

RECYCLING OF ELECTROLYZER SPENT CARBON-GRAPHITE LINING WITH ALUMINUM FLUORIDE REGENERATION

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The spent lining of aluminum electrolyzer is one of the most environmentally hazardous wastes of the aluminum industry due to its content of up to 0.2 wt.% cyanide and up to 40 wt.% fluorides. The majority of spent lining is accumulated near aluminum plants in specially equipped landfills, where it can interact with water and air, with formation of toxic compounds and alkaline solutions that could lead to ground water contamination. At the same time, spent lining is of specific value due to presence of fluoride and up to 30 wt.% carbon. Known technology for processing spent lining with preparation of cryolite in operation at some aluminum plants has lost its importance after introduction of dry gas cleaning and a change-over to electrolysis technology using acidic electrolytes. This has led to a substantial reduction of cryolite requirement. Therefore, at present more attention is devoted to technology for producing aluminium fluoride, including from spent lining. This article provides a brief review of known technology for processing aluminum electrolyzer spent lining. Technology is provided for preparing aluminium fluoride product containing fluorine of 55–59 wt.%; thus, there is a reduction in fresh AlF_3 consumption of about 4–6 kg/ton Al. Laboratory test results are provided.

Keywords: aluminum electrolyzer, spent lining, utilization, aluminum fluoride.

According to data in [1], spent lining contains on average about 30 wt.% carbon, 30 wt.% refractories, and 40 wt.% fluorine salts. The greatest content of fluorides, aluminum, and carbon is observed in the hearth and side blocks of the carbon part of an aluminum electrolyzer spent lining, whose quantitative composition is provided below [2], wt.%. 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_{met} 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, etc. 2–7.

For a long time, in many countries research is underway to find a most effective, simple, and economic method for neutralizing and regenerating fluorine from fluorine-containing waste [3–13]. The main methods are:

- neutralization of toxic inclusions and subsequent waste storage in dumps;
- production of fluorine-containing additives for the steel pouring branch;
- production of additives for the cement industry;
- burning;
- alkaline or acid leaching;
- flotation with cryolite extraction;

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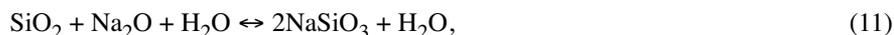
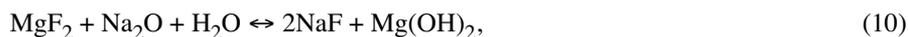
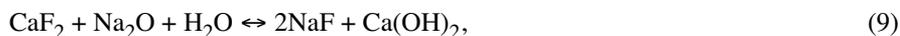
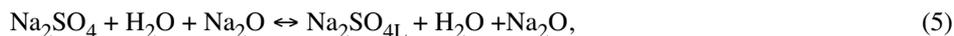
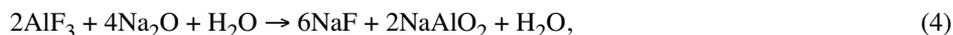
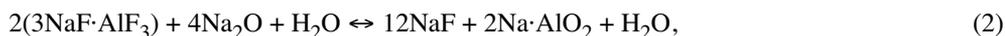
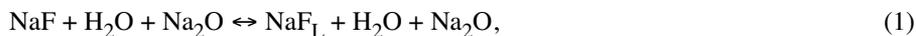
- pyrohydrolysis or pyrosulfolysis;
- extraction of the carbon part and its addition to a carbon cathode or carbon anode;
- addition to calcium fluoride in the production of hydrogen fluoride; and
- sulfuric acid decomposition at elevated temperature.

At the start of the 1990s, at the Achinsk Alumina Combine (AGK) cryolite production was started from spent lining by an alkaline method. About 15 thousand tons of lining per year were processed with preparation of 5000 tons of cryolite, although production ceased in view of the unwanted nature of cryolite and a high content of potassium within it due to use of caustic soda produced by AGK.

The main parameters for processing carbon-containing part of spent lining by an alkaline method were as follows. Lining is crushed and then refined to a size of 50–200 μm , which causes the desired increase in specific surface and reaction capacity of processed material, with provision the possibility of its subsequent separation from liquid phase in industrial vacuum filters or centrifuges. With inadequate refinement (size more than 200 μm), part of the useful components from spent material is not broken down and process efficiency is reduced. With fine grinding (less than 50 μm), there is no marked increase in valuable component extraction, and there is a significant increase in energy expended in milling.

With the aim of preventing refined material dust formation and premature start of the reactions of hydrogen (6) and methane (7) liberation, and also provision of process safety, refinement of spent carbon-containing refractory is carried out in an aqueous medium at up to 60°C and pH 6–8. The pulp is treated with a caustic soda solution with pH 10–12 and temperature 80–100°C for 4–10 h. With these process parameters, silica-free solution is achieved with maximum fluorine extraction efficiency.

On the whole, reaction of treated material with caustic soda solution occurs in accordance with the following main reactions:



as a result of which there is formation of pulp containing solid and liquid phases.

The solid phase, containing carbon, insoluble and an unreactive residue, i.e., alumina, part of the compounds of fluorine, calcium, magnesium, silicon and iron compounds, is separated by filtration or centrifuging and subsequently may be processed into carbon-containing products, for example, fuel or reducing briquettes.

Liquid phase is represented by a solution of sodium fluoride, sodium aluminate, sodium sulfate, and silicon compounds. After silica removal, accomplished in accordance with the reaction

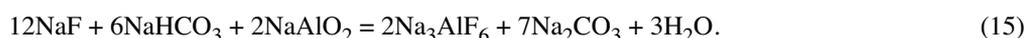


TABLE 1. Test Results for Extraction of Aluminum Fluoride from Regenerated Cryolite and Excess Electrolyte

Temperature, °C	Precipitate analysis, wt.%						Phase composition
	F	Al	Na	SO ₄	rest	calcination loss	
Original regenerated cryolite	45.6	14.32	31.0	4.8	1.8	2.48	Na ₃ AlF ₆ , Na ₂ SO ₄
400	31.73	17.01	16.39	30.25	2.3	2.32	Na ₃ AlF ₆ , Na ₅ Al ₃ F ₁₄ , Na ₂ SO ₄
500	49.3	26.67	8.4	10.2	2.9	2.53	AlF ₃ , Na ₅ Al ₃ F ₁₄ , Na ₂ SO ₄ , Al ₂ O ₃
550	57.1	32.92	2.12	2.3	3.16	2.4	AlF ₃ , Al ₂ O ₃
600	57.3	32.5	2.02	2.2	3.63	2.35	AlF ₃ , Al ₂ O ₃
700	50.1	35.2	4.2	3.1	5.5	1.9	AlF ₃ , Na ₅ Al ₃ F ₁₄ , Al ₂ O ₃
550	50.5	26.8	7.1	10.6	2.6	2.4	AlF ₃ , Na ₅ Al ₃ F ₁₄ , Na ₂ SO ₄
550	57.0	32.6	2.2	2.3	3.7	2.2	AlF ₃ , Al ₂ O ₃
550	49.3	25.5	7.8	12.1	2.5	2.8	AlF ₃ , NaAlF ₄ , Na ₂ SO ₄ , Al ₂ O ₃
550	50.2	37.1	1.7	2.1	6.1	2.8	AlF ₃ , Al ₂ O ₃
550	47.9	22.9	11.2	13.1	2.2	2.7	AlF ₃ , NaAlF ₄ , Al ₂ O ₃ , Na ₂ SO ₄
550	57.3	33.1	1.9	2.0	3.1	2.6	AlF ₃ , Al ₂ O ₃
Original electrolyte	52.63	15.5	25.7	0.08	4.89	1.2	Na ₅ Al ₃ F ₁₄ , Al ₂ O ₃ , Na ₃ AlF ₆
550	55.1	32.7	2.4	2.2	5.8	1.8	AlF ₃ , Al ₂ O ₃

Notes: 1. Treatment time, 2 h. 2. Excess of Al₂(SO₄)₃, % to stoichiometric content, 120. 3. Leaching conditions: T = 80°C; τ = 30 h; L:S = 4:1.

cryolite is precipitated from solution with sodium bicarbonate or carbon dioxide gas in accordance with reactions



Optimum cryolite formation reaction parameters are: temperature 80–90°C; pH 9.6–10.2; addition of aluminum-containing solution with calculation for residual sodium fluoride content in mother liquor of 4–7 g/liter [5, 14].

Other fluorine-containing waste, i.e., carbon-foam flotation tailings, gas cleaning slurry, and solid waste from slurry pits, can be processed by a similar technology [3, 5].

Thus, with alkaline processing of fluorine containing waste, it is possible to obtain cryolite not having sufficiently in demand in industry.

Under conditions of the contemporary aluminum industry using dry gas cleaning and acid electrolytes, preparation of aluminum fluoride from spent lining is most attractive. Work in this direction was started at the SibVAMI (Irkustsk) and subsequently continued at the Irkutsk National Research Technical University. Currently, technology for processing regenerated cryolite into aluminum fluoride has been developed, tested under laboratory conditions, and patented [9, 15, 16]. In essence the technology includes the fact that at 550–600°C cryolite reacts with aluminum sulfate by the following reactions:



The cake obtained in this way is leached with water. Sodium sulfate is transferred almost entirely into solution, but aluminum fluoride remains in the deposit and after filtration and drying it is a saleable product. Experimental data for testing the technology are provided in Table 1.

Data presented in Table 1 indicate that maximum extraction of fluorine is observed with treatment of original material for 2 h at 550–600°C. The product obtained by this technology contains, wt.%: 55–59 F, 32–34 Al, 2.0–2.5 Na, 2–3 SO₄, loss on calcining 2.5–3.0 wt.%. The content of iron and silicon impurities is within the limits of standard document specifications for aluminum fluoride quality.

Conclusion. It is possible to process by this technology other fluorine- and cryolite-containing products. Accomplishment of this technology makes it possible to reduce the requirement for “fresh” aluminum fluoride by 4–6 kg per ton of aluminum, to reduce the storage volume of fluorine-containing waste, and to improve the ecological situation in regions of aluminum plant location.

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