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PHYSICOCHEMICAL AND TECHNOLOGICAL BASES OF PRODUCTION OF DESULPHURISED CRYOLITE FROM MUSCOVITE-STAVROLITE SHALES OF TAJIKISTAN

Key words: cryolite, aluminium sulphate, potassium alum, sodium fluoride, muscovite-stavrolta shale, "Kurgovad" deposit, sulphatization, aluminium production.

Physicochemical and technological aspects of production of desulfurised cryolite from a mixture of water-dissolved $KAl(SO_4)_2$, $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ obtained by heat treatment of muscovite-stavrolite shale from the deposit "Kurgovad" with sulfuric acid have been investigated. According to the conducted laboratory tests at t – 85-95 °C, τ – 15-20 min. and NaF solution dosage 100% of stoichiometry, with two-fold washing with hot water at ratio S:L=1:4 and filtration with the help of vacuum-filtering unit, the degree of cryolite extraction reaches more than 94%. It was determined that relatively fine cryolite particles were formed at room temperature, which resulted in a prolongation of the filtration process and the absorption of relatively large amounts of sodium sulphate. At the same time the expediency of using a vacuum-filtering unit was established, because at increasing the temperature to 85 ° C sharply increases the removal of sodium sulphate from the composition of cryolite from 10.1 % to almost zero. In this case, the cryolite filtration time is reduced from 30 to 10 minutes. Physico-chemical methods of analysis proved the production of desulphurised cryolite corresponding to the normative requirements of GOST 10561-80 (artificial technical cryolite) and the mineral cryolite (PDF number 25-772). The chemical composition of the obtained cryolite consists mainly of 53.7% F, 12.5% Al and 31.8% Na. After separation of cryolite by filtration, the solid part of the evaporated filtrate was subjected to XRD, which determined the presence of sodium hydrosulphate, tenardite and aphthitalite minerals. The principal technological scheme of cryolite production from muscovite-stavrolite shales of the "Kurgovad" deposit was developed on the basis of the conducted research.

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ФИЗИКО-ХИМИЧЕСКИЕ И ТЕХНОЛОГИЧЕСКИЕ ОСНОВЫ ПОЛУЧЕНИЯ ОБЕССЕРЕННОГО КРИОЛИТА ИЗ МУСКОВИТ-СТАВРОЛИТОВЫХ СЛАНЦЕВ ТАДЖИКИСТАНА

Ключевые слова: криолит, сульфат алюминия, алюмокалиевые квасцы, фторид натрия, мусковит-ставролтовые сланцы, месторождение «Курговад», сульфатизация, производство алюминия.

Исследованы физико-химические и технологические аспекты получения обессеренного криолита из смеси, растворенных в воде $KAl(SO_4)_2$, $Al_2(SO_4)_3$ и $Fe_2(SO_4)_3$, полученных при термообработке мусковит-ставролитовых сланцев месторождения «Курговад» с серной кислотой. Согласно проведенных лабораторных исследований при t – 85-95 °C, τ – 15-20 мин. и дозировке раствора NaF 100% от стехиометрии, с двухкратной промывкой горячей водой при соотношении Т:Ж=1:4 и фильтрации с помощью вакуум-фильтрующей установки, степень извлечения криолита достигает более 94%. Определено, что при комнатной температуре образуются относительно мелкодисперсные частицы криолита, которые приводят к удлинению процесса фильтрования и поглощению относительно большого количества сульфата натрия. При этом установлено целесообразность использования вакуум-фильтрующей установки, так как при повышении температуры до 85 °C резко возрастает удаление сульфата натрия из состава криолита с 10,1 % практически до нуля. При этом продолжительность фильтрации криолита сокращается с 30 до 10 минут. Физико-химическими методами анализа, доказано получение обессеренного криолита, соответствующего нормативным требованиям ГОСТ 10561-80 (криолит искусственный технический) и минералу криолит (номер по картотеке PDF 25-772). Химический состав полученного криолита состоит в основном из 53,7% F, 12,5% Al и 31,8% Na. После отделения криолита фильтрованием, твердая часть упаренного фильтрата была подвергнута РФА, по результатам которого определено наличие гидросульфата натрия, минералов тенардита и афтиталита. На основе проведенных исследований разработана принципиальная технологическая схема получения криолита из мусковит-ставролитовых сланцев месторождения «Курговад».

Introduction

Cryolite is an important industrial product that is widely used in manufacturing, especially in the electrolytic process of aluminium production [1-9]. It is mainly synthesised by the interaction of hydrofluoric acid with aluminium hydroxide to give H_3AlF_6 from which it precipitates on introduction of sodium-containing salts [10]. The use of expensive components increases the cost of cryolite, because of this the practical use of these components is limited to some extent. Along with these methods, it is also possible to obtain Na_3AlF_6 from clarified liquid part of sludge, solid wastes of aluminium production, solutions of NaF and $Al_2(SO_4)_3$ and others [11-13]. There were also carried out works on obtaining Na_3AlF_6 from sulfate-containing solution [14], previously obtained from kaolinite-containing clays of Chashma-Sang deposit by sulfatisation method [15].

However, the presence of Na_2SO_4 in the cryolite leads to an increase in the alkalinity of the electrolyte, thereby causing a greater consumption of AlF_3, which is used to correct the electrolyte modulus. Also, the sulphate content leads to aluminium losses due to the reduction of sulphate ion and, consequently, to lower current yields [16-18].

In this connection, the aim of this work is the research and development of technology for obtaining synthetic desulphurised Na_3AlF_6 from a mixture of water-dissolved potassium alum and aluminium sulphate obtained during sulphatisation of muscovite-staurolite shale from the Kurgovad deposit.

Methodology of the experiment

A solution consisting mainly of $KAl(SO_4)_2$, $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ obtained by aqueous treatment of sulphatised sinter from muscovite-stavrolite shales of Tajikistan [19, 20] was used in the study of the present work. X-ray diffraction-phase analysis (XRD) of sulphatised sinter obtained from muscovite-staurolite shale is shown in Fig. 1.

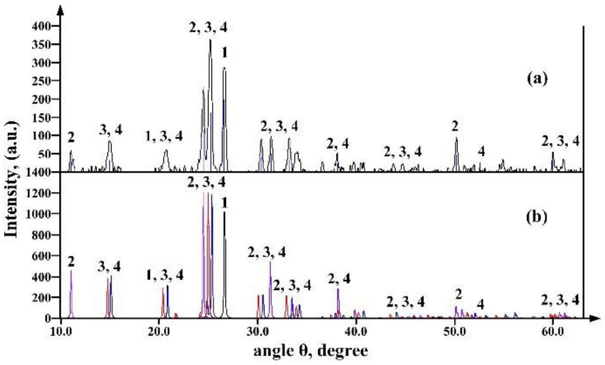

Fig. 1 - X-ray diffraction patterns of: sulphatised sinter (a) and standard sample (b): 1 - quartz (SiO_2), 2 - potassium alum ($KAl(SO_4)_2$); 3 - millosevichite ($Al_2(SO_4)_3$); 4 - mikasaite ($Fe_2(SO_4)_3$)

The XRD of the sulphatised sinter (Fig. 1a) shows the appearance of lines related to quartz (PDF number 85-335), potassium alum (PDF number 74-82), millosevichite (PDF number 42-1428) and mikasaite (PDF number 47-1774), which confirm the sulphatisation process and the formation of the corresponding sulphate-containing compounds.

For X-ray phase analyses, an X-ray apparatus "Drone-2" equipped with the software 'Crystallographica Search-Match' was used. The degree of yield of the investigated components during sulfatisation was determined by titrimetric (complexometric) method. Sodium fluoride used as a component in the synthesis of Na_3AlF_6 from sulfate-containing solution was obtained from a mixture of H_2SiF_6 and HF – a by-product of hydrofluoric acid production (TALCO Chemical Ltd.) [21].

Discussion of results

When sodium fluoride solution interacts with sulphate-containing solution, the following chemical reactions may occur.

$$3KAl(SO_4)_{2(l)} + 18NaF_{(l)} = 2Na_3AlF_{6(s)} + K_3AlF_{6(s)} + 6Na_2SO_{4(l)} \quad (1)$$

$$Al_2(SO_4)_{3(l)} + 12NaF_{(l)} = 2Na_3AlF_{6(s)} + 3Na_2SO_{4(l)} \quad (2)$$

Due to the relatively high potassium content in the composition of muscovite-stavrolite shales, in accordance with the first reaction, besides Na_3AlF_6, there is also a possibility of formation of a small amount of K_3AlF_6. The solubility of potassium cryolite in water at 80 °C is about 4.5%, apparently, this phenomenon causes its dissolution in water and transition to the liquid phase during filtration.

It is important to note that during thermal treatment of muscovite-stavrolite shales with H_2SO_4, in addition to potassium alum, iron (III) sulfate is formed, which according to XRD data belongs to the mineral mikasaite ($Fe_2(SO_4)_3$). According to the reaction below, when aqueous solutions of $Fe_2(SO_4)_3$ and NaF interact, there is a probability of formation of sodium hexafluoroferrate.

$$Fe_2(SO_4)_{3(l)} + 12NaF_{(l)} = 2Na_3FeF_{6(l)} + 3Na_2SO_{4(l)} \quad (3)$$

It should be noted that iron is an undesirable component in the composition of cryolite, but iron-containing cryolite is a colourless compound that is soluble in water. Therefore, it is likely that iron compounds are removed with the filtrate during washing.

To determine the physicochemical parameters of the technology for obtaining Na_3AlF_6 from aqueous solutions of potassium alum and aluminium sulphate using NaF solution, a series of studies of the dependence of Na_3AlF_6 extraction rate on temperature, process duration and NaF solution dosage were carried out, the results of which are shown in Table 1.

Table 1 - Parameters influencing the process of cryolite production from sulphate-containing solution and sodium fluoride

N	Influencing parameters			Cryolite recovery rate, %	Na_2SO_4 as an impurity, %
	t, °C	τ, min.	D_{NaF}, %		
1	25	15	100	97,3	10,1
2	45	15	100	96,8	5,3
3	65	15	100	95,9	1,8
4	85	15	100	94,1	-
5	85	5	100	94.8	0,7
6	85	25	100	93.5	-
7	85	35	100	93.1	-
8	85	15	80	77.4	-
9	85	15	90	88.9	-
10	85	15	110	94.5	-
11	85	15	120	94.6	-

As can be seen from Table 1, at temperature 85-95°C, duration of 15-20 minutes and sodium fluoride dosage 100% of stoichiometry, with two-fold washing with hot water at ratio S:L=1:4 and filtration with vacuum-filtering unit, the degree of cryolite extraction reaches more than 94%.

In order to determine the filtration rate and degree of desulphurisation of cryolite as a function of temperature using a conventional laboratory funnel and vacuum filtering device, a series of experiments were carried out, the results of which are presented in Table 2. It should be noted that using a conventional laboratory funnel, the cryolite paste was washed three times in the ratio S:L=1:5.

As can be seen from Table 2 (using an ordinary laboratory funnel), when increasing the temperature of the water used for washing from 25 to 85 ° C, the residual amount of sodium sulfate in the cryolite decreases from 27.9 to 12.6 %, while the time of filtration of cryolite decreases from 94 to 35 min. It should be noted that when cryolite is washed three times with hot water in the ratio S:L=1:5 and filtered using an ordinary laboratory funnel, sulphates are not completely removed from the cryolite composition (Table 2), which does not meet the requirements of GOST 10561-80, since according to this GOST the amount of sulphates in the cryolite composition should not exceed 1%. The use of an ordinary laboratory funnel leads to an increase in the duration of the filtration process, and the threefold washing of cryolite in the ratio S:L=1:5, to overconsumption of water.

Table 2 – Filtering time and degree of desulphatisation of cryolite as a function of temperature

№	Filtration conditions			Extraction rate of cryolite, %	Na_2SO_4 residual, %
	t, °C	Filtration time, min.	S:L		
Using an ordinary laboratory funnel					
1	25	94	1:5	97,2	27.9
2	45	76	1:5	96,7	22.4
3	65	43	1:5	95,8	17.9
4	85	35	1:5	94,2	12,6
Using a vacuum filter device					
5	25	30	1:5	97,3	10,1
6	45	21	1:5	96,8	5,3
7	65	15	1:5	95,9	1,8
8	85	10	1:5	94,1	-

Therefore, the effect of temperature and use of vacuum filter unit on the filtration and desulphurisation rate of Na_3AlF_6 was investigated (Table 2).

When the temperature increases from 25 to 85 °C, the residual amount of sodium sulphate in the composition of the washed cryolite decreases sharply from 10.1 % to almost zero. Thus, duration of filtration of cryolite is reduced from 30 to 10 min. that confirms efficiency of use of vacuum-filtering device.

After determining the optimum parameters, the chemical analysis of cryolite obtained from aluminous alum was carried out, and the result was compared with the normative requirements of standard cryolite (Table 3).

Table 3 – Comparison of chemical composition of cryolite obtained from sulphate-containing solution with standard cryolite

Name of indicators	Artificial cryolite technical GOST 10561-80			Cryolite obtained from muscovite-staurolite shales
	Norm for grades			
	Highest grade	First grade	KP	
Mass fraction of fluorine, %	Not less than 54	Not less than 54	Not less than 52	53.7
Mass fraction of aluminium, %	No more than 18	No more than 19	No more than 23	12.5
Mass fraction of sodium, %	Not less than 23	Not less than 22	Not less than 13	31.8
Mass fraction of silicon dioxide (SiO_2), %, not more	0,5	0,9	1,5	0,6
Mass fraction of iron oxide (Fe_2O_3), %, not more	0,06	0,08	0,1	0,07
Mass fraction of sulphates in terms of SO_4, %, not more	0,5	1	1	0,7
Mass fraction of water, %, not more	0,2	0,5	0,8	0.55

As can be seen from Table 3, the chemical composition of cryolite obtained from muscovite-stavrolite shale of the “Kurgovad” deposit corresponds to the chemical composition of standard cryolite and to the normative requirements of GOST 10561-80.

In order to confirm the technology of obtaining cryolite from sodium fluoride solution and salt mixture of sulfate-containing solution formed from muscovite-staurolite shales of “Kurgovad” deposit by sulfatisation, XRD was carried out, the results of which are shown in Fig. 2.

As can be seen from the X-ray diffraction (Fig. 2) almost all the lines found belong to the mineral cryolite (PDF number 25-772), thus confirming the chemical analyses, the technology of obtaining cryolite from aqueous solutions of potassium alum, aluminium sulphate and sodium fluoride, as well as desulphurisation of cryolite. However, traces of the mineral elpasolite (PDF file number 86-2057) are detected, which may partially lower the melting point of cryolite in the electrolytic production of aluminium.

Also, after filtration of cryolite, the liquid phase was evaporated and subjected to X-ray phase analysis (Fig.3).

It can be seen from the XRD (Fig. 3) that almost all of the detected peaks belong to the compound sodium hydrosulfate (PDF number 76-1110), partly to the minerals tenardite (PDF number 74-2036) and aphthitalite (PDF number 74-1742), which confirms the above reactions. At the same time, traces of iron fluoride compounds are observed in the composition of the evaporated salt.

On the basis of the conducted researches the basic technological scheme of processing of muscovite-staurolite shales of “Kurgovad” deposit by sulphatisation to obtain cryolite was developed (Fig. 4).

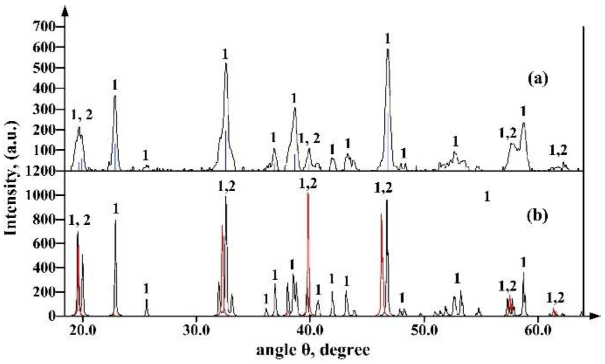

Fig. 2 - X-ray diffraction of cryolite obtained from sulphate-containing solution (a) and standard samples (b): 1 - cryolite (Na_3AlF_6); 2 - elpasolite ($K_2Na(AlF_6)$)

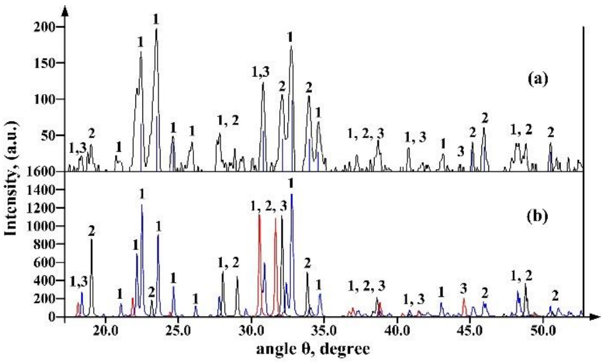

Fig. 3 - X-ray diffraction of the evaporated salt obtained from the filtrate after separation of cryolite (a) and standard samples (b): 1 - sodium hydrosulphate ($Na_3H(SO_4)_2$); 2 - tenardite (Na_2SO_4); 3 - aftitalite ($NaK_3(SO_4)_2$)

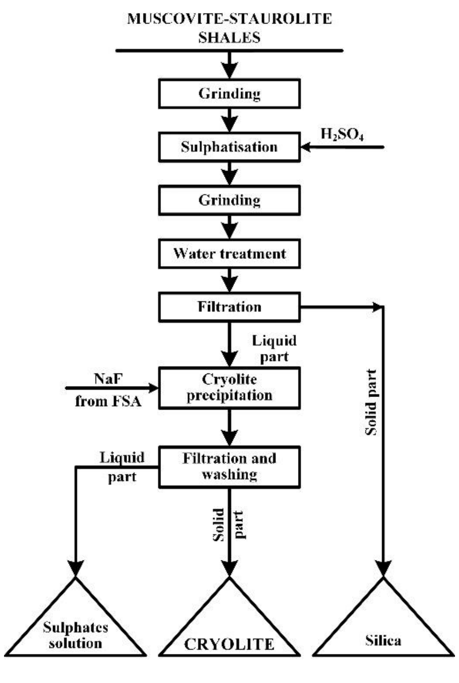

Fig. 4 - Principle scheme of cryolite production from sulphate-containing solution obtained during sulphatisation of muscovite-staurolite shale

As can be seen from the scheme (Fig. 4), after sulphatisation of muscovite-staurolite shale, the resulting spume is crushed and treated with water. The resulting pulp is filtered and washed to separate the solid part from the liquid part, which is treated with sodium fluoride solution to precipitate cryolite. The pulp is subjected to filtration and washing with separation in the solid part of cryolite and in the liquid part a mixture of sulphate solutions.

Conclusion

Cryolite obtained by this technology can be used in aluminium production, and the leachate consisting mainly of sodium hydrosulphate – in the production of detergents, mining and metallurgical industry, production of cryolite by hydrochemical method, production of construction materials and processing of secondary products of fluoride salt production – a mixture of fluorosilicic and hydrofluoric acids to obtain a mixture of silicofluoride and sodium fluoride.

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