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Review of Methods of Waste Lining Processing from Aluminum Electrolyzers

Kondratiev V.V.[1], Rzhechitskiy E.P.[2], Gorovoy V.O.[3], Shahray S.G.[4] and Karlina A.I.[5]

[1] *Kondratiev Viktor Viktorovich, Irkutsk National Research Technical University, Institute of physics and technology, Head of Department of innovative technologies, Ph.D.,*
E-mail: kvv@istu.edu

[2] *Rzhechitskiy Edvard Petrovich, Irkutsk National Research Technical University, Institute of physics and technology, senior researcher at the department of innovative technologies, Ph.D.,*
E-mail: epr523@gmail.com

[3] *Gorovoy Valeriy Olegovich, aspirant, engineer of scientific research Department, Irkutsk National Research Technical University, E-mail: vog@istu.edu*

[4] *Shahray Sergey Georgievich, Siberian Federal University, Ph.D., Associate Professor,*
E-mail: shahrai56@mail.ru

[5] *Karlina Antonina Igorevna, Irkutsk National Research Technical University, Deputy head of management of scientific activities,*
E-mail: karlinat@mail.ru

[1-3, 5]*Irkutsk National Research Technical University, 83, Lermontov street, 664074, Irkutsk, Russia.*
[4]*Siberian Federal University, 79 Svobodny av, 660041, Krasnoyarsk, Russia.*

Abstract

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

The presence of cyanide refers the SL to toxic wastes, warehousing and storage of which is possible only in specially engineered landfills, in compliance with the precautionary measures to prevent ingress of cyanide and fluoride in the environment, including in water bodies. However, construction of specialized polygons requires significant capital costs, which in turn is an incentive to develop the technical solutions and technologies for the disposal and recycling of the SL, and a list of components, which can be returned to production, makes the development perspectives of these technologies economically attractive.

SL processing technology developed IrNRTU can be implemented on existing shops equipment of fluoride salts production of aluminum smelters or on alumina production equipment or the equipment of chemical - metallurgical plants. SL technique involves its grinding, leaching with aqueous solutions of reagents of alkaline and acid nature, separation of liquid and solid phases of the pulp, the solution processing with releasing of fluoride product. Grinding and leaching are carried out in explosion-proof equipment. When grinding in an aqueous medium it is maintained at a pH of 6-8 and the temperature to 60ºC, then the pulp is processed by caustic alkali solution at a temperature of 80-100 ºC for 4-10 hours and the pH is maintained at 10-12. After phase separation solution treatment is carried out with an acids or salts. SL is grounded to a particle size of 50-200 microns. The solution processing may be carried out by aluminum sulfate in the presence of (or - without any) sulfuric acid, hydrofluoric acid or washing waters after purifying gases, containing fluorine, water.

The developed in IRNRTU technology enables the SL treatment to produce high quality demanded product - cryolite with reduced sodium content and the possibility of the solid phase recycling onto energy products.

Keywords: aluminum electrolytic; lining waste; recycling; aluminum fluoride.

The spent lining (SL) of aluminum electrolyzers contains significant amounts of carbon, refractories, fluorides. In addition, in the SL 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

The presence of cyanide refers the SL to toxic wastes, warehousing and storage of which is possible only in specially engineered landfills, in compliance with the precautionary measures to prevent ingress of cyanide and fluoride in the environment, including in water bodies. However, construction of specialized polygons requires significant capital costs, which in turn is an incentive to develop the technical solutions and technologies for the disposal and recycling of the SL, and a list of components, which can be returned to production, makes the development perspectives of these technologies economically attractive.

At this point in the global aluminum industry has developed a number of chemical and thermal processing technologies of SL recycling from aluminum electrolyzers. This article provides a brief overview of some of them.

THERMAL METHODS OF SL NEUTRALIZATION

Reynolds's technology [1], developed in the late 80's - early 90-ies the last century, includes a heat treatment for the destruction of cyanides in combination with a fluoride transfer to insoluble calcium fluoride CaF_2 (Fig. 1).

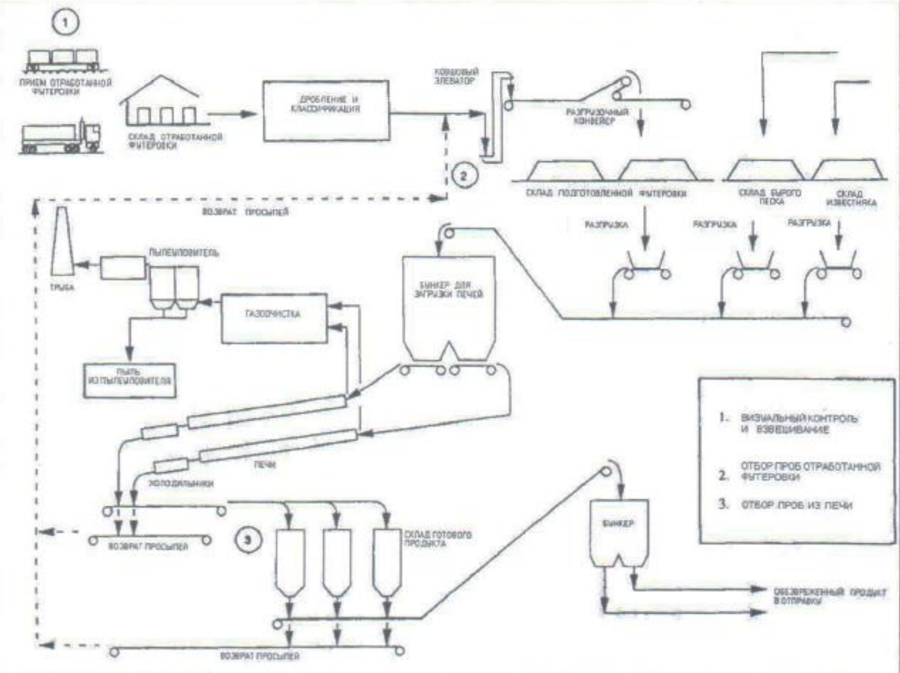

Figure 1. Technological diagram of the SL recycling by the Reynolds method

The technology is simple and flexible enough that allows to process a wide range of SL formulations. Incoming SL is milled to a particle size of 9.5 mm, charged with limestone (calcium source for the CaF_2 formation) and an anti-agglomerating additive (sand) and is fed into the rotary kiln, fired by natural gas. Furnace temperature 650 - 815^{0}C. Charge composition, temperature and residence time in the furnace is controlled due to the SL composition. The sinter, whose volume exceeds in 2.5-3 times the amount of recycled wastes, enters the siloses and is stored there until it is determined the residual content of CN and F, allowing to take them on the polygon. Thus, the obtained sinter is not toxic waste, but the potential raw material for commercial sale. However, the tightening of environmental regulations has led to the fact that since 1997, this type of waste is re-recognized as toxic. [2]

Vortec's technology [2] provides recycling of the SL to the glass by rapid heating in a two-stage reactor to 1200^{0}C with the introduction of glass-forming additives. The first step is the oxidation of organic material and preheating up to the melting temperature, on the second stage in a cyclone reactor there are reactions to produce liquid glass. Then liquid glass is adjusted to the desired state and sent for recycling in the form of semi-finished product. Vortec process provides 100% recycling of SL, which is pre-crushed to -0.42 mm size in the autogenous mill. Ground material from the mill is caught by the air stream and directed to the qualifier. The mill is equipped with a heater to remove moisture from the material.

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It also accumulates accidentally caught aluminum and silicon carbide, which is removed periodically. The prepared raw is mixed in a mixer with limestone and quartz sand to obtain a homogeneous mixture. Melting cyclone system consists of a periodic feed device, centrifugal countercurrent reactor, cyclone glassmaking device, the separator tank, the heat exchanger and a product transport system (Figure 2).

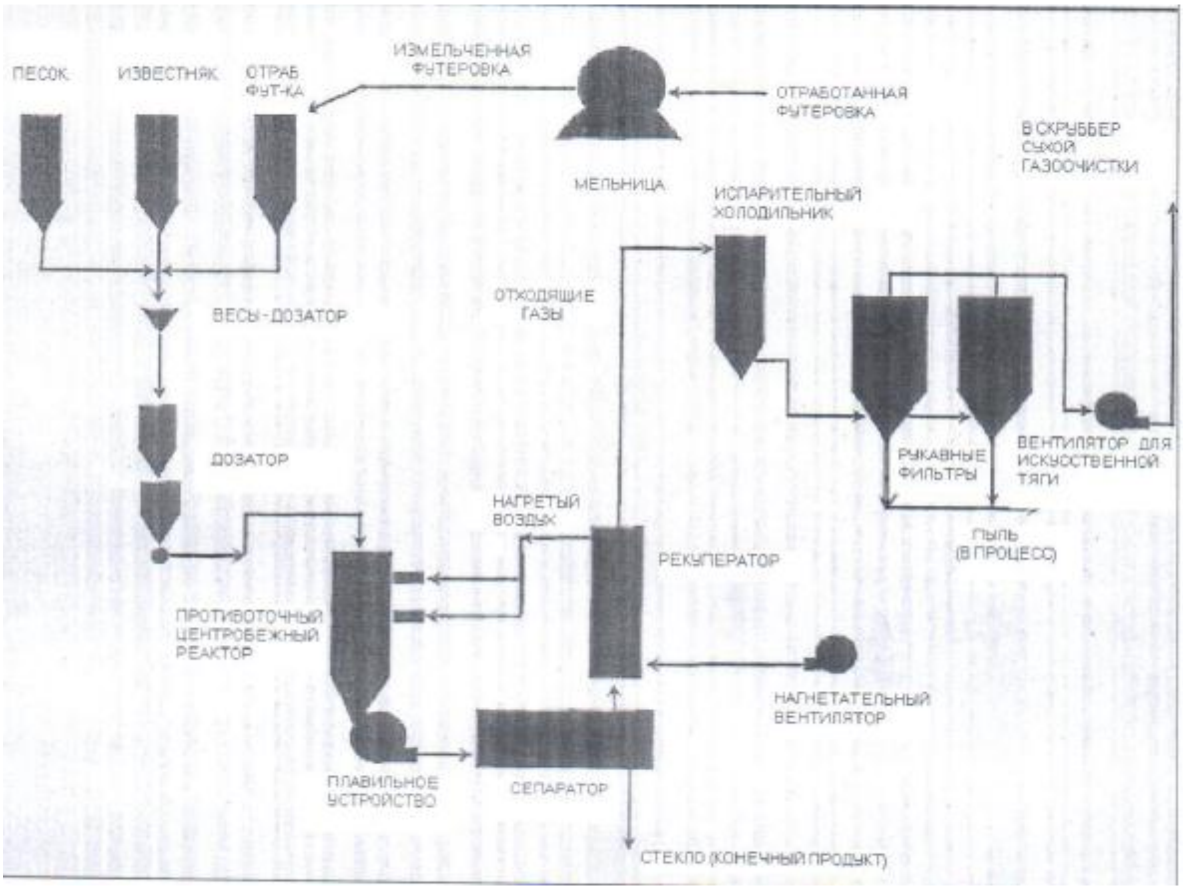

Figure 2. Diagram of SL processing by the Vortec method

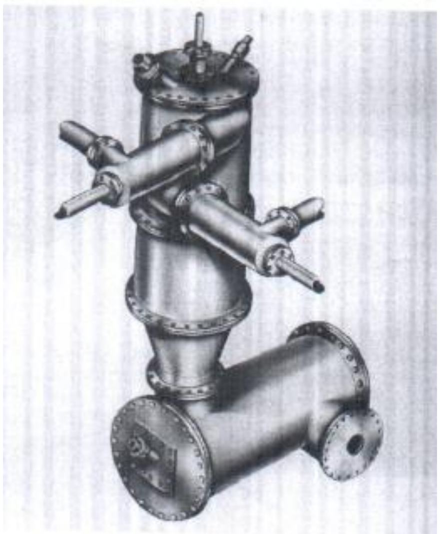

Figure 3. Reactor

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The raw material is supplied continuously into the reactor (Fig. 3). There also hot air is served from the heat exchanger and fuel (natural gas). In the reactor, it is created favorable conditions for the oxidation of inorganic substances, presented in the raw. The remaining raw material melts and flows down the reactor walls. To optimize the melting conditions, the temperature adjustment and the oxygen concentration are provided. Hot gases and the melt from the reactor are received in glassmaking device, where the melting process is completed. Here comes the initial separation of the liquid and gaseous phases. Final separation takes place in the separating tank, at that the hot gases are directed to the recuperator, and the melt goes in the quench tank, which is filled with water. [2]

Peciney Company in 1991 - 1992 developed a thermal process using a boiler for combustion of the vortex type. Cyanides thermally destroy in the vortex of hot air, rotating at supersonic speed with over 98% of fluorides are converted to CaF_2 by reaction with calcium sulfate or natural gypsum. SL, grounded to a particle size of 2.5 mm, passes through a furnace reactor for only 5 seconds, and carbon is not burn. Since 1997, the SL processing products are used on one of the cement plants on the north of France. [3-4]

Ausmelt method (Fig. 4) is as follows. SL, milled to approximately 25 mm fraction is treated in a batch furnace, that operate on a natural gas, with stirring the molten slag at a temperature 1300^{0}C. [5]

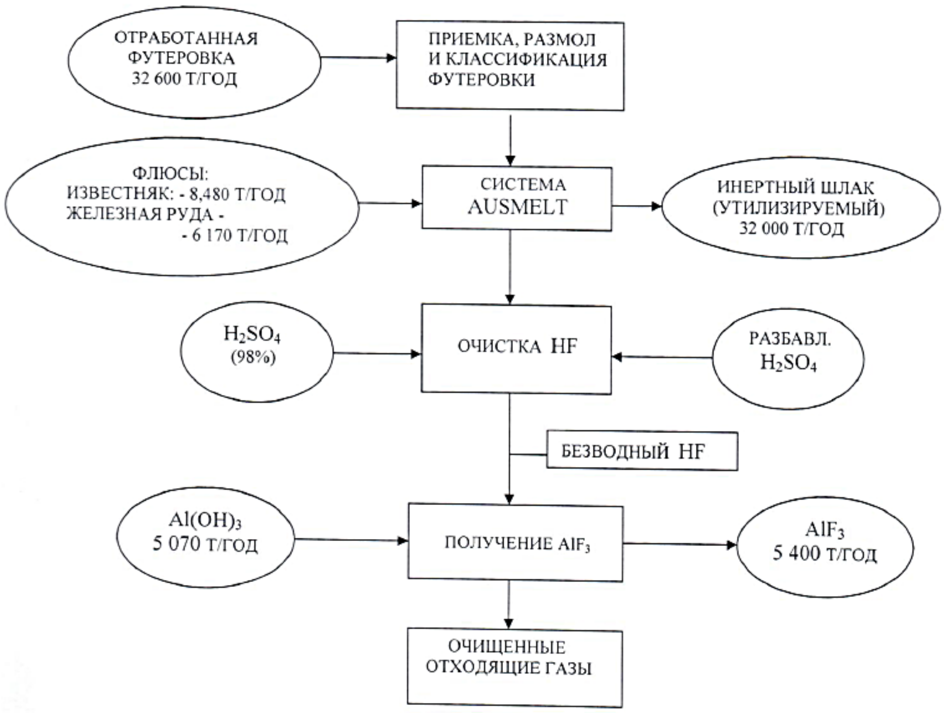

Figure 4. Scheme of Ausmelt process

Toxic components are destroyed, a stable slag is formed, which can be used for road pavement or as a cement filler. The gases from the furnace are cooled, filtered and fed to the fluorine recovery system where the aluminum fluoride is get. Sodium fluoride is separated and fed in aluminum production.

When processing in the fluidized bed, SL is subjected to two stage treatment at 650 - 900^{0}C with addition of calcium sulfate and magnesium sulfate. In the first step environment is slightly reducing, it goes to a second process at an oxygen content of more than 2%. Thus, it is obtained calcium fluoride and magnesium fluoride. Alumina is added to highly siliceous waste.

The firm Elkem [6] developed a method of SL processing in melting electrothermal furnaces of closed type. SL together with silica is melted at 1300 - 1700^{0}C. Oxidant is added in the furnace to the oxidation of carbon, metals, carbides contained in SL. Calcium oxide is also added in the furnace in a necessary amount to react all the fluorine compounds, contained in the lining to form calcium fluoride. Slag from calcium aluminate or calcium aluminate silicate, sometimes with a metallic phase, is poured from the furnace and cooled to blocks or granules. Molten slag is treated with steam to produce hydrogen fluoride, which was subsequently converted into aluminum fluoride and returns to the production of aluminum.

When processing by plasma, SL is heated to a temperature not lower 1000^{0}C. As a result, the carbon passes to a gaseous state - carbon monoxide, hydrocarbons or carbon dioxide. The inorganic material is melted with forming of slag. Fluorine compounds melt, evaporate or convert to gaseous hydrogen fluoride. Cyanides are destroyed, and other components, including sulfur compounds, melt or become gaseous. As a result, the non-toxic slag is received from SL with less weight and volume, hardly containing cyanides, leach resistant and safe, which can be found commercial implementation.

CHEMICAL METHODS OF SL NEUTRALIZATION

The process of the company Alcan [7]. C, F, Na and Al, containing in the SL, which are usually lost in the process of cyanide decomposition and leaching of soluble fluorine compounds before disposal, may be recovered in various mineral forms for reuse in the aluminum production. Alcan technology uses a number of proven methods for the cyanides destruction at full utilization of the chemical elements, which allows to reduce waste to zero. Caustic leaching technology of low concentration and lime processing consists of five steps:

- Dismantling and crushing of SL to -20 mm;
- Grinding and classification;
- Recovery and leaching SL by steam at 350^0C;
- The destruction of cyanide and sodium fluoride crystallization from leachate products;
- Causticizing of fluoride solution.

Fluoride can be converted into feldspar, while the sodium and aluminum are recovered in the form of sodium aluminate and caustic used in the Bayer process. The remaining components - the remains of the linnig and the coal fraction comply with environmental legislation.

Alcoa Company [8] developed a method of SL processing with an aqueous solution of aluminum sulfate and sulfuric acid with more than 90% recovery of fluorides. The method is based on the following reaction:

$$2Na_3AlF_6 + Al_2(SO_4)_3 = 4AlF_3 + 3Na_2SO_4$$

SL is crushed to 11 mm and grounded in a ball mill to 100 microns, then leached with a solution of 14 g / l NaOH to extract about 55% of fluorine. Part of the resulting solution is sent directly to the deposition of AlF_3, and the rest of the solution used for the wet grinding of fresh lining waste. The resulting slurry is subjected to acid decomposition by $Al_2(SO_4)_3/H_2SO_4$ mixture for extraction of remaining fluorine, is filtered with a graphite separation residue, and after removal of iron by extraction is also sent to the deposition of AlF_3. In this method, one can obtain 92% AlF_3 and graphite with commercial quality. In addition, by the electrolysis of Na_2SO_4 solution, sodium can be disposed in the form of a 50% NaOH caustic solution, usable in the production of alumina by the Bayer process.

THE EXPERIENCE OF THE DOMESTIC INDUSTRY IN THE FIELD OF SL PROCESSING

In the USSR in the 80-ies we were introduced hydrochemical and thermal processing methods using SL in steel production, and a method using SL during sintering of alumina-batch on alumina plant.

In Achinsk AGK it was processed 41 - 42 thousand tons / year of SL and produced 6,2 – 6,4 tons / year of secondary cryolite. Coal sinter from leaching was laminated in the raw mixture of sintering process of alumina production. Due to the decline in demand for secondary cryolite, high fluorine content in the soda products and sludge waters, in 1986, it was decided to terminate the processing of the SL on AGK. This technology does not solve the problem of cyanides, which had accumulated in the liquid phase of secondary cryolite production.

For many years, most of the SL smelters processed at Mariupol (Zhdanov) Metallurgical Plant, where a special crushing and sorting line for SL was built in open-hearth steel production.

After the collapse of the Soviet Union, due to the sharp rise in w / e rates, haul of SL from Russian plants, especially from Siberian, became unprofitable.

With the 90-ies, we began to apply SL at the West Siberian Metallurgical Combine (Novokuznetsk). Crushing of SL to a particle size of 20 - 80 mm arranged at the Krasnoyarsk Aluminum Plant. It was the intention of the whole SL processing from all Siberian smelters. But this raises a number of problems:

- The need for disposal of 20 mm fraction, the amount of which is 50 - 60% by weight of the SL, entrained in the processing;
- Explosiveness of SL crushing process;
- Environmental hazard of crushing processes, transportation and use of SL due to the presence in it of fluoride, alkalis and cyanides.

Since 1981, the Bogoslovsky Aluminum Plant recycled the wastes of dismantled cathode blocks of own electrolysis production in the sintering furnaces of alumina-containing charge in the amount of about 2000 tons / year (1% of the total sintering charge).

In the 90-ies, VAMI conducted industrial tests on the use of the SL fine fraction (-20 mm) in electro-melting production and the production of ceramic wall brick, confirmed the possibility of the SL use in these industries. Given the increasing demands from environmentalists, the Institute developed:

- Hydro-chemical method for processing of wastes, comprising grinding with subsequent alkali treatment in an autoclave at 180 - 200^0C. The method allows us to decompose cyanides, remove and utilize fluoride, sodium and aluminum and get an environmentally friendly solid residue is low in fluoride;

- Thermal processing method including thermal processing of produced wastes in special furnace units at certain temperatures with decomposition of cyanides, capture fluorine compounds in the gas cleaning system and its utilization, yield pure carbonaceous or other material.

SL processing technology developed IrNRTU can be implemented on existing shops equipment of fluoride salts production of aluminum smelters or on alumina production equipment (Fig. 5) or the equipment of chemical - metallurgical plants (Fig. 6). [9-10]

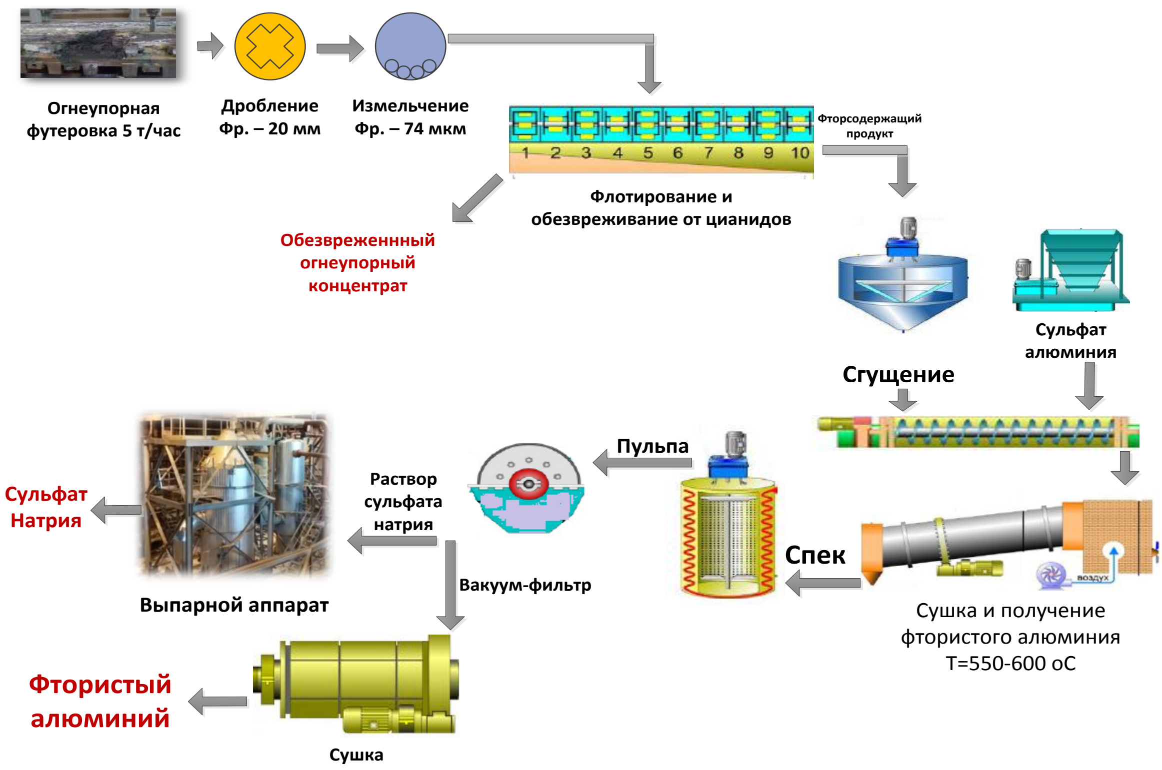

Figure 5. Hardware and technological scheme of SL processing on shops equipment of fluoride salts production of aluminum smelters

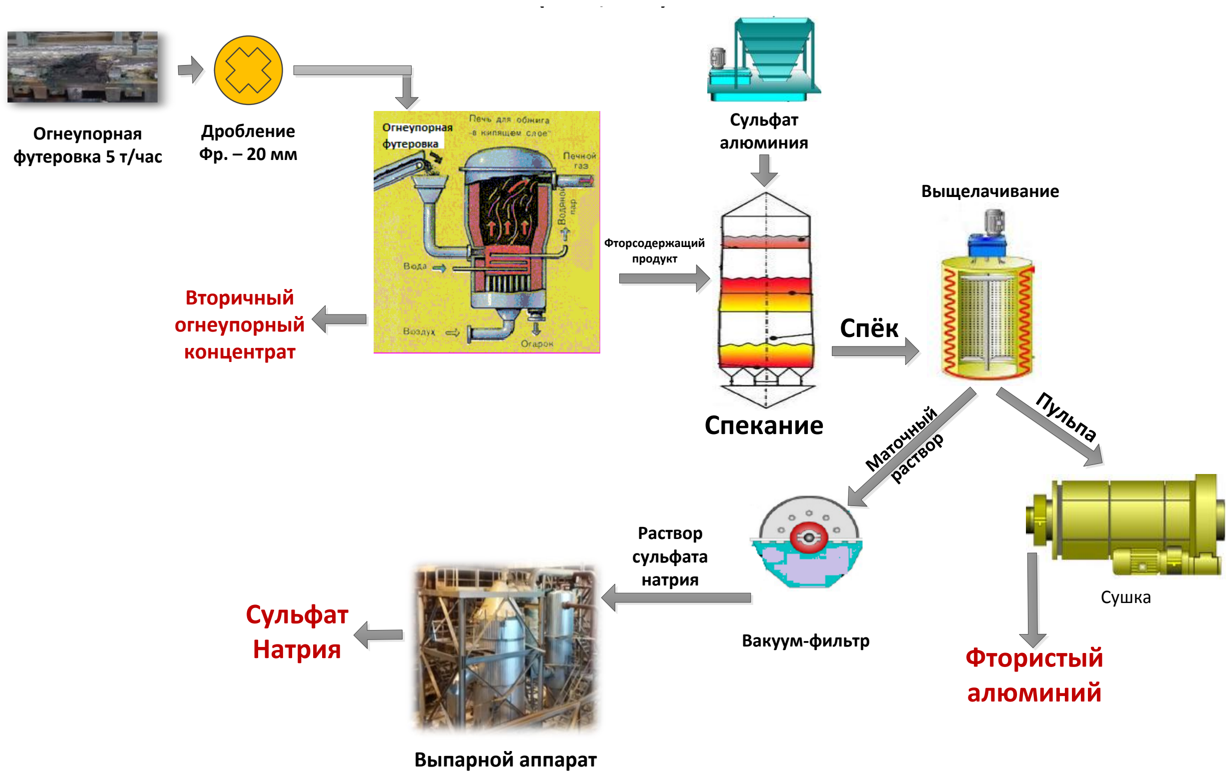

Figure 6. Hardware and technological scheme of SL processing on the equipment of chemical – metallurgical and alumina plants

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SL technique involves its grinding, leaching with aqueous solutions of reagents of alkaline and acid nature, separation of liquid and solid phases of the pulp, the solution processing with releasing of fluoride product. Grinding and leaching are carried out in explosion-proof equipment. When grinding in an aqueous medium it is maintained at a pH of 6-8 and the temperature to 60°C, thenthe pulp is processed by caustic alkali solution at a temperature of 80-100 °Cfor 4-10 hours and the pH is maintained at 10-12. After phase separation solution treatment is carried out with an acids or salts.

SL is grounded to a particle size of 50-200 microns. The solution processing may be carried out by aluminum sulfate in the presence of (or - without any) sulfuric acid, hydrofluoric acid or washing waters after purifying gases, containing fluorine, water. [11]

As a result of solid fluorine – carbon - containing wastes leaching, pulp is generated, consisting of solid and liquid phase. Solid phase contains a carbon component and insoluble residues - alumina, some fluorine compounds, calcium, magnesium, silicon and iron compounds. The solid phase is separated by filtration and may be recycled, for example, for fuels.

The liquid part contains sodium fluoride, sodium aluminate, sodium sulfate, silicon compounds, an excess of sodium hydroxide. [12]

In subsequent neutralization of solutions portion of the silicon compounds enters to the desired product - cryolite. Normative content of silica in cryolite is provided no more than 0.9%. The proposed technology defines the conditions of optimal implementation of desilication process:

- Conducting of desilication simultaneously with leaching;
- Additional contact of the sludge with solution for 4-10 hours;
- Treatment temperature - 80-100 °C

After desilication it is carried out the precipitation of cryolite from a solution of acidic aluminum salts, aluminum chloride or aluminum sulfate in the presence of sulfuric acid. The process is realized by the following reactions:

$$2 \cdot NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2 \cdot H_2O \qquad (1)$$

As a result of this reaction it is neutralized an excess of caustic alkali.

$$14 \cdot NaF + Na\,Al\,O_2 + Al_2\,(SO_4)_3 + 2 \cdot H_2SO_4 \rightarrow Na_5\,Al_3F_{14} + 5 \cdot Na_2SO_4 + 4 \cdot H_2O \qquad (2)$$

During the precipitation of cryolite by aluminum salts, it is precipitated chiolite $Na_5Al_3F_{14}$,, wherein the sodium content is at a level of 22-25%. This product is claimed to produce, since the sodium content in it is on 5-8% lower than in cryolite, that besieged sodium bicarbonate or carbon dioxide. [13-15]

Keeping on the first processing stage of shredded SL the pH = 6-8 and a temperature of not more than 60 °C in theexplosion-proof equipment is necessary to ensure the safety of the process, since in this case the evolution of hydrogen and methane is practically no. Reaction (3) of carbide decomposition with methane forming and (4) starts at a pH above 8.0, and intensified with increasing temperature above 60 °C. Hydrogen evolution by reaction (4) also begins at pH 8 - 10.

$$Al_4C_3 + 2 \cdot Na_2O + 6\,H_2O \rightarrow 2 \cdot (Na\,Al\,O_2) + 3 \cdot CH_4 \uparrow \qquad (3)$$

$$2 \cdot Al_{met} + Na_2O + 3\,H_2O \rightarrow 2 \cdot (Na\,Al\,O_2) + 3H_2 \uparrow \qquad (4)$$

Grinding is necessary to intensify the SL processing (increasing the contact surface of the processed material and reactant, increasing interaction efficiency, reduced processing time). With insufficient grinding (over 200 microns) the part of the useful components of the material being processed is not opened, the extraction decreases. More fine grinding (less than 50 microns) – impractical, because a significant effect on the recovery can't be achieved, but energy costs significantly increase, additional equipment is required.

The developed technology enables the SL treatment to produce high quality demanded product - cryolite with reduced sodium content and the possibility of the solid phase recycling onto energy products.

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