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Results of Carrying Out of Researches with Revealing of Technological Parameters of Processes of Recycling and Neutralization of the first and Second Cut of the Spent Pot Lining of Electrolyzers for Reception of Aluminum Fluoride

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Abstract

The spent pot lining (SPL) of aluminum electrolyzers contains significant amounts of carbon, refractories, fluorides. In addition, in the SPL contains metals, nitrides, carbides, hydroxides, carbonates, and free cyanides and iron cyanides.

The scales of technogenic impact of aluminum plants on the environment is determined by the technical level of production. Therefore, the solution of environmental problems is directly related to the technical improvement of existing production. The spent cathode lining of aluminum electrolyzers consists of carbonaceous and aluminosilicate parts, impregnated with electrolyte melt, metal and products of interaction of the listed components. In addition, the spent pot lining has the most complex material composition. Domestic aluminum plants, when dismantled, remove metallic aluminum, steel blooms and a peripheral layer of refractory bricks, and are sent to landfills of solid industrial waste for storage. To date, there has not been proposed a universal technical solution that would solve all the problems associated with spent lining.

Methods of analysis and instrumentation taking into account the features of the analyzed samples and in order to obtain the minimum error, it is expedient to use a combination of several methods for determining chemical and phase composition of the investigated substances. Also, the use of a set of methods in studies will allow us to determine the most effective analytical control scheme for process control in the practical implementation of technology.

Experiments with water and caustic are carried out in full. Experiments with sulfuric acid and aluminum sulfate are carried out at the zero level of factors. In the case of negative results (low level of fluoride extraction, high silica level) the work is suspended.

The obtained results of the experiments are processed with the derivation of conclusions and the determination of the possibility of patenting. Particular attention is paid to the content of cyanides and fluorides.

In the case of high cyanide content, additional studies are carried out to neutralize cyanides and use iron salts ($FeSO_4$ and others) or other methods.

Based on the data obtained, an environmental assessment of the application of hydrochemical methods is performed in comparison with thermal and flotation methods.

Keywords: aluminum electrolytic; lining waste; recycling, flotation.

INTRODUCTION

The spent pot lining (SPL) of aluminum electrolyzers contains significant amounts of carbon, refractories, fluorides. In addition, in the SPL contains metals, nitrides, carbides, hydroxides, carbonates, and free cyanides and iron cyanides. According smelters data, composition of SL varies within the following ranges (Table. 1).

Table 1: Fluctuations in the composition of PF

Component	Content, % wt.
Carbon	9,6 – 51,0
Sodium	7,0 – 20,0
Aluminum	4,7 – 22,1
Fluorine	6,0 – 18,9
Calcium	1,1 – 2,9
Lithium	0,3 – 1,1
Magnesium	0,3 – 0,9
Silicon	0,0 – 12,3
Iron	0,3 – 2,1
Sulfur	0,1 – 0,3
Cyanide	0,02 – 0,44

Program and methods of research trials

Table 2: Legend and abbreviations adopted in the text

FM	Flotation machine
LR	Laboratory Regulations
TD	Technological documentation
TP	Technological process
TO	Technological operation
TR	Process Requirements
NTD	Normative and technical documentation

GENERAL PROVISIONS

***Relevance and purpose of the work*.**

The scales of technogenic impact of aluminum plants on the environment is determined by the technical level of production. Therefore, the solution of environmental problems is directly related to the technical improvement of existing production. The spent cathode lining of aluminum electrolyzers consists of carbonaceous and aluminosilicate parts, impregnated with electrolyte melt, metal and products of interaction of the listed components. In addition, the spent pot lining has the most complex material composition. Domestic aluminum plants, when dismantled, remove metallic aluminum, steel blooms and a peripheral layer of refractory bricks, and are sent to landfills of solid industrial waste for storage. To date, there has not been proposed a universal technical solution that would solve all the problems associated with spent lining.

The purpose of the PM research trials is: To determine the optimum enrichment parameters for the fluorine-containing components of the spent lining, followed by sintering the enriched product with aluminum sulphate to produce aluminum fluoride and an aluminosilicate concentrate. The proposed equipment-technological schemes developed by RUSAL for research are presented in Figures 1 and 2.

Restrictions

The developed technology should be implemented using existing equipment. The cost of the produced aluminum fluoride should not exceed the cost of the purchased aluminum in terms of a valuable product.

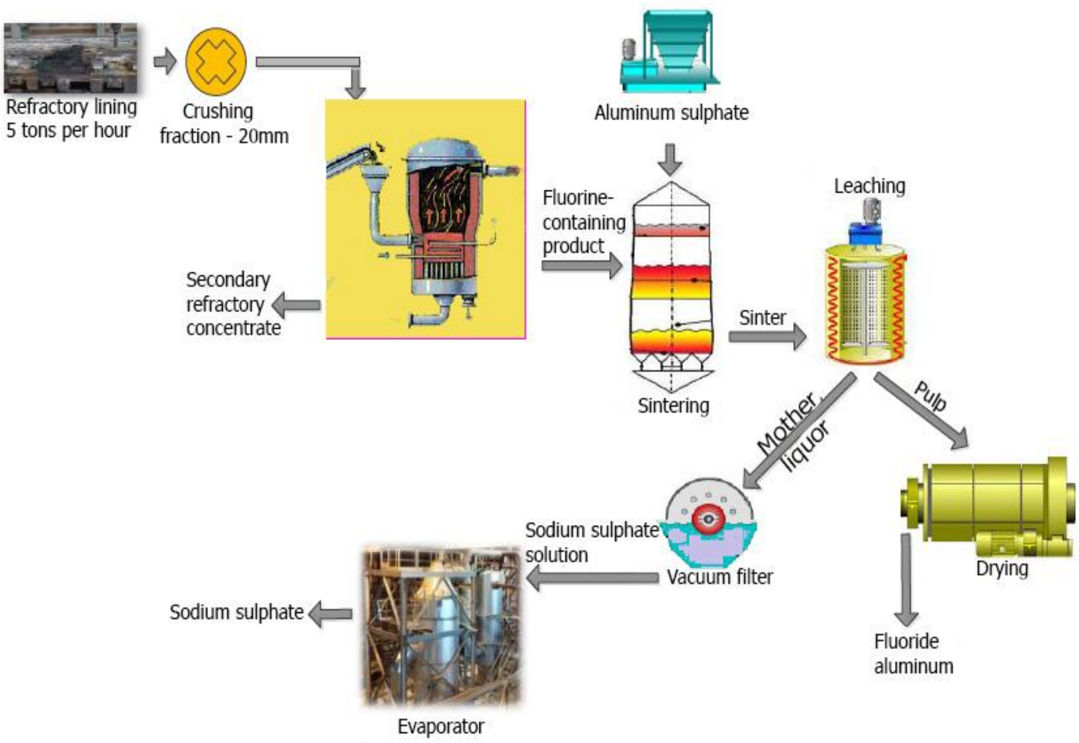

Figure 1: Perspective instrumentation technological scheme 1 of refractory lining processing with thermal enrichment.

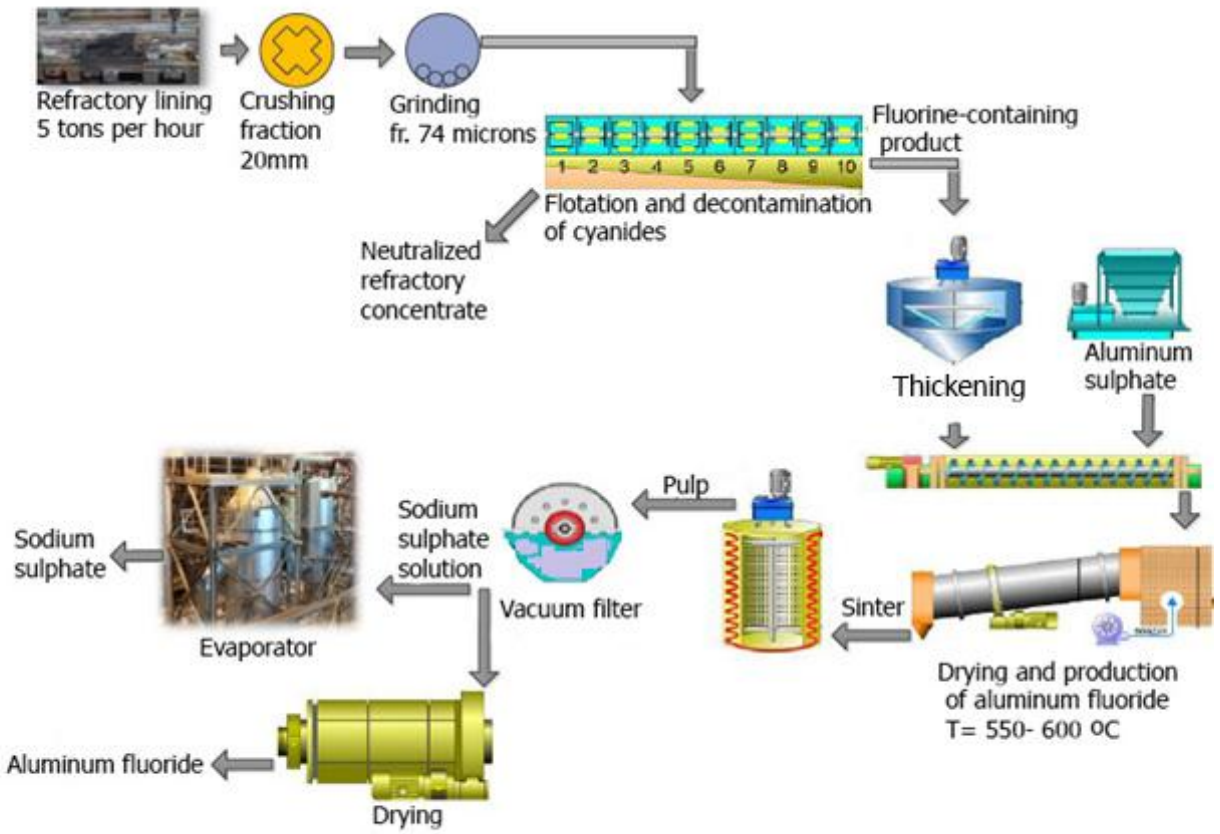

Figure 2: Perspective instrumentation technological scheme 2 of refractory lining processing with flotation enrichment.

Technological redevelopments requiring study

- Crushing;
- Grinding;
- Flotation;
- Thermal enrichment
- Sintering
- Water leaching
- Neutronization from cyanides and fluorides
- Development of industrial express methods for determination of elemental and phase composition

Analyzed materials

1) Spent refractory lining:
   - Elemental analysis of the solid part: C, F, Na, K, Al, Si, S, Fe, Ca, Mg
   - The amount and composition of the gaseous phase: V (m^3 / ton of lining); NH_3, CH_4, H_2S.
   - Phase analysis of fluorine-containing phases (NaF, Na_3AlF_6, CaF_2, AIF_3, SiF_4); Al_2O_3, SiO_2, CN-ion, AlC_3, AlN, CO_2, SO_4, Fe_2O_3, etc.
   - Granulometric analysis after crushing and grinding.
   - Index of capacity, hardness.
2) Flotation products (chamber and foam products), solid products of thermal enrichment and sintering):
   - Elemental analysis of the solid part: C, F, Na, K, Al, Si, S, Fe, Ca, Mg
   - The amount and composition of the gaseous phase: V (m^3 / ton of lining); NH_3, CH_4, H_2S.
   - Phase analysis of fluorine-containing phases (NaF, Na_3AlF_6, CaF_2, AlF_3, SiF_4); Al_2O_3, SiO_2, CN-ion, AlC_3, AlN, CO_2, SO_4, Fe_2O_3, etc.
3) Solutions after leaching, flotation, after washing (repulpation) of the sinter, thickening

   NaF, Na_2O, M_2O_3, SiO_2, CN-, SO4-, C (g-s / dm^3), L: S
4) Sludge of leaching and thickening: NaF, Na_2O, Al_2O_3, SiO_2, CN-, SO_4-, C
5) Aluminum fluoride: F, S, Na, Al, SO_4, C, Fe_2O_3, SiO_2, Moisture

6) Aluminosilicate product - elemental and phase composition, granulometric composition, CN-

7) Gases formed during grinding and leaching: CH_4, NH_3.

Methods of analysis and instrumentation

Taking into account the features of the analyzed samples and in order to obtain the minimum error, it is expedient to use a combination of several methods for determining chemical and phase composition of the investigated substances. Also, the use of a set of methods in studies will allow us to determine the most effective analytical control scheme for process control in the practical implementation of technology.

In the table 3. information on methods and instrumentation for conducting research is presented.

Table 3: Methodical and instrumental support of the experiment

№	Research object	Methods	Equipment	Note
1.1	Electronic microscopy	GOST R 8.635-2007	JEOL JIB-Z4500	1. Electron-optical system (EOS). Resolution: 2.5 nm (with accelerating voltage: 30 kV, high vacuum mode) 4.0 nm (with accelerating voltage: 30 kV, low-vacuum mode: 1 Pa) 2. Ion-optical system (IOS). Resolution: 5 nm (with accelerating voltage: 30 kV, working distance: 24 mm).
1.2	Spectrometry		Bruker S8 TIGER	
1.3	Titration	ISO 1693/GOST 10561-80		Determination of fluorine by the bulk fluorochloride method
1.4	Phase analysis	GOST 16865-79	X-ray diffractometer SHIMADZU XRD-7000	1. 1. X-ray tube: Max. Power: 3kW 2. 2. Generator: 3. - Max. Voltage 60kV 4. - Max. Current strength 80mA 5. 3. Goniometer: 6. Rotation speed: 1000 ° / min. Shooting speed 0.1-50 ° Minimum angle step 9: 0.0001 ° Angular repeatability 0.0002 °
2	Crushing	Operation manual JD-6	Jaw Crusher JD-6	
3	Grinding	Operation manual DE-65	Disk eraser DE-65	

Table 4: Research program

Name of event	Period	Experiment scope
Lining sampling	5 weeks	50kg
Preparation of samples, sorting of samples	5 weeks	20kg
Crushing of selected samples	4 weeks	20kg
Grinding of selected samples	2 weeks	20kg
Determination of element composition	15.09.	10 samples
Determination of the phase composition	1 week	10 samples
Research studies on possible processes of extraction of fluoride compounds from the refractory part of spent lining	4 weeks	
Development of the experiment matrix and methods for studying the processes of extraction of fluoride compounds the refractory part of spent lining:	1 week	
Water leaching	1 week	
Flotation	1 week	
Heat treatment	1 week	
Processing of results. Preparing of report	5 weeks	

FLOTATION

Purpose: extraction of the solid phase containing fluorine from the aluminosilicate matrix of the refractory lining with an efficiency of at least 90% using flotation

Equipment: LU-2 (FM)

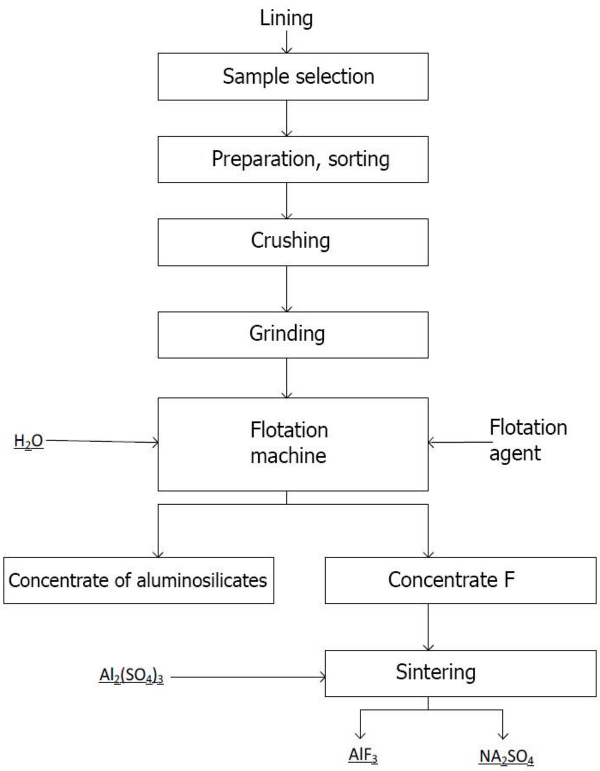

Figure 3: Functional scheme

The first stage of work: selection of representative samples of lining.

The second stage of work: preparation and sorting of samples for crushing

The third stage of work: crushing is performed on a jaw crusher (JD-6), designed for crushing brittle loose materials of various strength and hardness, according to the operating manual JD-6

The fourth stage of work: abrasion is performed on disk eraser (DE-65), intended for grinding brittle materials of different strength and hardness to finely dispersed state, according to the operating manual DE-65.

The fifth stage of work: flotation on the impeller flotation machine. The general view of the impeller flotation machine is shown in Fig. 4.

Figure 4: Impeller flotation machine

Before starting work, it is required to check the cleanliness (absence of contaminants or other substances) in the main capacity of the flotation machine and its integrity.

The order of the work: load the pre-conditioned raw material (pulp) preconditioned with reagents into the flotation machine. The ratio of the number of reagents to the raw material is taken according to the experimental matrix given in Table 5. Pour the pulp into the flotation machine to a level that is below the drain threshold. Prepare a container for the output of the resulting foam product. Switch on the pump and mix the pulp in the flotation machine with the tap closed on the air tube for 10-15 minutes. Make sure that air is sucked into the aerator-ejector. If there is no air in the air tube, then blow the aerator-ejector through the air connection with a compressor. Through the air tube, apply an emulsion of a foaming agent (pine oil or OPSB or any other foaming agent giving a finely bubbled, watered foam) in the desired ratio according to the experiment matrix.

The process of the main flotation and the release of the foam product into the previously prepared separate container will begin. The basic flotation is carried out from 5 to 45 minutes. During flotation, it is necessary to control the height of the foam layer in the flotation machine in front of the drain threshold. The height of the foam layer should be at least 20 mm and be controlled through the transparent wall of the flotation machine.

The sixth stage of the work: the chemical analysis of the chamber product and foam product. According to the results of the analysis, a possible control flotation of the chamber product is made in order to achieve the required concentration of aluminosilicates and purification of the foam product in order to achieve the required concentration of fluorine

To work at the stand, persons who have an engineering education and who have previously been acquainted with the device and the principle of operation of the stand equipment, who have been instructed in Safety engineering, are allowed.

Table 5. (The range of variation of the parameters in the experiment)

№	1	2	3	N
S:L	1:05	1:06	1:07	1:15
Flotation time (min.)	5	10	15	45
Flotation agent kerosene (kg / t)	1	1,2	1,4	3
Flotation agent sodium oleate (kg / t)	1	1,2	1,4	3
Foaming agent pine oil (mg / l)	10	15	20	40
Analysis of raw material (by various methods)				
Analysis of the chamber product (by various methods)				
Analysis of the foam product (by various methods)				

Note to Table 5:

The key criterion for selecting parameters is the maximum yield of fluorine from the aluminosilicate matrix of the feedstock. Control of fluoride yield is carried out by analyzing chamber and foam products, after flotation.

The first series of experiments (revealing the maximum effective S: L ratio):

The S: L ratio is a free parameter

Flotation time - fixed - 15 minutes

Flotation agent kerosene (kg / t) - the parameter value is fixed - 2 kg / t

Flotation agent sodium oleate (kg / t) - the parameter value is fixed - 2 kg / t

Foaming agent pine oil (mg / l) - the parameter value is fixed - 20 mg / l

The second series of experiments (revealing the most effective flotation time):

Flotation time - free parameter

The S: L ratio is the parameter chosen from the first series of experiments

Flotation agent kerosene (kg / t) - the parameter value is fixed - 2 kg / t

Flotation agent sodium oleate (kg / t) - the parameter value is fixed - 2 kg / t

Foaming agent pine oil (mg / l) - the parameter value is fixed - 20 mg / l

The third series of experiments (revealing the most effective amount of flotation agent (kerosene)):

Flotation time - the parameter is selected from the second series of experiments

The S: L ratio is the parameter chosen from the first series of experiments

Flotation agent kerosene (kg / t) - free parameter

Flotation agent sodium oleate (kg / t) - the parameter value is fixed - 2 kg / t

Foaming agent pine oil (mg / l) - the parameter value is fixed - 20 mg / l

The fourth series of experiments (revealing the most effective amount of flotation agent (sodium oleate)):

Flotation time - the parameter is selected from the second series of experiments

The S: L ratio is chosen from the first series of experiments

Flotation agent kerosene (kg / t) - selected from the third series of experiments

Flotation agent sodium oleate (kg / t) - free parameter

Foaming agent pine oil (mg / l) - the parameter value is fixed - 20 mg / l

The fifth series of experiments (the detection of the maximum effective amount of a foaming agent (pine oil)):

Flotation time - selected from the second series of experiments

The S: L ratio is chosen from the first series of experiments

Flotation agent kerosene (kg / t) - selected from the third series of experiments

Flotation agent sodium oleate (kg / t) - selected from the fourth series of experiments

Foaming agent pine oil (mg / l) - free parameter

Five series of experiments will allow to choose the most optimal value of the parameters of constituents of the reagents of the flotation process, which will maximize the yield of fluorine from the aluminosilicate matrix of the feedstock.

Sequence of experiments

Experiments with water and caustic are carried out in full. Experiments with sulfuric acid and aluminum sulfate are carried out at the zero level of factors. In the case of negative results (low level of fluoride extraction, high silica level) the work is suspended.

Analysis of results, environmental assessment, continuation of work

The obtained results of the experiments are processed with the derivation of conclusions and the determination of the possibility of patenting. Particular attention is paid to the content of cyanides and fluorides.

In the case of high cyanide content, additional studies are carried out to neutralize cyanides and use iron salts ($FeSO_4$ and others) or other methods.

Based on the data obtained, an environmental assessment of the application of hydrochemical methods is performed in comparison with thermal and flotation methods.

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