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Study of the Sulphuric Acid Decomposition of Fluorine-Containing Wastes of the Aluminium Production for the Purpose of the Isolation of Hydrogen Fluoride

I. V. PETLIN and A. N. DYACHENKO

Tomsk Polytechnic University,
Prospekt Lenina 30, Tomsk 634050 (Russia)

E-mail: petliniv@tpu.ru

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Abstract

Processing method of fluorine-containing wastes of the aluminium industry aimed at the preparation of hydrogen fluoride was considered. Thermodynamic parameters of the sulphatisation process of fluorine-containing wastes were calculated. The necessity of the stage of the preliminary oxidative roasting of wastes for the removal of the carbon constituent that hinders the interaction of sulphuric acid with fluorine-containing particles was established. Kinetic characteristics and optimal conditions of the sulphatisation process of fluorine-containing wastes in the static mode were determined.

Key words: hydrogen fluoride, aluminium industry, fluorine-containing wastes, sulphatisation, complex processing, oxidative roasting, thermodynamic parameters, kinetic characteristics

INTRODUCTION

Fluorine-containing wastes of the aluminium production for the industry of the Russian Federation are of interest, first of all, as an alternative source of hydrogen fluoride. The major source of hydrogen fluoride at the present time remains fluorite (fluorspar), CaF_2 . Prognostic resources of fluorspar ores in Russia are estimated in 148.2 million tons [1]. However, Russian deposits of fluorspar on the quality of ores are significantly inferior to foreign analogues: the average content of CaF_2 in established reserves is 3.9 %, while it exceeds 60 % [1] for analogous deposits of China.

In Russia, there are no large deposits with high-quality ores and reserves of deposits, on which lump fluorite can be extracted, are very small [2]. The absence of the domestic quality fluorspar products creates the following problems: 1) the unprofitability of the production of hydrogen fluoride in Russia; 2) the depen-

dence of domestic productions from imported raw materials.

Simultaneously with this, losses of fluorine on enterprises in the aluminium industry reach almost 18 kg per ton of aluminium produced. Annually, about 400 thousand tons of solid fluorine-containing wastes [3] are dropped on slime fields. Aside from fluorine, these wastes contain in large quantities carbon, alumina, cryolite, sodium sulphate and carbonate, suitable to the regeneration and return to technological limits.

There are various ways of processing of fluorine-containing wastes of the aluminium industry: leaching, flotation, pyrohydrolysis *etc.* Thus, tails together with the slimes of gas cleaning systems, formed in the course of flotation, are treated with a solution of NaOH, then the solution of leaching is used at the stage of the preparation of regeneration cryolite, the carbon-containing pasta is briquetted [4–6]. Flotation ways received the spread in the process of processing electrolysis coal foam [3].

The enrichment is carried out by the method of the reverse flotation, when the target is the chamber product, *i. e.* cryolite. After passing the main and control flotation it returns to the electrolysis process, and flotation tails are sent to slime fields. Additionally, the flotation enrichment and other types of fluorine-containing wastes were investigated [7, 8]. A number of works devoted to pyrohydrolysis of fluorine-containing wastes are described [9–11]. The basis of these ways is the extraction of fluorine from carbonaceous materials by the exposure on wastes of water vapour at the temperature. The method of the preparation of hydrogen fluoride by the sulphuric acid decomposition of the spent lining of the aluminium electrolyzer at the mass ratio of the lining and sulphuric acid of (0.25–0.33) : 1 at the temperature of 250 °C is known. However, none of the listed ways has received the industrial application, due to the complexity of the used equipment, specific conditions of carrying out the process and large capital investments into the construction of processing productions. In addition, these processing technologies allow extracting only a small proportion of valuable components not providing the complexity of the use and a substantial reduction in waste.

In this regard, the research directed at the development of scientific bases and technologies of the complex processing fluorine-containing wastes is of both the ecological and economic interests. The goal of this work is the study of the possibility of replacing the initial raw materials of the production of HF, fluor-spar on fluorine-containing wastes of the aluminium industry.

MATERIALS AND METHODS

Characteristic of the starting material

As fluorine-containing wastes the dust of electric filters of aluminium electrolyzers of the Irkutsk Aluminium Plant was selected. The phase composition of wastes (mass %): NaAlF₆ 25.08, Na₅Al₃F₁₄ 4.73, Al₂O₃ 19.53, C 35.23, Na₂SO₄ 13.31, Fe₂O₃ 1.04, SiO₂ 1.08. Electric filters dust is a fine powder of the dark grey colour, the average diameter of particles varies in the limits from 10 to 25 μm. The basis of the molecular composition of the dust is aluminium oxide Al₂O₃, predominantly of the α-modification, fluoride salts (basically, cryolite Na₃AlF₆ and chiolite Na₅Al₃F₁₄), carbon and sodium sulphate Na₂SO₄. A large amount of carbon in wastes of the aluminum production is due to the fact that when electrolytic obtaining metallic aluminium anodes made from oil coke are intensely destroyed. Cryolite chiolite mass is represented by fine intergrowths of the size of 70–80 μm. Free grains of the size from several micrometres to 10–80 μm are fixed in individual samples. Refraction indexes of cryolite and chiolite in wastes (N_{av}) are close on the value between each other and amount to 1.335 and 1.3422 for cryolite and chiolite, respectively. Aluminium oxide is presented, as a rule, by free light grey fine grains of α-Al₂O₃ with $N_{av} = 1.7650$ [3]. The granulometric composition of wastes is given in Table 1. The electrical resistivity of wastes is 4.10^7 – 10^8 Ohm · cm at the dew point of the gas from 10 to 40 °C. The true density (the density of the motes themselves) is on average 2.92 g/cm³. Values of the bulk density of dry wastes vary in the di-

TABLE 1
Granulometric composition of fluorine-containing wastes

Class fineness, μm	Content, mass %	Class fineness, μm	Content, mass %
0–1	0	12–16	0
1–2	4.9	16–24	27.0
2–3	2.4	24–32	2.3
3–4	0	32–48	24.9
4–6	5.5	48–64	4.5
6–8	3.0	64–192	16.5
8–12	9.0	d_{av}	22.9

apason of 0.86–1.15 g/cm³. The angle of repose depending on the bulk density changes within the limits of 35–40° [3].

Methods

The thermodynamic calculation of the possibility of proceeding sulphatisation reactions of the basic components was conducted for the mechanism study the process of the sulphuric acid decomposition of fluorine-containing wastes of the aluminium production.

To determine the optimal time and temperatures of the interaction of the reaction mixture under static conditions, the kinetic experiment using the method of the continuous weighing of the reacting mixture and automatic registration mass was conducted. The extent of reacting was determined on the mass loss that is due to the formation of gaseous hydrogen fluoride and water. A mixture consisting of 1 g of fluorine-containing wastes and 24.7 g of sulphuric acid (State Standard GOST 4204–77) by the stoichiometric amount was used during the experiment.

In order to determine the efficacy of using oxidative calcination to remove the coal constituent of fluorine-containing wastes, thermogravimetric and differential thermal analyses were conducted. Experiments were conducted on the coincident TGA/DSC/DTA analyser – derivatograph of the brand SDT Q600 with the data software processing TA instruments Universal V42E. The sample mass reached 25 mg. The sensitivity of the balance is 0.1 µg. The calorimetric precision/reproducibility is equal to ±2 % (according to metallic standards). The sensitivity of DTA is 0.001 °C. Thermocouples: Pt/Pt-Rh (type R). Crucibles: platinum (40 µL), ceramic (Al₂O₃, 40 µL). The control of the sample atmosphere is the atmospheric air.

In order to determine the completeness of the removal of the carbon component at different temperatures wastes were previously shredded. Shredding was implemented under laboratory conditions using the planetary mono mill Pulverisette 6 of the company Fritsch until the content of particles of the fineness of 0.15 mm did not reach 70 mass %. The pre-grinding is necessary for the increase of the surface of the interaction of the carbon component with oxygen of the air. Then, fulfilled wastes

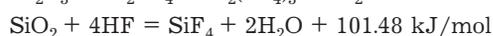
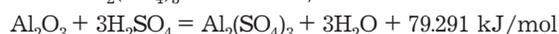
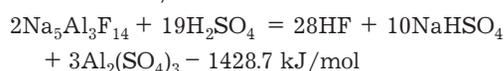
were laid out on the pallet (the layer thickness did not exceed 1 cm) and placed into a muffle furnace, where the roasting of the carbon component was conducted at temperatures of 400–900 °C with a step of 50 °C, the firing time was 1 h.

The analysis of the carbon amount in each sample was conducted by the method of gas spectroscopy using an elemental analyzer CHNS Flash 2000 Tresmo Scientific. The temperature of burning was 950 °C, atmosphere of burning samples was oxygen, helium; feed rate was 140 mL/s. The pressure in the apparatus is 3 atm; detector temperature is 65 °C. The mass of the sample is equal to 1 mg.

RESULTS AND DISCUSSION

Thermodynamic calculation

It was established that reactions of the sulphuric acid decomposition of cryolite and chiolite are endothermic and required a heat supply. The probability of their proceeding to the side of the formation of reaction products increases with the temperature increase. The temperatures of the start of direct reactions for cryolite and chiolite are equal to 81 and 236 °C, respectively. Reactions of the interaction of aluminium oxide, sodium sulphate and iron (III) oxide with sulphuric acid are exothermic and proceed with the heat evolution in the direction of the formation of reaction products already at room temperature. The heat effects of main reactions at the optimal temperature of carrying out the process of 250 °C will amount:



Kinetic experiment

The kinetic studies showed that opening a mineral component of aluminium production wastes passes only by 15–20 %. After the analysis of additional literature data, the assump-

tion was made that such low indicators are conditioned by the excessive amount of the carbon component that hampers the interaction of fluorine-containing components with the leaching agent [13]. Coal envelops fluorine-containing particles and thus prevents the penetration of sulphuric acid to the surface of reacting. Such a structure of wastes was formed due to the condensation of flying off fluorine-containing vapours in the developed surface of coal when electrolytic obtaining aluminium in systems of the dry and wet dust collection of electrolyzers [3]. Besides, the coal dust with a developed surface is an excellent adsorbent of liquid and gaseous substances. Consequently, sulphuric acid and the resulting hydrogen fluoride will be absorbed by coal, but not participate in the process. In order to remove coal and activate the surface of fluorine-containing particles, the stage of the preliminary oxidizing roasting before the sulphuric acid decomposition was used.

Thermogravimetric and differential thermal analysis

Results of thermogravimetric and differential thermal analysis are given in Fig. 1. It can be seen that when gradual heating wastes first, the hygroscopic moisture (endo effect at 100 °C) is removed. The further decrease of the weight sample to 363 °C is caused by desorption of gaseous impurities (CO, CO₂, HF, SO₂ etc.) adsorbed by solid particles of the dust, as well

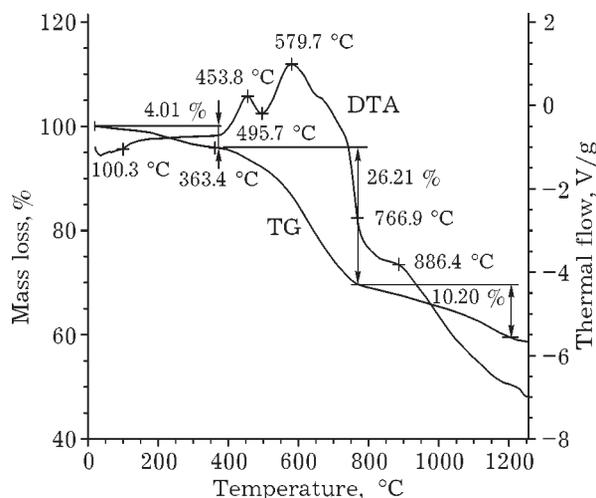


Fig. 1. Results of TGA and DTA of fluorine-containing wastes.

as by the evaporation and burnout of resinous substances concentrated on the dust. The loss of mass during these processes is almost 4 %. The exo effect occurring in the temperature interval of 360–750 °C is due to intense oxidation (burnout) of carbon. Reducing the mass herewith is approximately 26 %. The endo effect at 496 °C is caused by the process of the polymorphic transformation of cryolite. In the diapason of temperatures of 750–1200 °C, the mass loss and endo effect are associated with the process of pyrohydrolysis of fluorine-containing components of wastes (cryolite and chiolite). Reducing the mass at pyrohydrolysis is at the level of 11 %. The maximal overall mass loss during burning wastes of the aluminium industry up to 750 °C is 30–35 %, which is predominantly conditioned by the burnout of carbon and resinous substances, as well as desorption of accumulated gaseous admixtures. Judging by the absence of the endo-thermal effect in the studied interval of temperatures (up to 1200 °C), the liquid phase (meltdown the mineral component) is not formed [14].

Studies of the removal completeness of the carbon component

Results of experiments are presented in the form of the dependence of the content of carbon in the sample on the firing temperature (Fig. 2). It can be seen that oxidizing roasting passes most efficiently at 850–900 °C, the content of carbon at these temperatures in the sample is equal to 0.04 mass %. However, thermogravimetric studies showed that at these temperatures, the side process of pyrohydrolysis of fluorine-containing components that is accompanied by the loss of hydrogen fluoride is activated. In this regard, for the identification of the optimal temperature of the oxidizing roasting providing the minimal content of carbon at the maximal content of fluorine in the concentrate formed at the roasting, experiments on the determination of the content of fluorine in concentrates using the laboratory setup, were conducted (Fig. 3).

Cryolite-aluminous concentrate of the mass of 150 g obtained at a certain temperature of roasting, was uploaded into the chemical reactor (1) and sulphuric acid (State Standard GOST

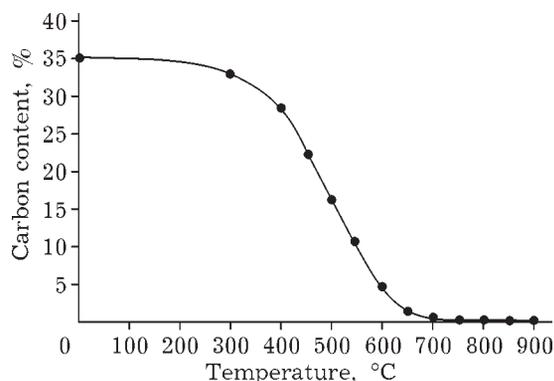


Fig. 2. Dependence of the content of carbon in the sample from the temperature of oxidative roasting.

4204-77) was poured with a 10% excess. The lid of the reactor was set, heated on the electric stove (6) up to 250 °C, the temperature was kept for 3 h; the temperature was measured using a thermocouple (3) (ChromelConstantan Thermocouple 2-3) and controlled using the microprocessor program regulator (7) (Aries TRM-1). The mixture in the reactor was constantly stirred using the electrical engine (2) with the paddle stirrer (4). Gases formed in the course of the decomposition of cryolite-aluminous concentrate were directed into the absorber (8), where they were absorbed by the soda solution (10) on the PTFE nozzle (9). The concentration of the

soda solution amounted to 20 g/L; the solution volume was 5 L. The constant irrigation of incoming gases and the nozzle was implemented using the pump (11) and sprayer (12). Unabsorbed gases went into the ventilation system bypassing the absorber. The duration of the experiment in total was 4 h: 3 h is heating up to 250 °C and sulphatisation at the set temperature; 1 h is cooling the mixture. The absorption of gases was conducted during the whole time of the experiment.

After the experiment, the sample of the volume of 50 mL was selected from the absorber and the concentration of the fluorine ion in the solution was determined by the potentiometric method using an ion selective electrode ELIS-131F and reference electrode ERE-10103/3.5 on GOST 4386-89. For this, the calibration of the fluorine-selective electrode by a solution of 0.1 M NaF was preliminarily conducted and then, the calibration curve of the dependence of EMF values from the concentration of sodium fluoride in the solution was constructed. The samples obtained at the temperatures of roasting of 450-900 °C were used. The experiments results are presented in Fig. 4. The yield value of fluorine ion were determined as the ratio of the practically identified amount of fluorine ion (m_{pr}) to the theoretically possi-

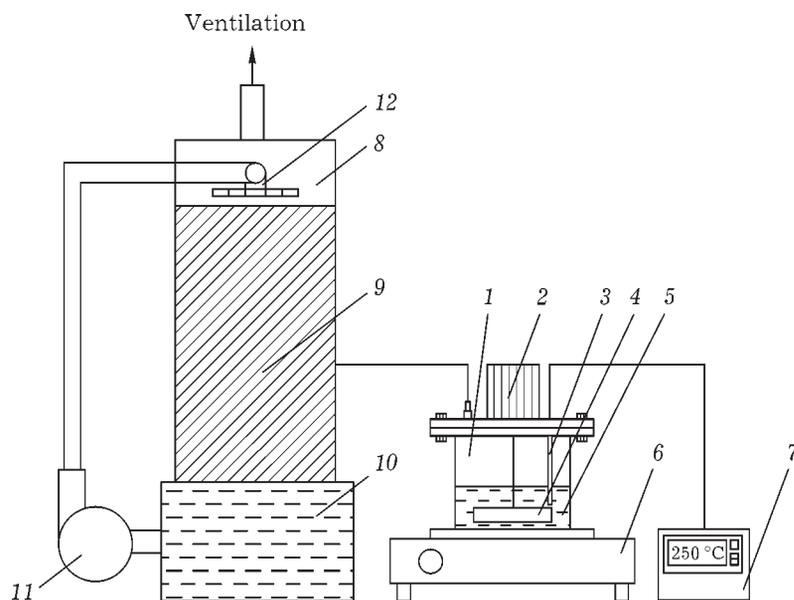


Fig. 3. Laboratory install of sulphatisation of cryolite-aluminous concentrate: 1 - chemical reactor; 2 - electrical engine; 3 - thermocouple; 4 - paddle stirrer; 5 - reaction mixture; 6 - electric hot plate; 7 - microprocessor program regulator of temperature; 8 - absorber; 9 - PTFE nozzle; 10 - reservoir with a soda solution; 11 - pump; 12 - sprayer.

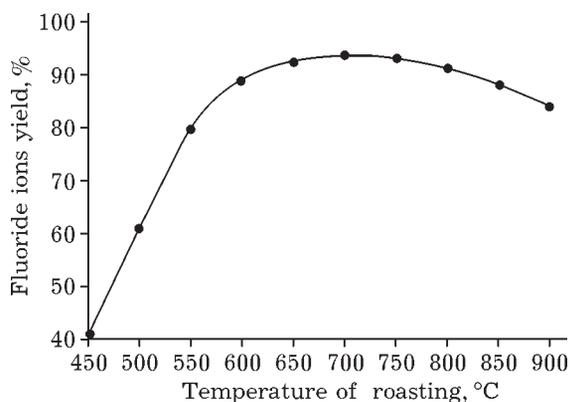


Fig. 4. Dependence of fluoride ions yield from temperature of oxidative roasting.

ble amount (m_{theor}), *i. e.* to the amount of fluorine ion that would have been contained in the sample in the absence of the process of pyrohydrolysis of fluorine-containing components: $\eta = m_{\text{pr}}/m_{\text{theor}} \cdot 100\%$.

When sulphuric acid decomposing concentrates obtained at the temperatures of 450–700 °C, the yield increase on fluoride ion is conditioned by the reduction of the negative effect of the carbon component due to its amount decrease. The yield reduction on fluorine ion when decomposing of concentrates obtained at 700–900 °C is associated with the activation of the process of pyrohydrolysis and, as a consequence, with the loss of fluorine ion when oxidizing roasting waste. The maximal yield on fluorine ion is observed at decomposing the cryolite alumina concentrate obtained at 700 °C and it is 93.79 %.

Thus, the optimal temperature of the preliminary oxidative roasting of fluorine-containing wastes is equal to 700 °C, roasting time is 1 h. The averaged phase composition of the obtained concentrate is (mass %): Na_3AlF_6 38.51, Al_2O_3 29.99, Na_2SO_4 20.44, $\text{Na}_5\text{Al}_3\text{F}_{14}$ 7.26, Fe_2O_3 1.60, SiO_2 1.66, C 0.54.

The dependence of the degree of reacting cryolite alumina concentrate with sulphuric acid from time is shown in Fig. 5. It can be seen that at the temperature of 200 °C (curve 1) on the section up to 14–15 min the active reacting occurred; further, the process slows down and practically stops. Sulphates formed cover cryolite by a crust and prevent the penetration of sulphuric acid to cryolite. In order to continue the reaction with an acceptable rate, increas-

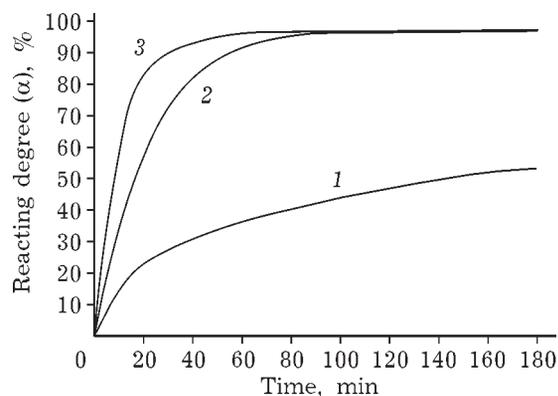


Fig. 5. Dependence of reacting degree (α) of concentrate from time. Process temperature (°C): 200 (1), 250 (2), 300 (3).

ing temperature and constant updating the surface of reacting are required. After 3 h, the experiment ended, the degree of reacting amounted to only 54 %. At the temperature of 250 °C (curve 2) at the section up to 27 min the active interaction is observed, further, the process slows down and after 40 min, transits into the diffusion area. The degree of reacting by the experiment end (3 h) amounted to 97 %. In the experiment at the temperature of 300 °C (curve 3), alongside with the reaction of the interaction of cryolite with sulphuric acid, the side reaction that is an intense evaporation of sulphuric acid occurs. Reacting was complete already in 30 min because of the shortage of the acid. The degree of reacting is 96 %.

This kind of dependence in the first 20 min of reacting is linearized most accurately according to the equation of the shrinking sphere [15, 16]. This equation describes the melting ball model and can be applied in processes of burning or dissolving, when a particle of the reacting compound reduces in the size when losing the mass. Usually, the equation of the shrinking sphere describes well processes proceeding in the kinetic area of reacting.

As a result of calculations and conversions, the apparent activation energy of the process ($E_a = 38.258$ kJ/mol) was determined and the equation of the dependence of the degree of reacting the cryolite-aluminous concentrate with sulphuric acid from time was deduced:

$$\alpha = 1 - [1 - 1.281 \exp(-38258/RT) \cdot t]^3$$

The sulphatisation process of the concentrate proceeds in the transition area of reacting and is limited by the chemical interaction

of reagents and diffusion of sulphuric acid from the volume to the surface of fluorine-containing particles.

Based on the resulting data in the static mode one can determine optimal conditions of the process that provide maximal opening on cryolite and minimal losses of the acid: the temperature is 240–260 °C, the duration is 2–3 h at intense stirring for updating the reacting surface of cryolite.

CONCLUSION

1. As a result of the thermodynamic calculation, the possibility of proceeding of the process of sulphatisation of wastes at a temperature, higher 236 °C was established.

2. The need of the introduction of the stage of preliminary oxidative roasting of wastes before the sulphuric acid decomposition was determined. Optimal conditions of roasting were determined: temperature is 700 °C, time is 1 h, and thickness of the sample is 1 cm.

3. As a result of kinetic studies, the apparent activation energy of the sulphatisation process ($E_a = 38.258$ kJ/mol) was determined and the equation of the dependence of the degree of reacting from time in the temperature interval of 200–350 °C was deduced. The sulphatisation process of the concentrate proceeds in the transition area of reacting.

4. Kinetic studies allowed establishing optimal conditions of the sulphuric acid decomposition of the cryolite-aluminous concentrate: the temperature was 250 °C (the degree of opening the concentrate was equal to 97 %), time

of reacting was 2.5–3 h, intense stirring for updating the reacting surface of cryolite.

5. The method of the preparation of hydrogen fluoride by the sulphuric acid decomposition of fluorine-containing wastes of the aluminium production with the stage of oxidative roasting to remove of carbon was proposed and studied.

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