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Extraction of Gallium and Vanadium from Alunite Residue (Red Mud) by Sulphating Roasting and Leaching

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Abstract

Red mud containing significant amounts of alumina, iron oxide, titanium dioxide and other valuable components (Ga 0.003–0.005 mass %, V 0.050–0.099 mass %) is the main waste in the alkaline extraction of alumina from alunites according to the Bayer method and a promising raw material for obtaining gallium and vanadium. The degree of sulphatization of gallium and vanadium from red mud during sulphating roasting was investigated. The technological scheme of sulphating process includes three main stages: 1) missing the moistened initial material with concentrated sulphuric acid; 2) sulphating roasting; 3) water leaching of the sulphated mass. The majority of minerals are transformed through sulphatization into the corresponding sulphate compounds. During subsequent roasting, unstable sulphates (mainly ferric sulphate) are decomposed to form the corresponding oxides, while other metals remain in the form of sulphates ($Al_2(SO_4)_3$, $Ga_2(SO_4)_3$, $VOSO_4$). As a result of leaching of the sulphated mass with water, iron and silicon oxides stay in the residue, while the sulphates of aluminium, gallium and vanadium pass into solution. The maximal degree of gallium and vanadium sulphatization under the conditions of laboratory experiments was detected within the range of 600–640 °C. The determination changes in the mineralogical composition of the sulphated mass of red mud were studied by means of thermogravimetry and differential thermal analysis. The developed method of gallium and vanadium extraction from red mud is distinguished by its simplicity and efficiency.

Keywords: busandem red mud, sulphating roasting, gallium, vanadium, leaching

INTRODUCTION

Recovery of alumina from aluminium-containing raw material (bauxite, alunite, nepheline) according to Bayer's method is accompanied by the formation of large-scale wastes in the form of red mud (RM). For instance, when 1 t of alumina is obtained from bauxite, the amount of resulting RM is 1.1–1.2 t, while 1 t of alunite gives 0.5–0.6 t of the waste. Red mud is among technogenic formations with the most complicated chemical and mineralogical compositions; its processing and utilization are very difficult. About 1 % of alumina, iron, substantial amount of rare and rare-earth metals, such as titanium (20–120 kg/t), gallium (60–80 g/t), vanadium (0.5–8 kg/t), scandium (60–120 g/t), yttrium (60–150 g/t) are usually lost with RM [1].

Essential components of RM are gallium and vanadium; their recovery from the wastes is a complicated technological problem. The demand for gallium and vanadium, as well as the consumption of these elements, are increasing all over the world, which provides the necessity to arrange their production from RM in the form of various compounds, for example in the form of oxides or salts.

Under natural conditions, gallium often accompanies alunite through the isomorphous substitution of aluminium. For instance, gallium content in alunite from Dashkesan deposit varies within the range of 0.0005–0.05 %, so its concurrent recovery is outlined [2]. The close ion radii of gallium, vanadium and aluminium (0.62, 0.67 and 0.57 nm, respectively) and pH of the precipitation of the hydroxides of these elements ($pH_{pre}(Ga(OH)_3)$ 3.4–9.7; $pH_{pre}(Al(OH)_3)$ 4.1–10.6) determine the possibility of their isomorphous substitution in rocks and minerals. Isovalent isomorphism $V^{3+} \rightarrow Al^{3+}$ providing the occurrence of more than 90 % of the total vanadium content in the lattices of aluminosilicate clay minerals is known [3]. Because of this, gallium and vanadium are recovered by treating bauxites, alunites and nephelines.

At present, many techniques have been proposed, allowing one to carry out both integrated and partial RM processing with the formation of some marketable products from its components [4–6]. The integrated treatment of RM is mainly based on the combination of pyro- and hydrometallurgical methods. The major areas of the use of RM are the iron industry (blast-furnace smelting of iron ores, a raw material for obtaining iron, a slug-forming reagent for refining cast iron and steel); the production of paints, fertilizers, sorbents, coagulants, catalysts, *etc.* [6].

Analysis of literature data showed that many versions of the integrated processing of RM have been developed, leading to a broad range of useful products. However, integrated RM with the utilization of all components has not been introduced yet. Insufficient attention is paid to the recovery of the most valuable components from RM, in particular gallium, vanadium and residual aluminium, with an exception of the work on the recovery of Ga and V from the RM obtained from bauxite at one of the Turkish aluminium processing plants [7]. Valuable components are leached from the RM containing 0.0055 % Ga_2O_3 and 0.026 % V_2O_5 in an autoclave with heating temperature up to 300 °C. The efficiency of gallium leaching was ~58 %, and after carbonization of the alkaline solution, gallium concentrate is obtained, which contains 0.32 % Ga. The degree of vanadium transition into the precipitate is 94.2–96.9 %. The authors of [8] carried out the acid leaching of bauxite and obtained RM having the composition, %: 0.0033 Ga and 0.034 V. After acid leaching of the slime with hydrochloric acid, the solution was processed using the ion exchange technology with a 5-fold increase in gallium concentration.

During the recent time, the method winning wider and wider application in nonferrous metallurgy and chemical technology is sulphatization of dust-like materials with sulphuric acid [9–14]. The use of H_2SO_4 allows processing of almost any kind of RM with a high degree of recovery of rare metals into solution. An increase in the concentration of H_2SO_4 and temperature causes an increase in the degree of recovery of scandium and other rare elements [9]. This process has also been developed for the selective recovery of nickel and cobalt from iron-rich lateritic [10–13] and polymetallic sulphide ores [14].

For the goal of developing new approaches to the recovery of valuable components (Ga and V) from RM of alunite works, and in order to eliminate the hazardous action of RM on the environment explained by its high alkalinity (pH_{RM} 11.3 ± 1), the technology of integrated processing of alunite raw material was put forward. This technology solves one of the major environmental problems of alumina production – the elimination of slime depositories, which is an urgent and important problem.

The technology implies the possibility to regenerate sulphuric acid and to return it to the start of the process.

The goal of the present work was to study the degree of sulphatization of aluminium iron, gallium and vanadium by sulphuric acid from RM of alunite ore, followed by leaching the sulphatized product with water, with gallium and vanadium passing into solution. The present work is the first systemic investigation aimed at the recovery of gallium and vanadium from RM. Experiments were carried out using a real sample obtained after alkaline leaching of alunite rocks.

EXPERIMENTAL

Objects of investigation

Alunite sample from the Zaglik deposit with the composition, mass %: Al_2O_3 24.09; SiO_2 31.09; Fe_2O_3 4.14; TiO_2 0.48; K_2O 5.15; Na_2O 0.23; SO_3 27.11; V 0.0594; Ga 0.003 was used in the work. According to the data of X-ray phase analysis (XRD), the major minerals of the technological sample of alunite raw material are alunite, dickite, hematite, and quartz (Fig. 1, *a*).

Alunite leaching was carried out under the following conditions: 10 % NaOH solution, temperature 90 °C; L : S = 5 : 1, duration 2 h. Leaching was carried out in a thermostatic reactor 3 dm^3 in volume. The amount of alunite leaching during one operation was 0.5 kg, and RM was obtained in the amount of 0.25 kg. The chemical

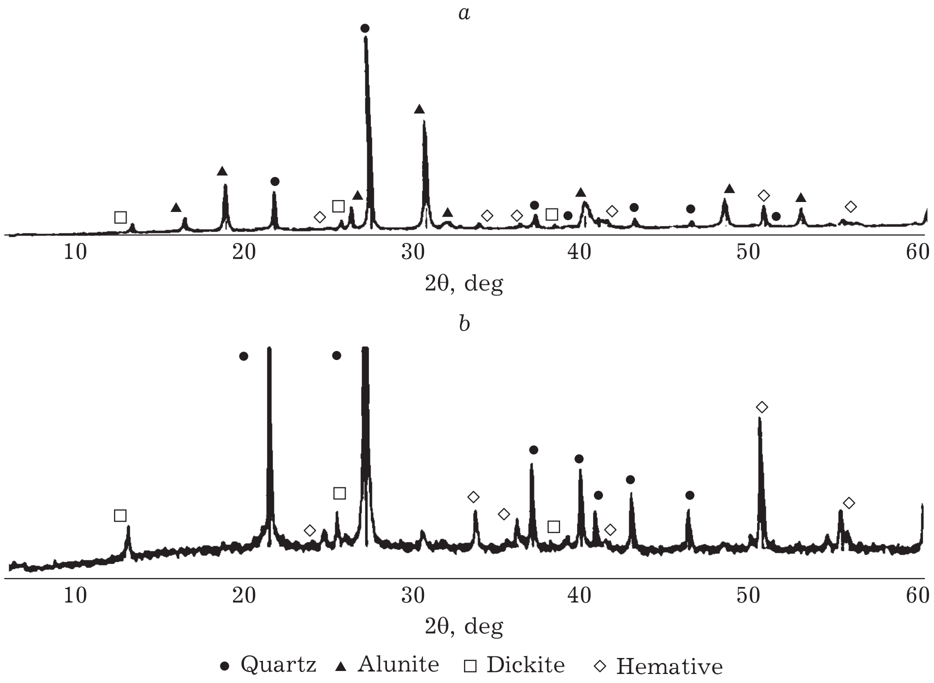

Fig. 1. Diffraction patterns of initial alunite ore from the Zaglik deposit (*a*) and the residue after red slime leaching (*b*).

composition of RM after alunite leaching was, mass %: Al_2O_3 4.53; SiO_2 82.21; Fe_2O_3 8.60; TiO_2 1.15; K_2O 0.07; Na_2O 0.23; SO_3 0.15; V 0.099; Ga 0.005; Rb 0.0012. The results of XRD of RM are presented in Fig. 1, *b*. One can see that the major minerals of RM are dickite ($Al_2Si_2O_5(OH)_4$), hematite (Fe_2O_3) and quartz (SiO_2) – 10, 8 and 78 %, respectively. It was established that aluminosilicates are the primary phases in the sample. Gallium- and vanadium-containing minerals were not discovered, probably due to insufficient sensitivity of the instrument for so low content.

The technological scheme of sulphatization consists of three major stages: 1) mixing of preliminarily wetted initial material with concentrated sulphuric acid; 2) roasting; 3) leaching with water. The RM sample dried at 105 °C for 12 h was ground to the powder state, passed through a sieve with a mesh size of 500 nm, and placed in a porcelain crucible. Then the sample was wetted with water, treated with sulphuric acid of different concentrations (density 1.06–1.84 g/cm^3), placed in the drying box 58/350 (SNOL, Lietuva) and kept for 1 to 12 h at a temperature of 130 °C. During sample mixing with the acid and subsequent stages of drying and roasting, macro- and microcomponents of RM are transformed into the corresponding sulphates. It should be stressed that sulphatization of iron, aluminium, vanadium and gallium starts at room temperature. However, under these conditions, the degree of gallium and vanadium sulphatization is comparatively low, and the amount of iron passing into the solution is rather substantial. After drying, the RM samples treated with sulphuric acid were roasted for 1 h at different temperatures (100–780 °C). Roasting causes the destruction of the lattice of minerals (mainly dickite and hematite) incorporated in RM. The degree of aluminium, gallium and vanadium recovery into the water-soluble form increases with an increase in temperature, while that of iron decreases. After sulphating roasting, the samples were cooled, treated with hot (80–90 °C) water under periodic intense mixing to achieve complete dissolution of gallium, vanadium and aluminium sulphates. The filtered solution and insoluble precipitate of the cake after leaching were subjected to chemical analysis for Ga, V, Al and Fe.

The concentrations of V (IV), Ga (III), Al (III) and Fe (III) in the aqueous phase were determined by means of atomic emission spectrometry with inductively coupled plasma (ICP-AES). To determine the degree of sulphatization and the initial temperature of the decomposition of metal sulphates, we used both literature data reported in [15–18] and experimental data (Fig. 2) of differential thermal analysis (DTA) of individual

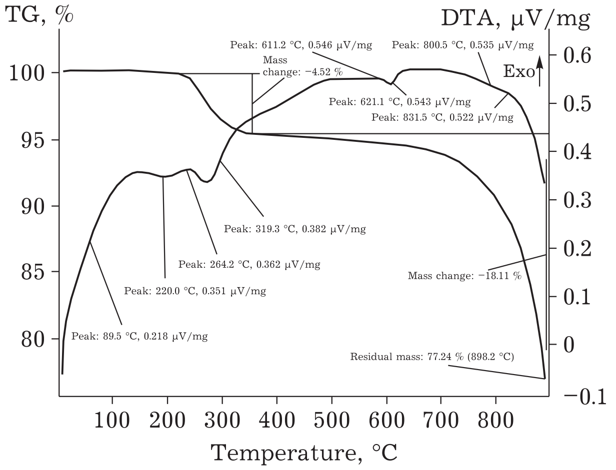

Fig. 2. Derivatogram of $Al_2(SO_4)_3$ (Kh. Ch. Reagent grade).

salts. Relying on the literature data on the thermal decomposition of the corresponding sulphates, we determined the optimal conditions for RM sulphatization with respect to the yields of gallium, vanadium, aluminium and iron sulphates. It was also revealed that $VOSO_4$ under a heating rate of 5 °C/min starts to decompose at 650 °C [15], $Fe_2(SO_4)_3$ – at 500 °C [16], $Ga_2(SO_4)_3$ – at 700 °C [17].

Methods of investigation

The properties of the initial raw material and processing products were studied using the following methods:

– phase identification was carried out by means of XRD with the help of an AXS diffractometer (Bruker, Germany);

– thermal analysis was carried out with a Yupiter STA 449F3 derivatograph (Netzsch, Germany);

– the content of elements in solutions was determined by means of ICP-AES with the help of ICP-AES 8300 spectrometer (Perkin Elmer, Germany).

Calculation procedure

The degree of metal sulphatization, which is the ratio (in per cent) of the mass (amount) of recovered useful substance in solution to its mass (amount) in the product under investigation, was calculated using equation:

$$\text{Sulphatization degree} = \frac{m_{\text{in}} - m_{\text{fin}}}{m_{\text{in}}}\,100~\%$$

where m_{in} and m_{fin} are the initial and final masses of metals, respectively.

RESULTS AND DISCUSSION

Effect of roasting temperature on the degree of sulphatization of iron, aluminium, gallium and vanadium

The data of thermal analysis (TG, DTA) of the sample dried at 130 °C and sulphated at the mass ratio of sulphuric acid to alunite residue 1 : 1 is shown in Fig. 3. During heating to 300 °C, the sample mass loss connected with the removal of physically adsorbed and chemically bound water and with the removal of excess sulphuric acid is detected. Further mass loss is due to the transi-

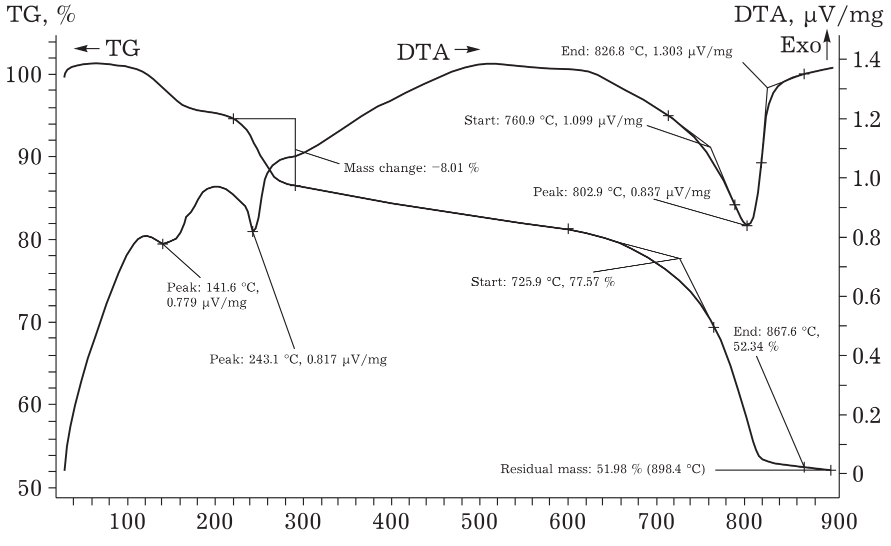

Fig. 3. The curves of thermal analysis (TG and DTA) of the sample of sulphated RM after drying (the ratio of sulphuric acid to RM residue is 1 : 1).

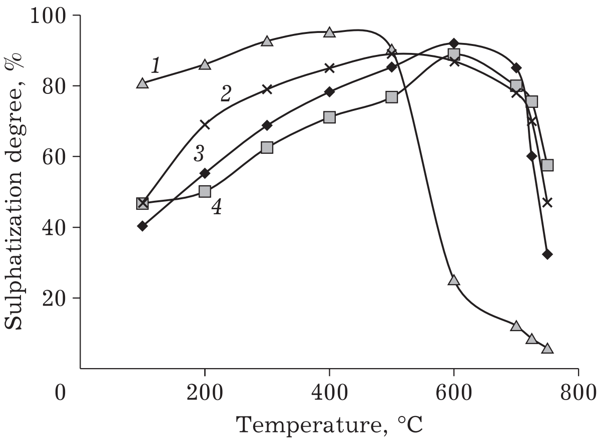

Fig. 4. Effect of roasting temperature on the degree of sulphatization of iron (*1*), aluminium (*2*), gallium (*3*), and vanadium (*4*).

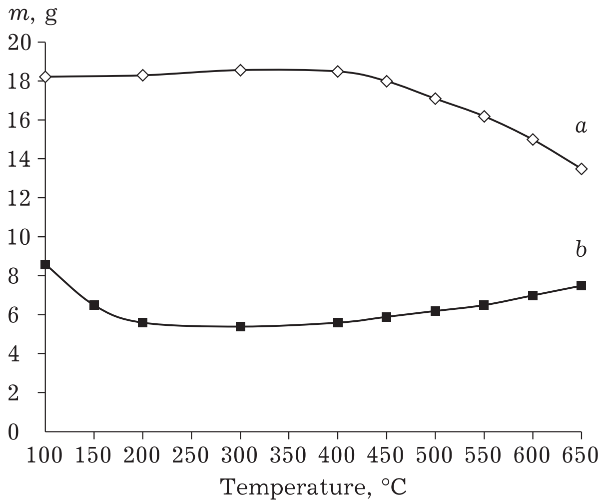

Fig. 5. Effect of roasting temperature on the mass of water-soluble part of cinder (*a*) and cake (*b*) formed during water leaching (the mass of initial RM is 10 g, the ratio of sulphuric acid to RM residue is 1 : 1, leaching temperature 80–90 °C).

tion of metal sulphates into oxides. A sharp mass loss is observed in the sample within a temperature range of 680–820 °C, mainly due to the active decomposition of aluminium gallium and vanadium sulphates. The endothermic effect within the temperature range 680–820 °C with the maximum at 802.9 °C corresponds to the final decomposition of metal sulphates. At the end of the experiment, the residual mass of the sample under investigation is 51.98 % (898.4 °C). The results of XRD of sulphated sample after roasting at 600 °C point to the absence of iron salts. This fact proves that the major fractions of Al, Ga and V pass into solution during water leaching of the product obtained by roasting the sulphated mass at 620 °C. These results confirm that aluminium, gallium and vanadium exist in the cinder after roasting within a temperature range of 500–650 °C in the form of sulphates ($Al_2(SO_4)_3$, $Ga_2(SO_4)_3$, $VOSO_4$).

One can see in the experimental results presented in Fig. 4 that the formation of iron, aluminium, gallium and vanadium sulphates is observed during mixing sulphuric acid (density 1.84 g/cm^3) with RM and roasting even at 100–120 °C. With an increase in roasting temperature to 350–450 °C, the degree of sulphatization of the indicated elements increases (see Fig. 4). The maximal recovery of the major components (Al, Ga, V) during water leaching is achieved as a result of roasting of the sulphated mass at a temperature of 400–600 °C, while 95.5 % of iron passes into the solution in the case if the roasting temperature is 450 °C.

Sulphatization of gallium and vanadium in the cinder (see Fig. 4) proceeds intensively at a roasting temperature within the range 400–650 °C, and then the degree of Ga and V sulphatization decreases with an increase in temperature. The maximal sulphatization of gallium and vanadium (under the conditions of laboratory experiments) is observed with the roasting temperature equal to 620 °C (90–93 %). As far as iron is concerned, with an increase in roasting temperature above 470 °C the degree of its sulphatization decreases, while at a temperature of 700 °C the cinder contains only the traces of water-soluble iron.

Figure 5 shows the effect of roasting temperature on the mass (*m*) of the parts of the cinder. An increase in the mass of the water-soluble part of the cinder (see Fig. 5, *a*) and a decrease in cake mass (see Fig. 5, *b*) during leaching of the sulphated mass confirm the successful sulphatization.

As we have already indicated above, at 120 °C the majority of RM components pass into the corresponding sulphates. The results of XRD of RM subjected to sulphatization (after roasting at 450 °C for 24 h) revealed the following phase composition (Fig. 6): SiO_2, $(H_3O)Al(SO_4)_2$, $Ca_6Al_3(OH)_{18}(SO_4)_{1.5}(H_2O)_9$, $Al_2(SO_4)_3(H_2O)_5$, $K_2SO_4 \cdot KHSO_4 \cdot H_2O$, $(H_3O)Fe(SO_4)_2$. Iron and aluminium sulphates are dissolved at the leaching stage because they are well soluble in water. Silicon was not observed in the solutions after leaching. XRD data showed that the cake after the dissolution of sulphated material is composed of only two minerals – quartz and hematite.

The behaviour of the shown curves (see Fig. 4) suggests that within the roasting temperature range of 200–650 °C the form of gallium and va-

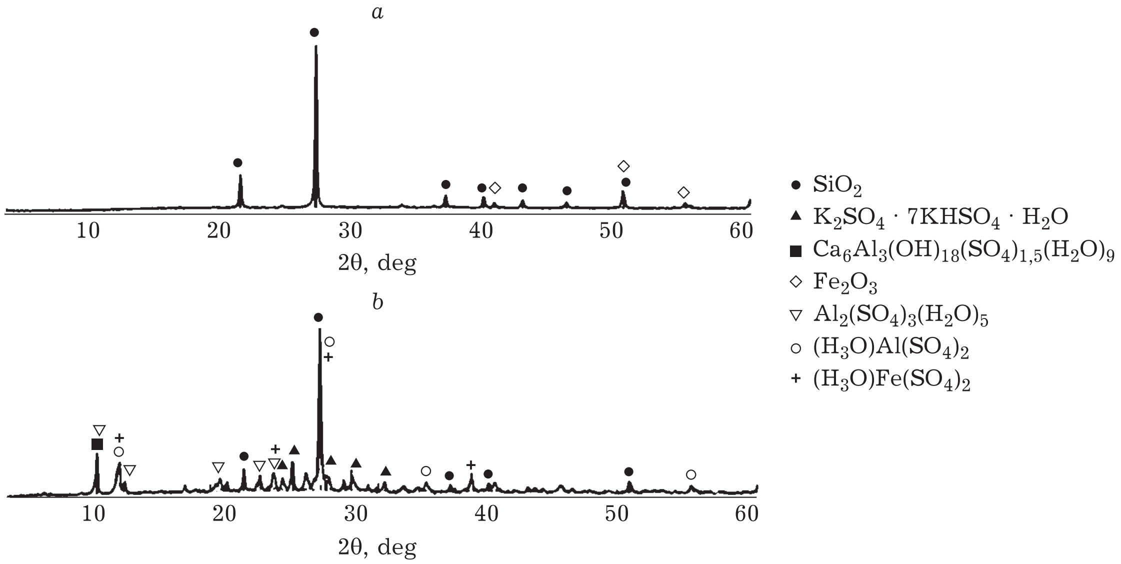

Fig. 6. Diffraction patterns of the cake (insoluble residue) (*a*) obtained after its water leaching, and sulphated RM after roasting at 450 °C for 24 h (*b*).

nadium occurrence in sulphated cinder changes with an increase in roasting temperature. A comparison of the curves of gallium and vanadium transition into solution shows that the recovery of these metals is connected with the leaching of the soluble forms of cinder macrocomponents, namely aluminium. Sulphatization of gallium and vanadium starts under the same conditions as aluminium. This is explained by the fact that gallium and vanadium are present in sulphated material at a roasting temperature below 620 °C in readily leachable forms, that is, as sulphates. An increase in the temperature of sulphating roasting (>700 °C) has unfavourable effect on the parameters of leaching of sulphated material. The recovery of gallium and vanadium into solution decreases from 93 to 60 % with an increase in sulphatization temperature from 620 to 700 °C. However, the yield of cake (insoluble part of the cinder) after leaching increases (see Fig. 5, *b*). A decrease in the recovery of gallium and vanadium into solution is due to the fact that the formation of poorly water-soluble compounds into which Ga and V are incorporated occurs during roasting as a result of the interaction between separate components of the cinder. One type of these compounds is metal ferrites. It was stressed in [19] that gallium may enter ferrites that are formed during roasting; these ferrites are only partially dissolved during water leaching and remain in the precipitate from sulphated product leaching.

TABLE 1

Estimated expenses for the reagents used for processing 1 t of red slime (alunite residue)

	Mass, t	Cost per unit (US dollars/t)	Cost (US dollars)
Expenses			
Acid	0.261	−200.00	−52.20
Water	10	−1.00	−10.00
Total			−62.20
Income			
Red slime	1	10.00	10.00
Ga	$46 \cdot 10^{-6}$	$2.81 \cdot 10^5$	12.93
V_2O_5	$910.8 \cdot 10^{-6}$	$5.50 \cdot 10^4$	50.05
Al_2O_3	$45.3 \cdot 10^{-3}$	$0.70 \cdot 10^3$	31.71
TiO_2	$11.5 \cdot 10^{-3}$	$1.86 \cdot 10^3$	21.39
Rb	$10 \cdot 10^{-6}$	$11.18 \cdot 10^6$	111.80
Total			237.88
Profit			175.68

The economic efficiency of RM processing according to the proposed procedure was estimated. Calculations based on experimental data including the estimated expenses for reagents and the values for generated products are shown in Table 1. The profit from processing 1 t of red slime is 175.68 US dollars. The prices of the used reagents for calculations were taken from open sources [20, 21].

CONCLUSION

The results obtained in the present work allow us to conclude that sulphuric acid sulphatization of red slime (wastes from alumina recovery from alunite) under corresponding conditions allow one to transform the accompanying elements (gallium, vanadium, and aluminium) into water-soluble form with simultaneous minimal sulphatization of iron. For instance, for the mass ratio of red slime and sulphuric acid (1 : 1), the temperature of sulphating roasting equal to 620 °C and roasting time 1 h under laboratory conditions, 90–93 % of gallium and vanadium may be successfully transformed into water-soluble form, while the degree of aluminium sulphatization is 85 %, and iron not more than 18 %.

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