

Composition of the heat insulating part of the spent lining – waste of overhaul of aluminum electrolyzers

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Abstract. The main part of losses of fluorine during the electrolytic production of aluminum accounts for the wastes of the overhaul of electrolyzers - spent lining. To assess the possibility of creating a technology for the regeneration of fluorine from the heat insulating part of the spent lining of aluminum electrolyzers, its chemical and phase composition was studied. Presence of water-soluble fluorides in the heat insulating part of the spent lining makes it possible to extract from it up to 70% of fluorine by leaching.

1. Introduction

At the present time, the main type of solid wastes in the production of aluminum are materials for the overhaul of electrolyzers, including spent lining. Annually, in Russia, it is formed and stored in storage tanks, or exported to the dump about 130-150 thousand tons of lining of dismantled electrolyzers [1]. The spent lining during being stored in landfills can interact with water and air, forming toxic compounds and alkaline fluoride-containing solutions. In this regard, spent lining is an environmentally hazardous waste.

2. Study of the material

To study the material composition and properties of the heat insulating part of spent lining of aluminum electrolyzers, dismantling products of the cathode device of five C8BM with different operating times were used at the Krasnoyarsk and Irkutsk alluminium smelters.

Samples, with the exception of chamotte backfill, which was taken from different locations along the perimeter of the pool, were taken from each product by a point method in terms of area and cross-section. Samples were crushed with a hydraulic press, then crushed into powder with a jaw crusher and rubbed in a disk attritor since the fraction is of -0.2 mm. Then, by quartizing several samples in certain ratios, an average representative sample was obtained. Heat insulating part of the spent lining has a complex phase and material composition. That's why, various modern analysis methods were used to estimate the material and phase composition of the averaged samples: micro-X-ray one, X-ray phase one and X-ray fluorescence one.

Chemical composition according to the results of the analysis of samples performed on a S8 TIGER X-ray fluorescence spectrometer from five C8BM electrolyzers of various plants is given in table 1.



Table 1. Results of X-ray fluorescence analysis of samples from five C8BM electrolyzers of various plants, % wt.

Electrolyser	C	F	Na	Mg	Al	Si	Ca	Fe	K	Others
1	1.60	13.30	10.30	0.17	16.20	21.40	0.60	1.20	0.90	34.33
2		33.90	24.52	0.21	8.20	10.00	3.10	2.60	0.60	17.08
3		1.80	3.90	0.16	16.20	26.10	0.27	0.78	0.57	50.22
4	0.4	9.42	18.36	0.21	9.72	22.42	0.36	1.32	0.61	37.18
5		2.1	4.1	0.17	16.12	26.3	1.11	1.349	0.53	48.22
At average	0.40	12.10	12.24	0.18	13.29	21.24	1.09	1.45	0.64	39.31

As follows from the data given, composition of the heat insulating part of the spent lining for each electrolyser is individual and can vary significantly. Average values were used in the study.

Elemental composition of constituents of the heat insulating part of the spent lining of the electrolyser No. 1 is shown in table. 2

Table 2. Elemental composition of constituents of the heat insulating part of spent lining,% wt.

Sample	C	F	Na	Mg	Al	Si	Ca	Fe	K	Others
Dissolved chamotte	3.20	20.60	17.20	0.12	16.30	16.80	0.70	0.70	0.90	23.48
First layer of chamotte	2.80	12.80	19.10	0.14	16.00	19.50	0.90	1.50	0.70	26.56
Second layer of chamotte	-	1.30	3.60	0.23	16.50	26.10	0.27	0.78	0.44	50.78
Third layer of chamotte	-	0.20	2.20	0.30	16.50	26.90	0.68	1.90	0.44	50.88
Diatomite	-	6.90	3.00	8.40	4.50	22.40	0.47	7.20	3.00	44.13

The others are mainly represented by oxygen in the form of Al_2O_3 , SiO_2 . The diffractograms, obtained with the help of Shimadzu XRD-7000S powder diffractometer, of the averaged sample of the heat insulating part of the spent lining of electrolyzers 2 and 5 of the Irkutsk and Krasnoyarsk aluminum smelters of OK "RUSAL" are shown in figure 1 and 2, respectively.

In the first diffractogram, the peaks which correspond to sodium fluoride are most intensively isolated, since the electrolyser was emergency and the fluorine content in this sample was very high. As seen in the second diffractogram, peaks which correspond to nepheline, cristobalite and mullite are more pronounced.

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As main phases, with the help of the X-ray phase analysis, the following substances were found in the heat insulating part of the spent lining were found: mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, sodium fluoride NaF, cryolite Na_3AlF_6 , kyolite $\text{Na}_5\text{Al}_3\text{F}_{14}$, silicon oxide SiO_2 in the form of cristobalite, quartz, tridymite, calcium fluoride CaF_2 , aluminum oxide Al_2O_3 , nepheline NaAlSiO_4 , albite $\text{NaAlSi}_3\text{O}_8$.

Below, we consider the main properties of the phases which appear in the heat insulating part of the spent lining of the aluminium electrolyser.

The solubility data are presented in figure 3 [3].

Cryolite Na_3AlF_6 and chiolite $\text{Na}_5\text{Al}_3\text{F}_{14}$ are slightly soluble in water 0.41 g/dm^3 (at 200°C). They react with strong acids to form salts of aluminum and sodium and hydrogen fluoride. Cryolite and chiolite are decomposed by strong alkalis with the formation of metal tetrahydroxoaluminates of the corresponding alkalis and fluoride. Under normal conditions, silicone dioxide SiO_2 is most often found in the polymorphic modification of α -quartz, which at a temperature above $+573^\circ\text{C}$ reversibly passes into β -quartz.

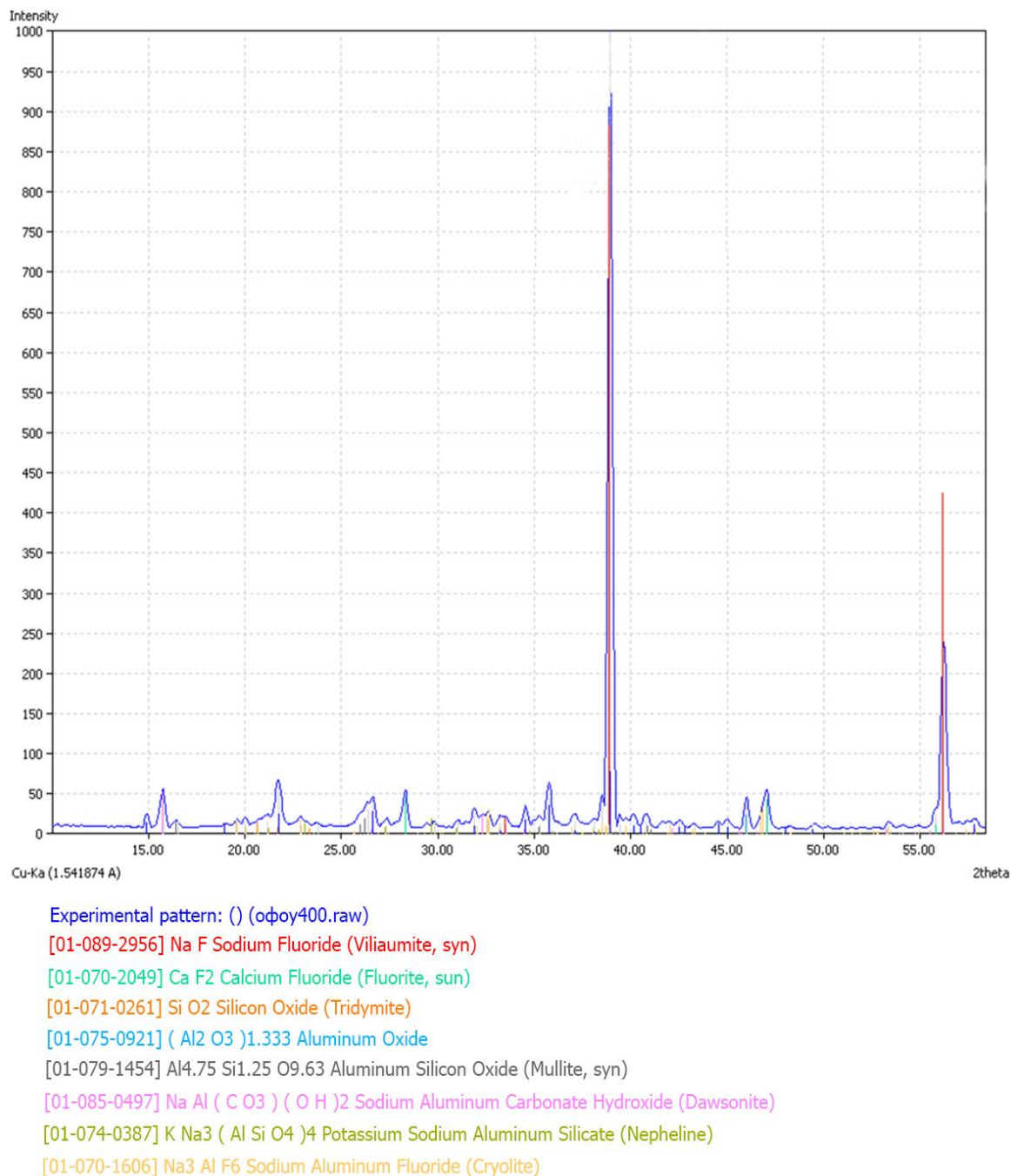


Figure 1. Diffractogram of the sample of the heat insulating part of the spent lining (electrolyser No. 2).

With a further increase in temperature, quartz becomes tridymite and cristobalite. These polymorphic modifications are stable at high temperatures and low pressures. Cristobalite is more stable than tridymite at temperatures below 1770 °C [8]. Silicon dioxide practically does not dissolve in water, solubility is, mg/dm³: 7 for quartz, 12 for cristobalite, 16 for tridymite, 120 for amorphous silica [9]. However, as the pH increases, solubility of silicon dioxide in water sharply increases.

Calcium fluoride CaF_2 is practically insoluble in water 0.017 g/dm^3 (at 200°C) Calcium fluoride is chemically relatively passive. It reacts with sulfuric acid to form calcium sulphate and hydrogen fluoride, which is used in industry to produce hydrofluoric acid. At high temperatures, it undergoes hydrolysis.

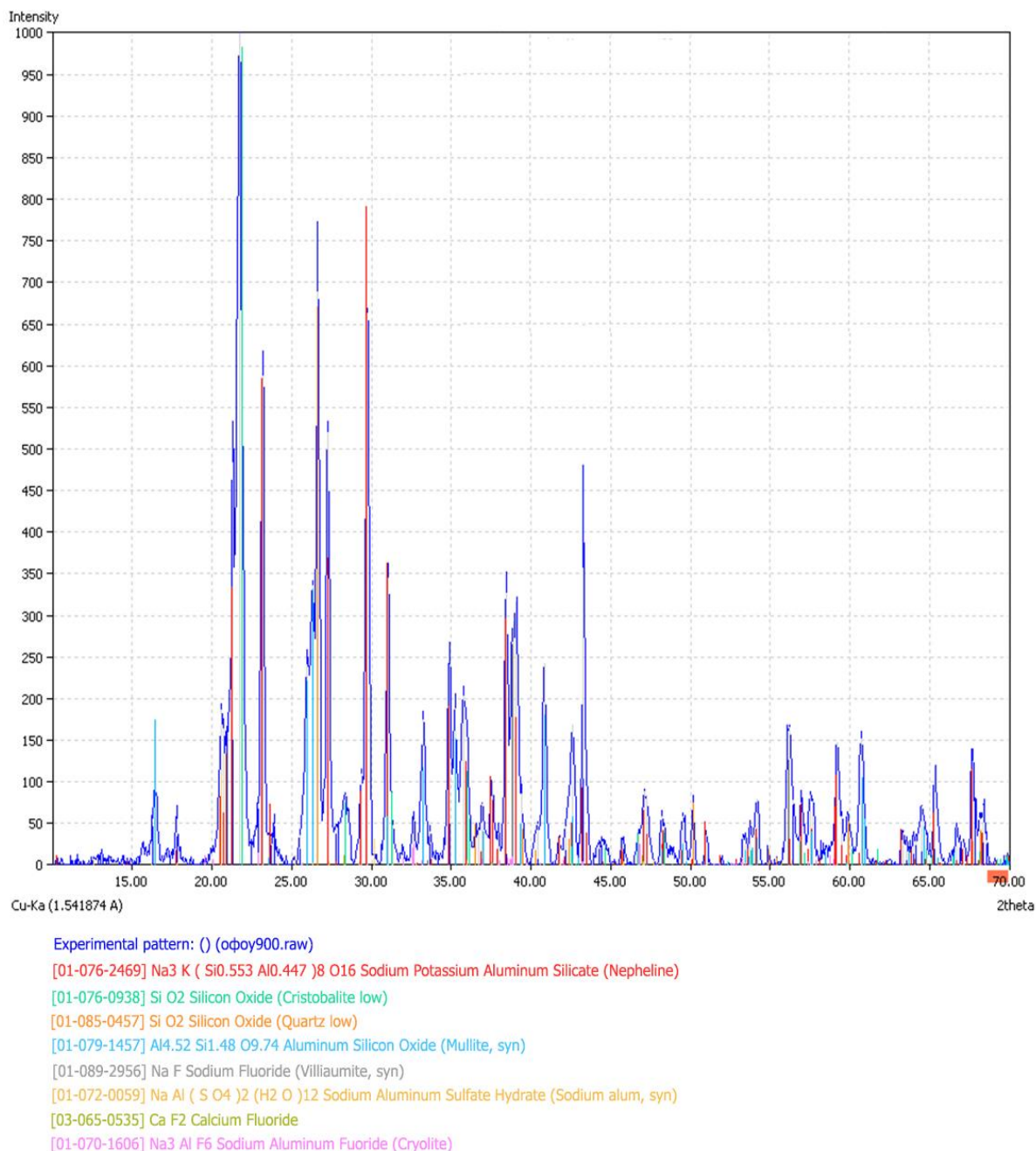


Figure 2. Diffractogram of the sample of the heat insulating part of the spent lining (electrolyser No. 5).

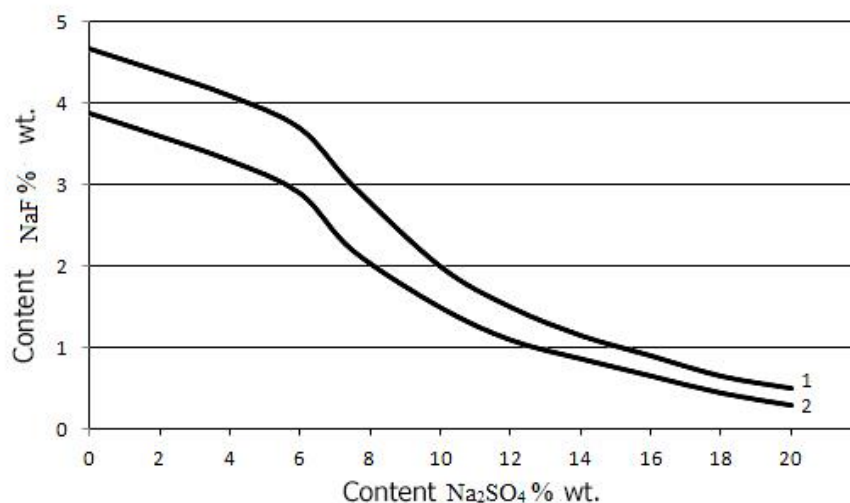


Figure 3. Solubility in the NaF-Na₂SO₄-Na₂CO₃-NaHCO₃-H₂O system: 1 – isotherm of the NaF-Na₂SO₄-H₂O system; 2 – the same in the presence of a constant sum of salts (about 4%) of Na₂CO₃ and NaHCO₃.

3. Conclusion

Aluminum oxide Al₂O₃ in the heat-insulating part of the spent lining is represented by α and β phases (corundum and alumina, respectively). Both phases are insoluble in water, but interact with acids to form aluminum salts and water. Reacting with water solutions of alkali, alumina forms tetrahydroxoaluminate, which decomposes in air to aluminum hydroxide and bicarbonate.

Nepheline NaAlSiO₄ is easily decomposed by mineral and organic acids with the release of gelatinous silica. In case of prolonged boiling in water, the solution acquires an alkaline reaction. Nepheline does not interact with alkalis.

Albit NaAlSi₃O₈ is insoluble in water, slightly soluble in acids, decomposed by hydrofluoric acid with the release of gelatinous silica.

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