 552.1°C and 767.4°C in comparison with the pattern of raw

ash are indicated for phase changes in the process.
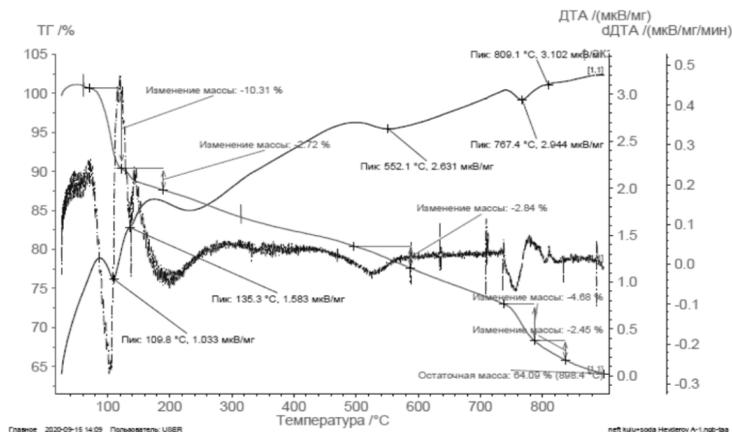
Fig. 8 (b). Derivatogram of a mixture of ashes:soda = 1: 1

Subsequent studies focused on the study of factors affecting the release of gallium and vanadium from the sol sample: baking temperature, duration, aimed at studying the mass ratios of ash to soda. Table 4 shows the effect of cooking temperature on the yield of vanadium and gallium in solution. As can be seen from the table, raising the cooking temperature from 500°C to 800°C increases the yield of both vanadium and gallium. When a mixture of ash and soda, mixed in a 1:1 ratio, is burned at 800°C for 1.5 hours, 91.9% vanadium and 92.4% gallium are dissolved. Raising the temperature to 900°C reduces the release of both elements into solution due to the formation of ferrite. In practice, it was assumed that the cooking time was 1.5 hours, and the mass ratio of soda ash was 1:1.

On the basis of research, the optimal conditions for the separation of a solution of vanadium and gallium from an ash sample were found. Baking temperature 750-800°C, duration 1.5 hours, mass ratio of ash:soda = 1:1, water solubility temperature of the mass 80-95°C, ratio of solid: liquid 1: 5-10, dissolution time 2 hours. Under the proposed optimal conditions, the yield of vanadium and gallium in solution is 98.6% and 97.5%, respectively.

Table 4

Influence of the cooking temperature on the yield of vanadium and gallium. Ash samples 2.5 g, soda 2.5 g, time 1.5 hours

№	Baking temperature, °C	Output percentage, %	
		V	Ga
1	500	50.00	49.80
2	500	50.10	50.20
3	600	56.90	56.90
4	600	56.50	57.20
5	700	62.00	66.40
6	700	63.10	65.00
7	750	71.30	82.00
8	750	77.80	82.30
9	800	91.70	91.00
10	800	91.90	92.40
11	900	90.10	90.20
12	900	89.60	90.40

After filtration, the suspension mixture is separated into a solid ($Fe(OH)_2$, $Fe(OH)_3$, $Ni(OH)_2$, $Mg(OH)_2$) and a (VO_3^-, GaO_2^-, AlO_2^-, SiO_3^{2-}). At the next stages, the separation of vanadium and gallium was studied by precipitation of silicon and aluminum in solutions with pH 12 in the form of H_2SiO_3 and $Al(OH)_3$.

When the alkaline solution is neutralized with 1 N H_2SO_4, more than 90% of Al and Si are precipitated as $Al(OH)_3$ and H_2SiO_3 at pH 10.5, while more than 98% of vanadium and gallium remain in solution.

$$SiO_3^{2-} + 2H^+ \rightarrow H_2SiO_3 \downarrow$$
$$2\,AlO_2^- + 2\,H^+ + 2H_2O \rightarrow 2\,Al(OH)_3 \downarrow$$
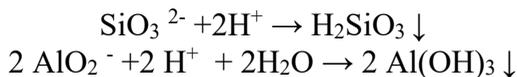
After filtration and separation of precipitates of H_2SiO_3 and $Al(OH)_3$, the galate and vanadate solutions are again neutralized with H_2SO_4 to pH 7.5. In this case, the amorphous $Ga(OH)_3$ precipitate is separated from the vanadate ion in the form of a finished product. At the next stage, NH_4VO_3 is precipitated at pH = 6-7 by adding ammonium chloride salt to the vanadium solution (g/l: V_2O_5-10.10; Na_2O-54.35; SiO_2-0.066; Al_2O_3-0.075). When the pellet is washed, dried and incubated at 500°C, V_2O_5 can be obtained as the final product.

When the solid residue, consisting of Fe and Ni hydroxides, dissolves in sulfuric acid (C_{H2SO4} =5M, t = 98°C, T = 3 hours, S:L= 4:1), these components go into solution in the form of sulfate salts. By adding Fe(OH)$_3$ at pH = 5-6 and adding soda (Na$_2$CO$_3$), NiCO$_3$ salt at pH = 7 can be obtained as a finished product.

In laboratory experiments, the conditions for the dissolution of gallium in samples of fly ash, an increase in the concentration of components in the resulting solutions due to the return to the technological process, and the production of gallium concentrate by two-stage carbonization were studied.

As a result of the research, a technological scheme was proposed for obtaining concentrates of Ga(OH)$_3$, V$_2$O$_5$ and NiCO$_3$ from the ash residue by processing it in two stages (baking soda and dissolving the fired mass in water) (Figure 9).
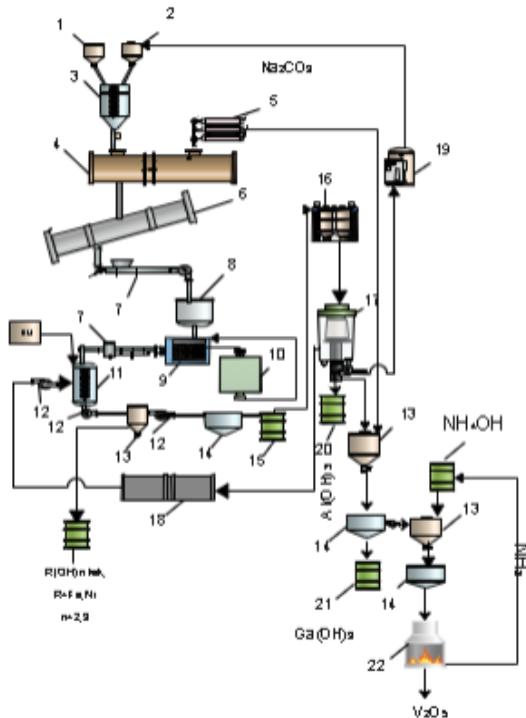
Fig. 9. Apparatus-technological scheme for the extraction of Ga, Ni and V from the ash of fuel oil combustion.
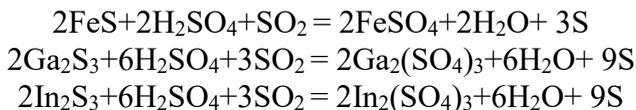
heated to the required temperature, and at the end of the experiment, the tube was cooled to room temperature while maintaining inertia. After determining the exact weight of the burn, its composition was analyzed for the content of Fe, Zn, Pb, Cu, S, Ga and In. Changes in time and temperature cause the formation of pyrrhotines of various compositions in the burn. In this case, in addition to sulfur, 97.78% of arsenic is sublimated and passes into the gas phase.

The optimal conditions for pyrrhotisation were determined: temperature 700°C, test time 60 min, particle size 0.1-0.3 mm. Sublimation of gallium and indium sulfides at temperatures up to 700°C was not observed during the study, and under the optimal conditions found, these elements are added to the pyrrhotised product. If the original ore contains Ga-0.0027%; if it was 0.002%, then in the pyrrhotised product this amount increases to 0.0036 and 0.0026%, respectively, and thickens 1.3 times. At a temperature of 700°C, the pyrite crystal lattice in the ore is captured and completely decomposed into pyrrhotite, which is confirmed by the results of phase analysis.

The lines observed on the obtained X-ray diffraction pattern correspond to the hexagonal modification of pyrrhotite (d (A°) = 2.95; 2.627; 2.068; 1.718; 1.324).

At the next stage of research, the distribution and thickening of gallium in the processed products during the autoclave dissolution of pyrrhotite ore with SO_2 gas was studied. Carrying out the solution in an autoclave at high temperature (110°C) and pressure (0.25 MPa) increases the rate of reactions in the process, increases the yield of products and eliminates environmental problems.

The treatment of a mixture of pyrotechnic products with water was carried out in a laboratory autoclave equipped with an electric heater and a mechanical stirrer. Experiment temperature (25-110°C); pressure (0.1-0.25 MPa); the ratio of solid and liquid phases (1: 5-10); carried out at different times (1-5 hours). The experimental results showed that sulfides of non-ferrous metals (ZnS, CuS, PbS) in the pyrrhotised product do not interact with sulfur dioxide, and iron, gallium and indium compounds are sulfated into the solution:

$$2FeS+2H_2SO_4+SO_2 = 2FeSO_4+2H_2O+ 3S$$
$$2Ga_2S_3+6H_2SO_4+3SO_2 = 2Ga_2(SO_4)_3+6H_2O+ 9S$$
$$2In_2S_3+6H_2SO_4+3SO_2 = 2In_2(SO_4)_3+6H_2O+ 9S$$

In the process of solving, the optimal conditions for the transition of non-ferrous metals to the solid phase were determined: temperature -100°C, P_{SO_2}=0.25MPa, time = 2 hours, density horra-S:L = 1:4. Under these conditions, 84 % iron (Fe^{2+}-81.9 g/l), 70% gallium (6.57 mg/l) and 2.8% zinc (Zn^{2+}-0.22 g/l). Copper solidifies as a concentrate with lead and zinc.

It is known that the complete deposition of each metal hydroxide occurs within a certain concentration of the deposited metal ions and hydrogen ions. The deposition of gallium and indium from solutions containing iron 2-sulfate was carried out at 70°C using ZnO powder. Experiments have shown that $Fe(OH)_3$ precipitation begins at pH = 1.7, and complete precipitation occurs at pH = 3.5. While the precipitation of 2-iron hydroxide occurs at pH 5.6, the precipitation of rare metals occurs at pH 3.8-4.8.

Ingredients 100.76 g/l $FeSO_4$; 0.25 g/l Zn; 70.8g/l S, 0.089 g/l SiO_2; 10.87 mg/l Ga və 12.17mg/l İn are added to 1 liter of a solution (pH = 1.2) containing 10.87 mg / l Ga and 12.17 mg / l In by stirring at 70-90°C. In this case, the pH of the solution rises to 4.8 and part of gallium, indium and oxidized iron precipitates in the form of an amorphous sulfate base salt ($Fe_2O_3 \cdot SO_3 \cdot xH_2O$). In such a hydrated cake, rare metals thicken 50-67 times (table 5).

The cake of rare metals, presented in the table, can be obtained as a separate product by processing it using existing metallurgical methods and separating it from impurities.

Table 5

Chemical composition of cakes obtained from iron-containing sulfate solutions of ZnO, (%)

Components	Fe	Zn	Pb	Ga	İn	CuO	SiO2
Pyrrhotic burns	50.71	7.44	3.9	0.0036	0.0026	0.73	2.1
Cake rich in unique elements	11.5	22.9	0.4	0.163	0.17	0.1	1.12

fuel oil with soda and the dissolution of the boiled mass in water have been studied. As a result of the research, a new environmentally friendly technology was proposed that provides high yields of Ga, V and Ni from the ash residue of heavy oil. The optimal conditions for the process are found. It was determined that the yield of gallium and vanadium in solution is 97.5 and 98.8%, respectively. The conditions for the extraction of Ni were studied by treating the ash after the separation of Ga and V with acid [7, 11].

6. Regularities of distribution of gallium from processing products during processing of ore polymetallic sulfide ore (combustion and dissolution of pyrrhotite in an autoclave in the presence of SO_2) have been investigated. It was found that during pyrrhotics combustion in an inert gas atmosphere at 700° C, the bulk of gallium remains in the ore, and its density increases 1.3 times compared to the original ore. After the separation of iron from the solution by high-temperature crystallization, the Ga and In concentrate is precipitated at a pH of 3.4-4.8. Studies have shown that a rich concentrate of gallium and indium is obtained (Ga-0.163%, In-0.17%) [1-3].

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