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Recycling of Spent Pot Lining of Electrolysis Cells with Regeneration of Aluminum Fluoride

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Abstract

Metallurgical production at the present time are undergoing modernization of technological processes and production capacity, which leads to the introduction in the industry automation systems. The spent pot lining (SPL) of aluminum cell is one of the most environmentally hazardous waste of the aluminum industry due to its content of up to 40 wt. % fluorides. At present most of the SPL is accumulated near aluminum factories in specially equipped landfills, where it can interact with water and air, with formation of toxic compounds and alkaline solutions, which could lead to groundwater contamination.

At the same time, the SPL is of some value because of the presence of fluoride and up to 30 wt. % carbon. Known technology for processing spent lining with obtaining cryolite, operated at some aluminum plants, has lost its applicability after introduction of dry gas cleaning unit and transfer of electrolysis technology on the use of acidic electrolytes. This has led to a substantial reduction of cryolite consumption. Therefore, at present more attention is paid to technologies for production of aluminium fluoride, including from the SPL.

This article presents a brief review of known technologies for processing spent lining of aluminum cell. The technology of obtaining aluminium fluoride is presented as well as the results of laboratory tests, allows obtaining product with a fluorine content from 55 to 59 wt. %, and thus to reduce the consumption of fresh AlF_3 about 4–6 kg/t Al.

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

Metallurgical production at the present time are undergoing modernization of technological processes and production capacity, which leads to the introduction in the industry automation systems. Their main feature, due to the nature of metallurgical production is a systematic approach to all procedures within the framework of the whole enterprise:

- thermal engineering;
- metallurgical;
- environmental;
- management [1]

In the paper [2] investigated foreign experience of development of small innovative business. Small businesses represent an increasing share in the number of companies engaged in research and development including in the use of technical devices for automation of control over protection of labour at the metallurgical enterprises. The author pays special attention to the Japanese model of integration of science and production. It involves the construction of completely new cities, technopolises, combining R & d and knowledge-intensive industrial production.

In the steel industry, it is extremely important not only to build the management processes, but also to ensure their uninterrupted flow. As a consequence, increase the quality of the product, increases productivity and saves finances.

None of the benefits can not be compared with the damage that enterprises of metal can cause to the environment, health and even human life. One of the main missions of the systems of automation of metallurgical production should be aimed at reducing hazardous waste (technological dust, carbon oxides, nitrogen oxides, sulfur oxides, and others). The set of tasks that have to solve the system of automation of metallurgical production:

- ensuring rational modes of activity of the enterprise in General and each individual of the technological process;
- ensuring specified operation of the enterprise;
- ensuring improved quality of products by reducing costs, delays, emergency situations and other adverse factors.

RUSAL (the main producer of aluminium in Russia) directions environmental strategy are:

- Reduction of pollutant emissions in atomsfera, including greenhouse gas emissions;
- Creating a closed water recycling systems for the main production processes of enterprises;
- Increasing the share of recycling and the use and safe storage;
- Replacement and disposal of electrical equipment containing polychlorinated biphenyls;
- Restoration of disturbed lands and promoting the conservation of biological diversity;
- Creation of the corporate management system for the management of environmental issues and risk. [3]

The organization of these processes and monitoring their implementation entrusted to the Department of labor protection.

According to [4], the SPL has an average of about 30 wt. % of carbon, 30 wt. of refractories% and 40 wt. % of fluoride salts. The highest content of fluorides, alumina and carbon is observed in the hearth and side blocks of the coal portion of the spent coal lining in the aluminum cell, qualitative composition of which is given below by weight. %:

C 40–55; Na_3AlF_6 15–25; NaF 10–20; Al_2O_3 5–6; CaF_2 1–3; Al_4C_3 5–10; Fe_2O_3 2–3; $Al_{мет}$ 0,5–1,0; SiO_2 1–2; CaO 0–1,0; AlF_3, $Na_3Al_3F_{14}$, NaCN, LiF, Na_2SO_4, Ca, Mg and others. 2-7.

For a long time in many countries, researches are underway to find the most effective, simple and economical method of disposal and recovery of fluorine from fluoride-carbon-containing wastes [6-16]. The main ones are:

- Neutralization of toxic impurities and further storage of waste in dumps;
- Production of fluxing agents for the steel industry;
- The production of additives for cement industry;
- Incineration;
- Alkaline or acid leaching;
- Flotation with extraction of cryolite;
- Pyrohydrolysis or pirosulfoliz;
- Extraction of the carbon additive and its additive in carbon cathode or carbon anode;
- Addition to calcium fluoride in the hydrogen fluoride production;
- Sulfuric acid decomposition at elevated temperatures.

In the early 1990s, the Achinsk Alumina Refinery (AAR) cryolite production was mastered from a SPL by alkaline way. It was processed for about 15 thousand t per year of lining to obtain 5000 tons of cryolite, but production has been closed due to lack of demand of cryolite, and potassium high content therein because of the use of caustic soda in AAR's production.

The main parameters of the technology for processing carbon-containing waste lining by alkaline manner are the following. The lining is crushed and then ground to a particle size of 50-200 microns, which is caused by increasing the feasibility of the specific surface area and reactivity of the material being processed, ensuring the possibility of further separation from the liquid phase at the industrial vacuum filters or centrifuges. With insufficient grinding (particle size 200 microns) part of the mineral components of the material are not open being processed, and the process efficiency reduces. When fine grinding (less than 50 microns) substantial increase of the components extraction efficiency is not achieved, but significantly increases the energy consumption for grinding.

In order to prevent dusting of the crushed material and a premature start of the following hydrogen evolution reactions (6) and methane (7) and for providing the security process, grinding of the waste carbonaceous lining is carried out in aqueous medium at temperatures up to 60 ° C and pH 8.6. Next, the pulp is treated with a solution of caustic soda at a pH of 10-12 and a temperature of 80-100 ° C for 4-10 hours. Under these process parameters, solution desiliconization and maximum extraction efficiency of fluorine are achieved

Overall interaction of the material being processed with caustic soda solution is in accordance with the following general reactions:

$$NaF + H_2O + Na_2O \longleftrightarrow NaF_{ж} + H_2O + Na_2O, \quad (1)$$

$$2(3NaF \cdot AlF_3) + 4Na_2O + H_2O \longleftrightarrow 12NaF + 2Na \cdot AlO_2 + H_2O, \quad (2)$$

$$2(5NaF \cdot 3AlF_3) + 12Na_2O + H_2O \longleftrightarrow 2NaF + 3(Na_2O \cdot Al_2O_3) + H_2O, \quad (3)$$

$$2AlF_3 + 4Na_2O + H_2O \rightarrow 6NaF + 2NaAlO_2 + H_2O, \quad (4)$$

$$Na_2SO_4 + H_2O + Na_2O \longleftrightarrow Na_2SO_{4ж} + H_2O + Na_2O, \quad (5)$$

$$2Al_{мет} + Na_2O + 3H_2O \rightarrow 2NaAlO_2 + 3H_2\uparrow, \quad (6)$$

$$Al_4C_3 + Na_2O + 6H_2O \rightarrow 2NaAlO_2 + 3CH_4\uparrow, \quad (7)$$

$$Al_2O_3 + Na_2O + H_2O \rightarrow 2NaAlO_2 + H_2O, \quad (8)$$

$$CaF_2 + Na_2O + H_2O \longleftrightarrow 2NaF + Ca(OH)_2, \quad (9)$$

$$MgF_2 + Na_2O + H_2O \longleftrightarrow 2NaF + Mg(OH)_2, \quad (10)$$

$$SiO_2 + Na_2O + H_2O \longleftrightarrow 2NaSiO_3 + H_2O, \quad (11)$$

as a result of which is a pulp, comprising a solid and a liquid phase.
Solid phase containing carbon, insoluble residues and unreacted - alumina, some fluorine compounds, calcium, magnesium, silicon and iron compounds, separated by filtration or centrifugation and subsequently can be recycled to the carbon-containing products, such as fuel or reduction briquettes.
The liquid phase is represented by sodium fluoride, sodium aluminate, sodium sulfate, silicon compounds. After desilication, prepared in accordance with reaction

$$2Na2SiO3 + 2NaAlO2 + H2O \rightarrow Na2O \cdot Al2O3 \cdot 2SiO2 + 2Na2O + H2O, \quad (12)$$

cryolite precipitated from a solution of sodium bicarbonate or carbon dioxide according to the reactions

$$2NaOH + CO2 \rightarrow Na2CO3 + H2O, \quad (13)$$

$$NaOH + NaHCO3 \rightarrow Na2CO3 + H2O, \quad (14)$$

$$12NaF + 6NaHCO3 + 2NaAlO2 = 2Na3AlF6 + 7Na2CO3 + 3H2O. \quad (15)$$

The optimal cryolite formation reaction parameters are the temperature of 80-90 ° C; pH 9,6-10,2; Dosage aluminum solution - calculate residual content of sodium fluoride in the mother liquors 4.7 g / l [8, 17].

For the same technology can be processed and other fluorine-containing waste - tailings flotation of coal foam, sludge gas cleaning, solid waste from sludge fields [6; 8].

Thus, when alkaline processing of fluoride-carbon-containing wastes, cryolite can be prepared, without significant demand in the industry.

In the modern aluminum industry, which uses dry treatment of gases and acidic electrolytes, the most attractive seems to receive from the SPL aluminum fluoride. Work in this direction have been launched in JSC "SibVAMI" (Irkutsk), and later continued in Irkutsk State Technical University. To date, the processing technology of regeneration cryolite in aluminum fluoride designed, tested in laboratory conditions and patented [12, 18, 19]. The technology is in the fact that at a temperature 550-600 ° C cryolite reacted with aluminum sulfate by the following reactions:

$$2Na3AlF6 + Al2\ (SO4)\ 3 = 4AlF3 \downarrow + 3Na2SO4, \quad (16)$$

$$6Na5Al3F14 + 5Al2\ (SO4)\ 3 = 28AlF3 \downarrow + 15Na2SO4. \quad (17)$$

The thus obtained frit is leached with water. In this case sodium sulphate is almost entirely into the solution, and aluminum fluoride remains in the precipitate and, after filtration and drying, is a commercial product. Experimental data of testing technology is shown in Table.

Technology test results of extraction of the aluminum fluoride from regeneration cryolite and excess electrolyte *

Temperature, °C	**Sediment analysis, wt.%**						**Phase composition**
	F	**Al**	**Na**	**SO_4**	**rest**	**calcination loss**	
Source regeneration cryolite	45,6	14,32	31,0	4,8	1,8	2,48	Na_3AlF_6, Na_2SO_4
400	31,73	17,01	16,39	30,25	2,3	2,32	Na_3AlF_6, $Na_5Al_3F_{14}$, Na_2SO_4
500	49,3	26,67	8,4	10,2	2,9	2,53	AlF_3, $Na_5Al_3F_{14}$, Na_2SO_4, Al_2O_3
550	57,1	32,92	2,12	2,3	3,16	2,4	AlF_3, Al_2O_3
600	57,3	32,5	2,02	2,2	3,63	2,35	AlF_3, Al_2O_3
700	50,1	35,2	4,2	3,1	5,5	1,9	AlF_3, $Na_5Al_3F_{14}$, Al_2O_3
550	50,5	26,8	7,1	10,6	2,6	2,4	AlF_3, $Na_5Al_3F_{14}$, Na_2SO_4
550	57,0	32,6	2,2	2,3	3,7	2,2	AlF_3, Al_2O_3
550	49,3	25,5	7,8	12,1	2,5	2,8	AlF_3, $NaAlF_4$, Na_2SO_4, Al_2O_3
550	50,2	37,1	1,7	2,1	6,1	2,8	AlF_3, Al_2O_3
550	47,9	22,9	11,2	13,1	2,2	2,7	AlF_3, $NaAlF_4$, Al_2O_3, Na_2SO_4
550	57,3	33,1	1,9	2,0	3,1	2,6	AlF_3, Al_2O_3
Source electrolyte	52,63	15,5	25,7	0,08	4,89	1,2	$Na_5Al_3F_{14}$, Al_2O_3, Na_3AlF_6
550	55,1	32,7	2,4	2,2	5,8	1,8	AlF_3, Al_2O_3

Notes: 1. The processing time - 2 hours.
2. Excess Al_2 (SO_4) 3,% of the stoichiometric content - 120.
3. The leaching conditions: T = 80 ° C; τ = 30 hours; the ratio of W: T = 4.1.

The data presented in the table show that the maximum recovery of fluorine observed when processing the starting materials for 2 hours at a temperature of 550-600 ° C. The product obtained by this technology, comprises by weight. %: F 55-59; Al 32-34; Na 2,0-2,5; SO4 2-3; LOI 2.5-3.0 wt. %. The content of iron and silicon impurities are within the requirements of normative documents on the quality of aluminum fluoride [20-25].

CONCLUSION

This technology can be processed and other fluoro- and cryolite-containing products. The implementation of this technology will reduce the consumption of "fresh" aluminum fluoride at 4-6 kg per ton of aluminum, to reduce the storage capacity of fluorine-containing waste, to improve the ecological situation in the aluminum smelters location areas.

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