AN APPROPRIATE METHOD FOR PROCESSING LOW-QUALITY FLUORITE CONCENTRATE AND FLUORINE-CONTAINING WASTE OF ALUMINUM PRODUCTION

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Abstract

The technology of reception cryolite and fluoride of aluminum from alumina-, fluorine containing aluminum production wastes. In the present article technology of reception cryolite and fluoride of aluminum from alumina and fluorine containing wastes of aluminum production is descried. The physical and chemical analysis is carried out optimum condition of process passing and defined compositions of raw materials and products.

Keywords

aluminum production, alumina and fluorine containing wastes, aluminum manufacture, acidic decomposition, fluoric acid, criolite and aluminum fluoride production.

1. Introduction

The primary consumption of extracted fluorspar, a natural mineral of fluorite, is in the production of fluorine compounds used for primary aluminum manufacturing. Modern methods for processing fluorine-bearing ores are based on the beneficiation of fluorite ores by flotation techniques, followed by decomposition with concentrated sulfuric acid [1, 2]. For the production of technical hydrofluoric acid, fluorspar with a CaF_2 content of not less than 92% is typically used, while the production of anhydrous hydrogen fluoride requires concentrate containing 96–97% of the main component.

In recent years, due to the growing demand for fluorine salts, the reserves of fluorite ore have become noticeably depleted. Moreover, in the aluminum industry, valuable fluorine-containing secondary raw materials accumulate, including gas-cleaning sludge, spent electrolyzer linings, and other by-products. The processing of these materials would not only reduce environmental impact but also enhance the efficiency of aluminum production by lowering emission-related costs.

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In previous studies, the sulfuric acid decomposition of solid alumina–fluorine-containing aluminum production wastes was investigated, and a technology for producing hydrofluoric acid from these wastes was developed [3–6].

Objects of the Study

At present, a plant for the production of cryolite and aluminum fluoride is operating in Yavan, Republic of Tajikistan (LLC TALCO Chemical), using fluorite concentrate supplied by LLC TALCO Fluorite as fluorine-containing raw material, in accordance with GOST 29220-91.

The process flow diagram of the plant provides for the implementation of a technology for producing hydrofluoric acid directly from fluorine-containing aluminum production wastes. Partial substitution of fluorite concentrate with such wastes not only reduces the production cost but also improves the environmental situation in the region. Due to the insufficient amount of calcium fluoride required for HF production, it is considered reasonable to carry out the sulfuric acid decomposition of fluorine- and alumina-containing wastes (washed sludge — sodium sulfates and carbonates) from the aluminum plant of State Unitary Enterprise TALCO in a mixture with fluorite concentrate from LLC TALCO Fluorite. The chemical composition of these materials, determined by standard chemical analysis, is presented in *Table 1*.

Table 1. Chemical composition of the batch materials used

Name	Component content, wt.%								
	Al_2O_3	Na_3AlF_6	NaF	MgF_2	C	Fe_2O_3	SiO_2	CaF_2	$CaCO_3$
Washed gas-cleaning sludge from the TALCO aluminum plant (State Unitary Enterprise)	9-15	20-27	1-3	0,6-0,9	16-30	1,0-1,6	0,3-0,6	0,7-1,0	-
Fluorite concentrate from LLC TALCO Fluorite	0,25	-	-	-	-	0,25	0,5	97,0	2,0

To determine the mineralogical composition of the raw materials used, X-ray phase analysis was carried out on a DRON-2.0 diffractometer with Cu_α radiation. The analysis results are presented in *Figure 1*.

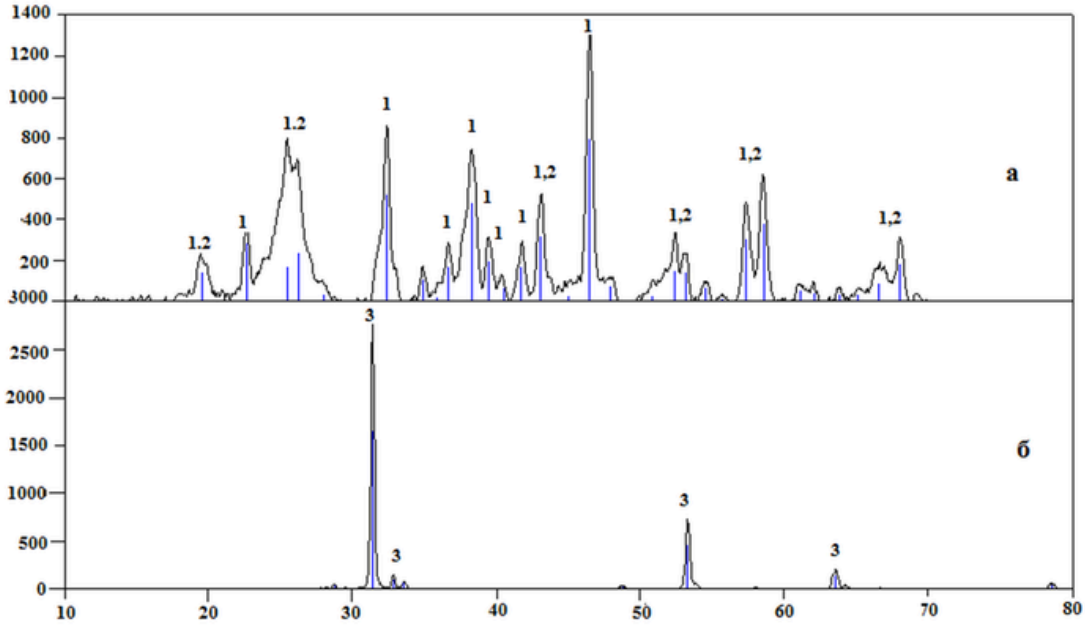

Fig. 1. X-ray diffraction patterns: (a) washed gas-cleaning sludge from the TALCO aluminum plant (State Unitary Enterprise) and (b) fluorite concentrate from LLC TALCO Fluorite. 1 – Na_3AlF_6 (cryolite); 2 – Al_2O_3; 3 – CaF_2 (fluorite).

Experimental Procedure for Acid Decomposition

The method for producing hydrogen fluoride is based on the decomposition of fluorine-containing wastes mixed with fluorite concentrate using sulfuric acid, according to the following reaction equations [1–8]:

$$2Na_3AlF_6+6H_2SO_4=3Na_2SO_4+Al_2(SO_4)_3+12HF, \quad (1)$$

$$Al_2O_3+3H_2SO_4=Al_2(SO_4)_3+3H_2O, \quad (2)$$

$$Fe_2O_3+3H_2SO_4=Fe_2(SO_4)_3+3H_2O, \quad (3)$$

$$2NaF+H_2SO_4=Na_2SO_4+2HF, \quad (4)$$

$$2AlF_3+3H_2SO_4=Al_2(SO_4)_3+6HF, \quad (5)$$

$$CaF_2+H_2SO_4=CaSO_4+2HF, \quad (6)$$

$$MgF_2+H_2SO_4=MgSO_4+2HF, \quad (7)$$

$$CaCO_3+H_2SO_4=CaSO_4+H_2O+CO_2. \quad (8)$$

The laboratory setup for acid decomposition of the charge, consisting of fluorine- and alumina-containing washed sludge from aluminum production and fluorite concentrate (*Figure 2*), is a sealed cylindrical steel vessel with a capacity of 800 mL. The vessel is internally lined with carbon–graphite material and equipped with a screw cap, which is internally lined with fluoroplastic.

To remove the product gas from the reactor, a fluoroplastic gas outlet tube is used, with one end immersed in a polyethylene vessel containing distilled water. As the gas passes through the water, gaseous HF is absorbed, forming hydrofluoric acid.

The presence of SiO_2 in the composition of the technogenic raw material leads to the formation of H_2SiF_6, which contaminates the hydrofluoric acid. To remove silica impurities, a certain amount of soda is added to the solution. As a result of the reaction

$$H_2SiF_6 + Na_2CO_3 = Na_2SiF_6\downarrow + CO_2 + H_2O \quad (9)$$

an insoluble sodium fluorosilicate is formed, which can further react with an excess of soda to yield sodium fluoride, silica, and carbon dioxide:

$$Na_2SiF_6 + 2Na_2CO_3 = 6NaF + SiO_2\downarrow + 2CO_2. \quad (10)$$

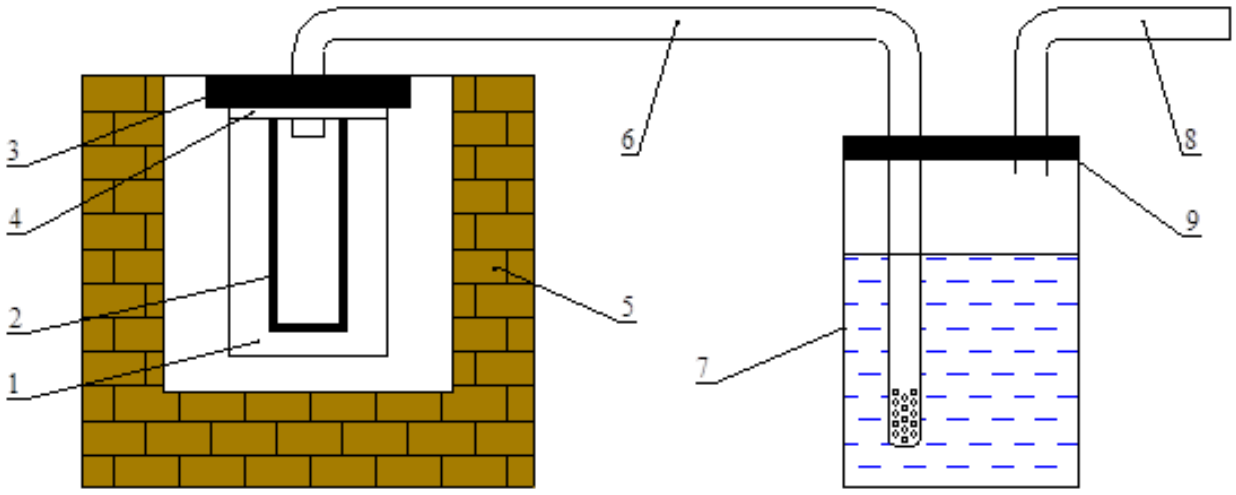

Figure 2. Schematic of the laboratory setup for acid decomposition of fluorine–alumina-containing technogenic raw material:

1 – steel vessel; 4 – fluoroplastic lining; 7 – polyethylene vessel with water;
2 – carbon lining; 5 – shaft muffle furnace; 8 – polyethylene tube for exhaust gas release;
3 – steel lid; 6 – fluoroplastic gas outlet tube; 9 – polyethylene stopper.

The purified hydrofluoric acid, containing only minor amounts of H_2SiF_6 and H_2SO_4, is directed to the production of cryolite in accordance with GOST 10561-80 or aluminum fluoride in accordance with GOST 19181-78.

A series of studies was carried out on the processing of technogenic raw materials from the aluminum plant by sulfuric acid decomposition of a charge consisting of fluorite and fluorine–alumina-containing technogenic materials in various mass ratios, with the aim of reducing the environmental burden in the vicinity of primary aluminum production facilities.

Table 2 presents the values of fluorine recovery into solution at different mass ratios of the components, depending on process parameters such as temperature, duration, sulfuric acid concentration, and solid-to-liquid ratio (S:L).

Table 2. Dependence of fluorine recovery from the charge under various parameters of acid decomposition

No.	Mass ratio of fluorite to technogenic raw material	Solid-to-liquid ratio (S:L)	Process duration, min	Temperature, °C	H_2SO_4 concentration, wt.%	Fluorine recovery, %
1	10:90	1,0:1,5	20	260-280	90-92	64,7
2	20:80	1,0:1,5	20	260-280	90-92	76,8
3	30:70	1,0:1,5	20	260-280	90-92	81,7
4	40:60	1,0:1,5	20	260-280	90-92	86,3
5	50:50	1,0:1,5	20	260-280	90-92	91,3
6	60:40	1,0:1,5	20	260-280	90-92	93,9
7	70:30	1,0:1,5	20	260-280	90-92	94,2
8	80:20	1,0:1,5	20	260-280	90-92	94,8
9	90:10	1,0:1,5	20	260-280	90-92	95,1
10	60:40	1,0:1,5	20	260-280	90-92	93,9
11	60:40	1,0:1,0	20	260-280	90-92	93,9
12	60:40	1,0:0,8	20	260-280	90-92	87,3
13	60:40	1,0:1,0	15	260-280	90-92	84,4
14	60:40	1,0:1,0	20	260-280	90-92	93,9
15	60:40	1,0:1,0	25	260-280	90-92	91,2
16	60:40	1,0:1,0	30	260-280	90-92	87,4
17	60:40	1,0:1,0	20	160-180	90-92	61,0
18	60:40	1,0:1,0	20	200	90-92	74,2
19	60:40	1,0:1,0	20	240-260	90-92	93,9опт
20	60:40	1,0:1,0	20	260-280	90-92	93,9
21	60:40	1,0:1,0	20	240-260	80	85,2
22	60:40	1,0:1,0	20	240-260	70	71,9

As can be seen from the data in *Table 2*, the optimal parameters for fluorine recovery, ensuring subsequent production of hydrofluoric acid from the proposed raw material mixture, are as follows: mass ratio of fluorite to technogenic raw material = 60:40; temperature = 240–260 °C; sulfuric acid concentration = 90–92 wt.%; solid-to-liquid ratio (S:L) = 1:1; and process duration = 20 min. Under these conditions, the degree of fluorine recovery from the charge reaches its maximum value of 93.9%.

The cake obtained after sulfuric acid decomposition consists mainly of aluminum, sodium, iron, and calcium sulfates, along with carbon. To extract the most valuable component—aluminum sulfate—the cake was subjected to aqueous treatment under the following conditions: solid-to-liquid ratio (S:L) = 1:5, temperature = 95 °C, and process duration = 30 min. Under these conditions, the degree of aluminum sulfate recovery (calculated as Al_2O_3) reached 97.7% (*Table 3*).

Table 3. Values of the main parameters of the aqueous leaching process

No.	Solid-to-liquid ratio (S:L)	Temperature, °C	Duration, min	Sulfate content in solution, g/dm³			Al_2O_3 recovery, %
				$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$	Na_2SO_4	
1	1:1	95	30	0,80	0,13	3,10	24,0
2	1:2	95	30	1,68	0,21	4,90	51,0
3	1:3	95	30	2,57	0,38	7,10	78,0
4	1:4	95	30	3,07	0,46	8,51	93,1
5	1:5	95	30	3,22	0,58	10,10	97,7
6	1:6	95	30	3,22	0,58	10,10	97,7
7	1:5	50	30	1,61	0,43	4,20	49,0
8	1:5	75	30	2,41	0,53	6,50	73,2
9	1:5	95	30	3,22	0,58	10,10	97,7
10	1:5	95	20	2,89	0,54	9,95	87,9
11	1:5	95	30	3,22	0,58	10,10	97,7опт
12	1:5	95	40	3,22	0,58	10,10	97,7

To extract aluminum hydroxide, the sulfate solution was treated with a sodium carbonate solution. As a result of the reactions

$$Al_2(SO_4)_3 + 3Na_2CO_3 + H_2O = 2Al(OH)_3\downarrow + Na_2SO_4 + 3CO_2 \quad (11)$$

and

$$Fe_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Fe(OH)_3\downarrow + 3Na_2SO_4 + 3CO_2, \quad (12)$$

aluminum and iron ions are precipitated in the form of hydroxides.

Table 4 presents the results on the precipitation degree of aluminum and iron hydroxides from sulfate solutions after treatment with a Na_2CO_3 solution.

As can be seen from *Table 4*, the most favorable conditions for the precipitation of aluminum hydroxide are: solution volume ratio = 0.4:1.0; sodium carbonate concentration = 1 g-eq/L; temperature = 25 °C; and process duration = 15 min. Under these conditions, the precipitation degree of aluminum hydroxide reaches 97.4%, while that of iron hydroxide reaches 98.8%.

The resulting precipitate of aluminum and iron hydroxides was dried at 100–120 °C to constant weight. Subsequently, in order to separate aluminum hydroxide (by obtaining sodium aluminate) from iron hydroxide, the material was treated for 5–15 min with sodium hydroxide solutions of varying concentrations and volume ratios at temperatures ranging

from 25 to 60 °C.

Table 4. Values of the main parameters of the precipitation process of aluminum and iron hydroxides from sulfate solutions

No.	Volume ratio of soda solution to sulfate solution	Concentration of soda solution, g-eq/L	Temperature, °C	Duration, min	Precipitation degree, %	
					$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$
1	0,2:1,0	1	25	15	64,6	71,2
2	0,3:1,0	1	25	15	82,3	89,0
3	0,35:1,0	1	25	15	92,1	94,1
4	0,4:1,0	1	25	15	97,9	98,3
5	0,5:1,0	1	25	15	98,6	98,5
6	0,4:1,0	0,7	25	15	91,0	88,3
7	0,4:1,0	0,8	25	15	94,3	94,7
8	0,4:1,0	1	25	15	97,4	98,3
9	0,4:1,0	1,2	25	15	98,7	98,8
10	0,4:1,0	1	25	15	97,4	98,3
11	0,4:1,0	1	40	15	97,4	98,8
12	0,4:1,0	1	60	15	94,2	98,8
13	0,4:1,0	1	25	10	91,2	93,0
14	0,4:1,0	1	25	15	97,4опт	98,3
15	0,4:1,0	1	25	20	97,4	98,8

Table 5. Aluminum recovery from the hydroxide precipitate during alkaline treatment of sulfate solution

No.	Solid-to-liquid ratio (S:L)	NaOH concentration, g/dm³	Temperature, °C	Duration, min	Al_2O_3 recovery, %
1	2:10	100	25	15	54,0
2	2:15	100	25	15	68,0
3	2:20	100	25	15	86,0
4	2:30	100	25	15	86,1
5	2:35	100	25	15	86,1
6	2:20	80	25	15	83,7
7	2:20	100	25	15	86,0
8	2:20	120	25	15	86,4
9	2:20	100	30	15	93,7
10	2:20	100	40	15	97,2
11	2:20	100	60	15	97,2
12	2:20	100	40	5	93,1
13		100	40	10	97,2опт
14	2:20	100	40	15	97,2

As shown in *Table 5*, the optimal parameters for the process are: solid-to-liquid ratio = 2:20 (2 g precipitate: 20 mL solution), NaOH concentration = 100 g/dm³, temperature = 40 °C, and process duration = 10 min. Under these conditions, the degree of aluminum recovery from the cake into solution (calculated as aluminum oxide) reaches 97.2%.

When treating the mixture of aluminum and iron hydroxide precipitates with sodium hydroxide solution, the following reaction may occur.

$$Al(OH)_3 + NaOH = NaAl(OH)_4 \quad (13)$$

The sodium aluminate solution was carbonized with gaseous CO_2 in order to obtain aluminum hydroxide. As shown in *Table 6*, the most efficient conditions for carbonization of the sodium aluminate solution are: temperature = 20 °C, CO_2 flow rate = 2 L/min, and process duration = 3 min. Under these conditions, the precipitation degree of aluminum hydroxide reaches 97.3%.

Table 6. Values of the main parameters of the carbonization process of sodium aluminate solution (per 100 mL of solution)

No.	Sodium aluminate content in solution, g/dm³	Duration, min	Temperature, °C	CO_2 flow rate, L/min	Precipitation degree of aluminum hydroxide, %
1	10,9	1	20	2	69,5
2	10,9	2	20	2	89,5
3	10,9	3	20	2	97,3
4	10,9	4	20	2	97,3
5	10,9	5	20	2	93,4
6	10,9	3	20	2	97,3
7	10,9	3	40	2	88,0
8	10,9	3	60	2	81,7
9	10,9	3	20	1,5	73,9
10	10,9	3	20	2	97,3опт
11	10,9	3	20	3	97,3

4. Conclusion

As a result of the experiments, the optimal conditions for sulfuric acid decomposition of a mixture of aluminum production gas-cleaning sludge and fluorite concentrate (containing 97.0 wt.% CaF_2) were determined: mass ratio of fluorite to technogenic raw material = 60:40; temperature = 240–260 °C; sulfuric acid concentration = 90–92 wt.%; solid-to-liquid ratio (S:L) = 1:1; and process duration = 20 min. Under these conditions, the degree of fluorine recovery from the charge reaches 93.9%. The remaining mixture of sulfates can be selectively separated to obtain individual chemical compounds that may be utilized in various industries [8].

The method developed on the basis of this research can be implemented without significant modifications using the existing equipment at LLC TALCO Chemical.

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