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Determination of Optimal Fluorine Leaching Parameters from the Coal Part of the Waste Lining of Dismantled Electrolytic Cells for Aluminum Production

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When aluminum is obtained by electrolysis of cryolite-alumina melts when the baths are sent for capital repairs, a solid technogenic product is formed – waste lining of electrolytic cells (WLEC). The volume of formation of WLEC is 30-50 kg per 1 ton of aluminum. Currently, it is mainly stored at landfills near industrial enterprises, causing harm to the environment. However, this technogenic raw material contains valuable components (fluorine, aluminum, sodium) that can be extracted to produce fluoride salts, which are in demand during the electrolytic production of aluminum. The objects of research were samples of the coal part of the waste lining of dismantled S-8BM (E) type electrolytic cells of «RUSAL Krasnoyarsk» JSC (Krasnoyarsk) of RUSAL company. According to the X-ray experiment diffraction analysis (using a Bruker D8 ADVANCE diffractometer) of the phase composition of the samples, it was found that the main fluorine-containing compounds are cryolite, chiolite, sodium and calcium fluorides. The total fluorine content in the studied samples averaged 13.1 %. We conducted studies on the leaching of fluorine from WLEC with a solution of caustic alkali (NaOH concentration – 17.5 g/dm^3). The process was carried out in a mechanically agitated reactor using a BIOSAN MM-1000 top drive laboratory stirrer with a two-blade nozzle. By the method of mathematical planning of a three-factor experiment, the mutual influence of three leaching conditions on the optimization parameter was established – the extraction of fluorine in solution (in percent). The maximum recovery of fluorine from WLEC to the leach solution averaged 86.4 % and was achieved with the following indicators: process temperature – 95 °C, the ratio of liquid to solid phase – 9:1, duration – 210 min.

Key words: aluminum production; electrolytic cell; cathode device; technogenic raw materials; waste lining; leaching

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Introduction. The aluminum industry, being an integral part of the Russian economy, is steadily developing due to the improvement of technological processes at enterprises producing alumina [16, 22], primary aluminum [9, 21] and alloys based on it [23], practical experience in implementing projects to expand raw materials base [5, 20] and improving environmental performance indicators [3, 4, 15, 18, 26].

The production of primary aluminum by electrolysis of cryolite-alumina melts – the current commonly used industrial method [13, 24] – is accompanied by the formation of significant waste that is harmful to the environment. These technogenic by-products of primary aluminum production include the following: dust from electrostatic precipitators, gas treatment residues, skim, anode butts, alumina-containing sweepings, dismantling materials of electrolyzes disconnected for major repairs. The largest solid industrial man-made product is the waste lining of electrolytic cells (WLEC) (coal blocks and refractory materials), which is related to waste of the 4th hazard class [6]. The production volume of this type of technogenic raw materials is 30-50 kg/t Al [19, 29]. It is known, that the electrolyte used in the preparation of aluminum by the Hall–Héroult method consists of cryolite, alumina and corrective additives – aluminum fluoride and calcium fluoride. During electrolysis, the cathode lining is impregnated with electrolyte components, cathode metal, and gases dissolved in the electrolyte [27, 28]. According to previous analytical studies, WLEC contains the following components on average, % by weight: 30 – carbon, 40 – fluor sulphates (mainly cryolite, chiolite, calcium and sodium fluorides, etc.), 30 – refractories (mullite, quartz, tridymite, etc.) [7].

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This technogenic raw material also contains a small amount of aluminum metal, sodium cyanides and iron NaCN and $Na_4[Fe(CN)]$ [7, 27], aluminum nitride AlN, aluminum carbide Al_4C_3, iron aluminide Al_3Fe, hydroxides and carbonates of alkaline and alkaline-earth metals and other components.

The life cycle of the electrolysis cell in Russia is 1000-1500 days, and in modern foreign plants, it is much longer. However, to date, the recycling of the coal and refractory components of WLEC in our country and abroad has not been properly organized. Currently, a small amount of the coal portion of the WLEC of aluminum production is sold for the needs of ferrous metallurgy [21], but most of it remains unclaimed. But this technogenic raw material must be processed to extract valuable components (in particular, fluorine) to produce fluoride sulphates for electrolysis process, thereby increasing the efficiency of the existing production.

Formulation of the problem. For this research we took samples of WLEC from the cathode device, which was previously installed at the electrolysis cell stopped for major repair with Soderberg type S-8BM (E) anode of RUSAL Krasnoyarsk JSC (Krasnoyarsk) of RUSAL company. The service life of this electrolytic cell was 4.4 years (Fig.1).

At the initial stage, the dismantled WLEC was divided into coal and refractory parts, the bottom blocks were separated from lumpy blooms and aluminum scrap. To remove small metal inclusions, magnetic separation was carried out. Then the sample was crushed in a PE900 × 1200 jaw crusher with a complex swing of the cheek and was sent to an SMD 108 crusher, where the material was crushed to a particle size of 20-30 mm. The size of the input material for the SMD-108 should not exceed 200 mm. After crushing, the material was sent to a ball mill of the MShR1500 × 1600 type, where the WLEC was ground at L:S = 2.5÷2:1 (% by weight). The technical water was supplied to the mill to maintain a given ratio of liquid and solid phases.

The selected average material sample was sent for analytical studies. A comprehensive analysis of the chemical composition of WLEC samples showed the presence of the following compounds: NaF (sodium fluoride), Na_3AlF_6 (cryolite), $NaAlSiO_4$ (nepheline), C (graphite), $Na_2O \cdot 11Al_2O_3$ (sodium polyaluminate), $K_{1.44}Al_{10.88}O_{17.23}$ (potassium aluminate), CaF_2 (calcium fluoride), $Na_5Al_3F_{14}$ (chiolite), Al, Fe $(Fe_{1.24}Ti_{0.61})O_4$ (titanomagnetite) [26]. The X-ray diffraction analysis was performed on a D8 ADVANCE diffractometer (Bruker, Germany) equipped with a Gobel mirror and a VANTEC-1 PSD detector. The survey was performed step by step in a range of angles 2θ from 5 to 70° using Cu-K_α-radiation (Fig.2). The fluorine content in the samples was 13.1 % in average.

The main fluorine-containing compounds are cryolite, chiolite, sodium and calcium fluorides. According to previous thermodynamic calculations and studies [1, 7, 11, 14], it was found that fluorine from WLEC is completely (at least 80 %) extracted when the material is processed with caustic alkali solutions.

Leaching of fluorine from WLEC samples with a caustic alkali solution (with a NaOH concentration of 17.5 g/dm^3) was carried out in a reactor with mechanical stirring using a BIOSAN MM-1000 top drive laboratory stirrer with a two-paddle nozzle.

According to theoretical and practical studies in the field of hydrometallurgical processes, it is known that the transfer of impurity elements into a solution depends on several factors [10]: leaching duration, solvent concentration, suspension mixing intensity, the ratio of liquid and solid phases, particle size, leaching temperature, etc. It is quite difficult to conduct a full factorial experiment considering all the above factors, however, practical experiments with all factors are inappropriate tedious process.

In this regard, we adopted the following process parameters as constant values: particle size of the WLEC particles – 200 microns; the concentration of caustic alkali solution is 17.5 g/dm^3, the stirrer rotation frequency is at the level of 800 min^{-1} (peripheral speed 0.2 m/s).

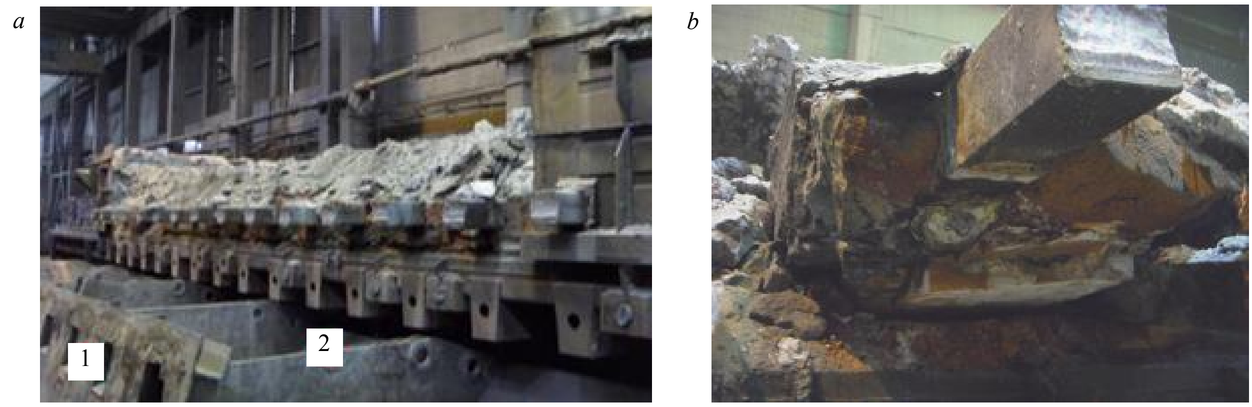

Fig.1. In the shop of major repair (JSC «RUSAL Krasnoyarsk»): *a* – dismantled electrolytic cell;
b – bottom block with blooms

1 – steel wall of the cell; 2 – container for collecting disassembled materials

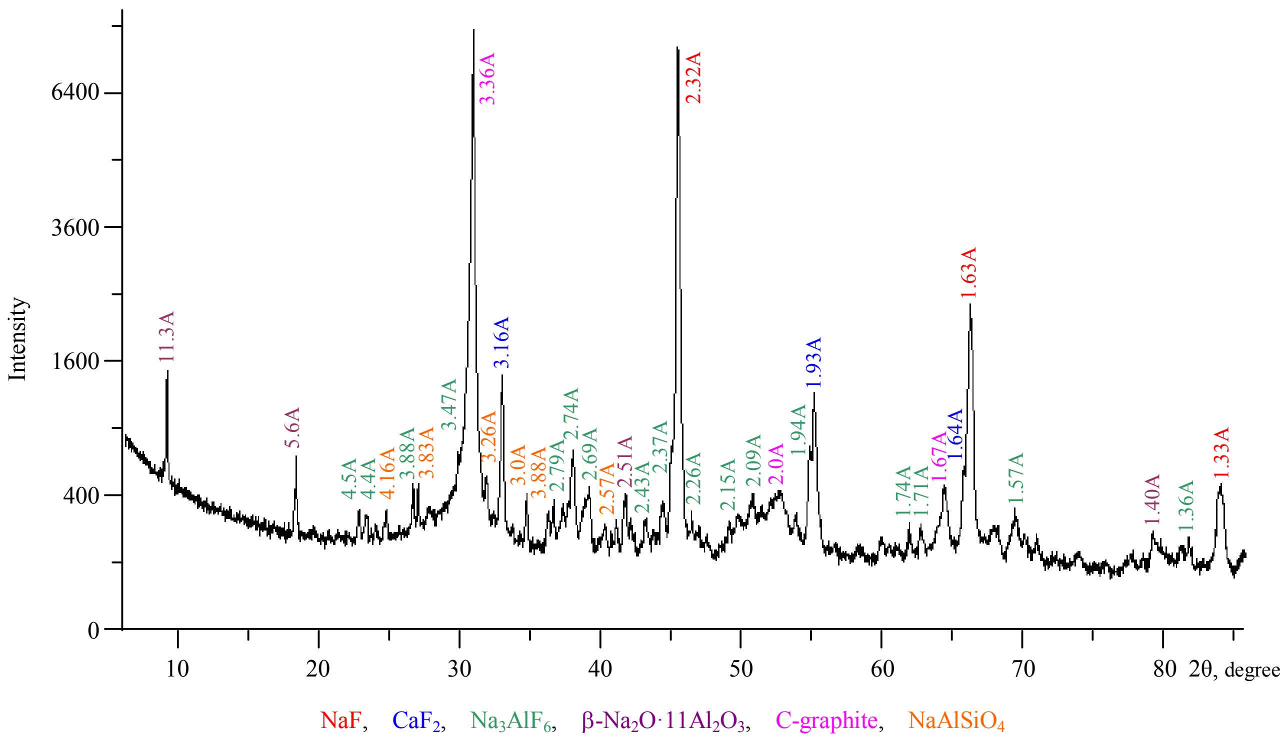

Fig.2. The XRD pattern of the WLEC coal sample

The aim of the research was to select the optimal parameters for leaching fluorine from WLEC during alkaline treatment with maximum extraction of fluorine into solution using the method of planning a three-factor experiment. The indicator was taken as the optimization parameter: fluorine recovery (ε_F, in percent) to the leach solution.

As the variable parameters during leaching of fluorine from the WLEC sample, we assumed the following parameters: temperature (t) – 75÷95 °C, the ratio of liquid and solid phases (r) – 6.0:9.0; duration (τ) – 30÷210 min. Preliminary studies showed the inappropriateness of using the process temperature below 75 °C and the duration of the process less than 0.5 hours: fluorine extraction (with the constancy of other parameters) did not exceed an average of 62.5 %.

Discussion and results. The experimental design and results of fluorine extraction during alkaline processing of WLEC are presented in Table 1.

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As a result of the analysis of experimental data, it was found that the best results on ε_F were obtained under the following conditions (Table 1): process temperature – 95 °C, L:S = 7.5:9.0; leaching time – more than 120 min.

To determine the specific values of the optimal process parameters, as the main (null) level and variation intervals (J_i), respectively, were selected: t = 85 and 10 °C; r = 7.5 and 1.5; τ = 120 and 90 min (Table 2).

Next, we compiled a plan of a three-factor experiment of type 3^3, the total number of experiments in the plan was 27. But the results of eight experiments that correspond to the highest and lowest factors are significant for calculating the mathematical model of the leaching process: these are experiments numbered 1, 3, 7, 9, 19, 21, 25, 27, respectively (see table 1). Based on these experiments, a code-design experiment planning matrix of type 2^3 is constructed. When planning the experiment, a duplication of the entire series of experiments was provided: it was decided to duplicate all eight experiments twice.

After calculating the coefficients of the mathematical model and their confidence intervals, we obtained the equation of the multidimensional polynomial of this model, showing the mutual influence on the fluorine extraction into the solution during alkaline treatment of the WLEC of three leaching parameters:

$$\varepsilon_F = 83.38 + 0.61t + 0.61r + 0.61\tau + \\ + 0.34tr + 0.41tr\tau.$$

The adequacy (suitability) of the model was carried out according to the Fisher criterion:

$$F = S_{ad}^2 / S_r^2,$$

where S_{ad}^2 – variance characterizing the deviation of the experimental values of the optimization parameter from its theoretical value calculated using the studied model; S_r^2 – variance of repeatability dispersion of ε_F.

Table 1

The experimental design and the obtained values for extracting fluorine into solution

Batch number	Temperature, °C	L:S	Duration, min	Fluoride extraction, %
1			30	81.90
2		6.0	120	82.60
3			210	82.80
4			30	83.40
5	75	7.5	120	85.10
6			210	85.10
7			30	82.90
8		9.0	120	83.10
9			210	83.50
10			30	82.00
11		6.0	120	82.70
12			210	82.80
13			30	83.60
14	85	7.5	120	85.90
15			210	85.00
16			30	83.00
17		9.0	120	83.10
18			210	84.90
19			30	83.10
20		6.0	120	83.40
21			210	83.30
22			30	85.30
23	95	7.5	120	85.80
24			210	85.90
25			30	83.20
26		9.0	120	85.70
27			210	86.40

Table 2

Experiment conditions

Factor	Null level	Variablity interval	Factor level	
			High (+)	Low (–)
t	85	10	95	75
r	7.5	1.5	9.0	6.0
τ	120	90	210	30

The table value of the Fisher criterion (F_{table}), adopted at a significance level of α = 0.05, the number of degrees of freedom for the variance of deviation f_{dev} = 1 and the number of degrees of freedom for the variance of repeatability f_y = 8, is

$$F_{table}(\alpha;\ f_{dev}; f_y) = 5.3.$$

The calculated value of the Fisher test (F_{calc}) for our data at $S_{ad}^2 = 0.02$ and $S_r^2 = 0.19$ was 0.105. Since $F_{calc} < F_{table}$, the hypothesis of the adequacy of the obtained model is not rejected at a 5 % significance level [12].

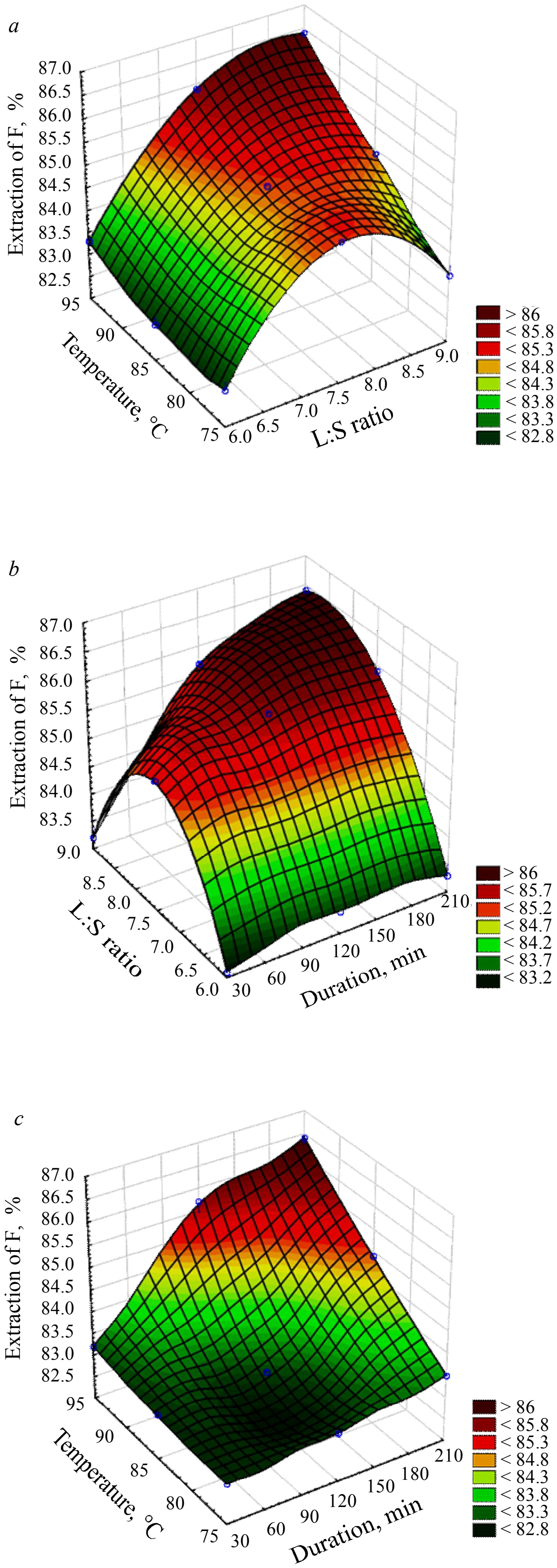

Fig.3. Extraction of fluorine in solution with leaching parameters: *a* – duration of 210 min; *b* – temperature of 95 °C; *c* – L:S = 9:1

To visualize the results of the experiment, the data obtained are presented in the form of yield surfaces made using the Statistica 10.0 computer program [2] (Fig.3). As can be seen from the figure, the best results on the extraction of fluorine from WLEC samples during their alkaline processing were obtained for experiments in which the process duration was 210 min, the ratio of liquid to solid phases was 9:1, and the temperature was 95 °C; under these process conditions, fluorine extraction averaged 86.4 %.

Thus, cryolite can be extracted from the obtained fluorine-containing solutions [8], which meets the requirements of electrolysis of cryolite-alumina melts, according to the traditional technology using sodium bicarbonate and aluminate solution.

Conclusion. One of the main types of technogenic raw materials in the production of primary aluminum is the waste lining of electrolytic cells, the volume of which can reach 50 kg/t Al. During the operation of the bath, the lining is saturated with fluoride salts and other components, which, when stored at specially designated landfills, causes a serious threat to the environment. One of the ways to solve this problem is the processing of WLEC with the transfer of fluorine-containing compounds into a solution during alkaline processing with the possible production of cryolite for the further electrolysis process.

As a result of mathematical processing of the experiments performed on the treatment of phosphoric acid by a solution of caustic alkali, the multivariate polynomial equation of the model of the leaching process was obtained, showing the mutual influence on the extraction of fluorine into the solution of three parameters, and the values of these optimal process factors were determined: duration – 210 min, L:S = 9:1, temperature 95 °C; under these leaching conditions, fluorine extraction averaged 86.4 %.

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