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Technology of the Thermal Extraction of Fluorosols from Spent Refractory Lining

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Abstract

Described methods of analysis and instrumentation taking into account the features of the analyzed samples and in order to obtain the minimum error, it is expedient to use a combination of several methods for determining chemical and phase composition of the investigated substances. Also, the use of a set of methods in studies will allow us to determine the most effective analytical control scheme for process control in the practical implementation of technology.

The scheme, part of the carbon is crushed and ground to a size of 0.2 mm and dispensed for mixing, which also receives the aluminum sulfate. Delivery of aluminium sulphate in the form of slurry or in solution. The mixture is fed into a furnace where it is sintered at a temperature of 600-700 ° C for one hour, cooled and directed to leaching with water to dissolve the salt. The pulp after leaching is fed to a thickening. As a result of leaching the sodium sulfate goes into solution and a small amount of fluorine and aluminum (aluminium fluoride and cryolite is slightly soluble) solution processed in the original scheme of obtaining fluorine-containing substances and removal of sulfates. Deposits are received at the flotation, where the separation of carbon and fluorine compounds-alumina, which is filtered, dried, and returned to the aluminium production. Fluoride-alumina mixture contains aluminum fluoride, cryolite and hilic (flowable cryolite). Carbon deposits come into the burning process via the new technologies. Perspective diagram of the sintering of the carbon lining of aluminum sulfate. However, it should be improved from the point of view of getting the best product for carbon, sodium and sulfur.

Keywords: aluminum electrolytic; lining waste; recycling, flotation.

INTRODUCTION

The scales of technogenic impact of aluminum plants on the environment is determined by the technical level of production. Therefore, the solution of environmental problems is directly related to the technical improvement of existing production. The spent cathode lining of aluminum electrolyzers consists of carbonaceous and aluminosilicate parts, impregnated with electrolyte melt, metal and products of interaction of the listed components. In addition, the spent lining has the most complex material composition. Domestic aluminum plants, when dismantled, remove metallic aluminum, steel blooms and a peripheral layer of refractory bricks, and are sent to landfills of solid industrial waste for storage. To date, there has not been proposed a universal technical solution that would solve all the problems associated with spent lining.

Program and methods of research trials

Table 1: Legend and abbreviations adopted in the text

FM	Flotation machine
LR	Laboratory Regulations
TD	Technological documentation
TP	Technological process
TO	Technological operation
TR	Process Requirements
NTD	Normative and technical documentation

Thermal extraction of fluorosols from spent refractory lining. Instrumental support of research.

Figure 1: Jaw crusher JD-6

Provides crushing of solid materials with an average size of 1mm with the minimum gap size.

Figure 2: Disk eraser DE-65

Provides grinding of brittle materials of different strength and hardness to an average particle size of 50 μm.

Figure 3: Electric muffle furnace EKPS-10

Provides heating and maintaining the temperature of 200-1300 ° C in programmable mode.

Figure 4: Wave X-ray fluorescence spectrometer S8 TIGER

Provides accurate express analysis of the elemental composition of the test substance

Figure 5: X-ray diffractometer Shimadzu XRD-7000 with system of polycapillary optics

Provides an accurate phase express analysis of the test substance

Procedure for conducting research

Study 1:

1.1 The refractory lining under investigation is crushed in a JD-6 crusher to a size <10 mm.

1.2. The material obtained after grinding is heated to temperatures of 1000-1300 ° C in a muffle furnace until the phases are obtained and separated into solid (aluminosilicates) and liquid (nNaF x m(AlF3)) phases.

1.3 We make the sintering of nNaF x m (AlF_3) + $Al_2(SO_4)_3$ + ... => $yAlF_3$ + ...

At each stage, samples are taken and analyzed

1.1. The test refractory lining is crushed in a JD-6 crusher to a size <10 mm

1.2. The material obtained after grinding is sintered in a muffle furnace with $Al_2(SO_4)_3$: nNaF x m(AlF_3) + $Al_2(SO_4)_3$ + ... => $yAlF_3$ + ...

At each stage, samples are taken and analyzed

3.1. The test refractory lining is crushed in a grinder JD-6 to a size <10 mm.

3.2. The material obtained after grinding is heated to a temperature of 1300 ° C with the evolution of HF (sublimation).

3.3. The captured gaseous HF is converted to a cryolite cooking solution: Na_2CO_3 + HF = NaF + $NaHCO_3$ + ...

3.4. We get cryolite from solution

3.5. We make sintering of nNaF x m(AlF_3) + Al2(SO_4)$_3$ +. => $yAlF_3$ + ...

Study 2, is performed in the absence of separation into solid and liquid phases in paragraph 1.1 of the research:

Study 3 is performed in the absence of isolation of AlF_3 in Study 2:

The structural scheme of the thermal separation of fluorosols from the aluminosilicate matrix and the investigations is shown in Figure 6.

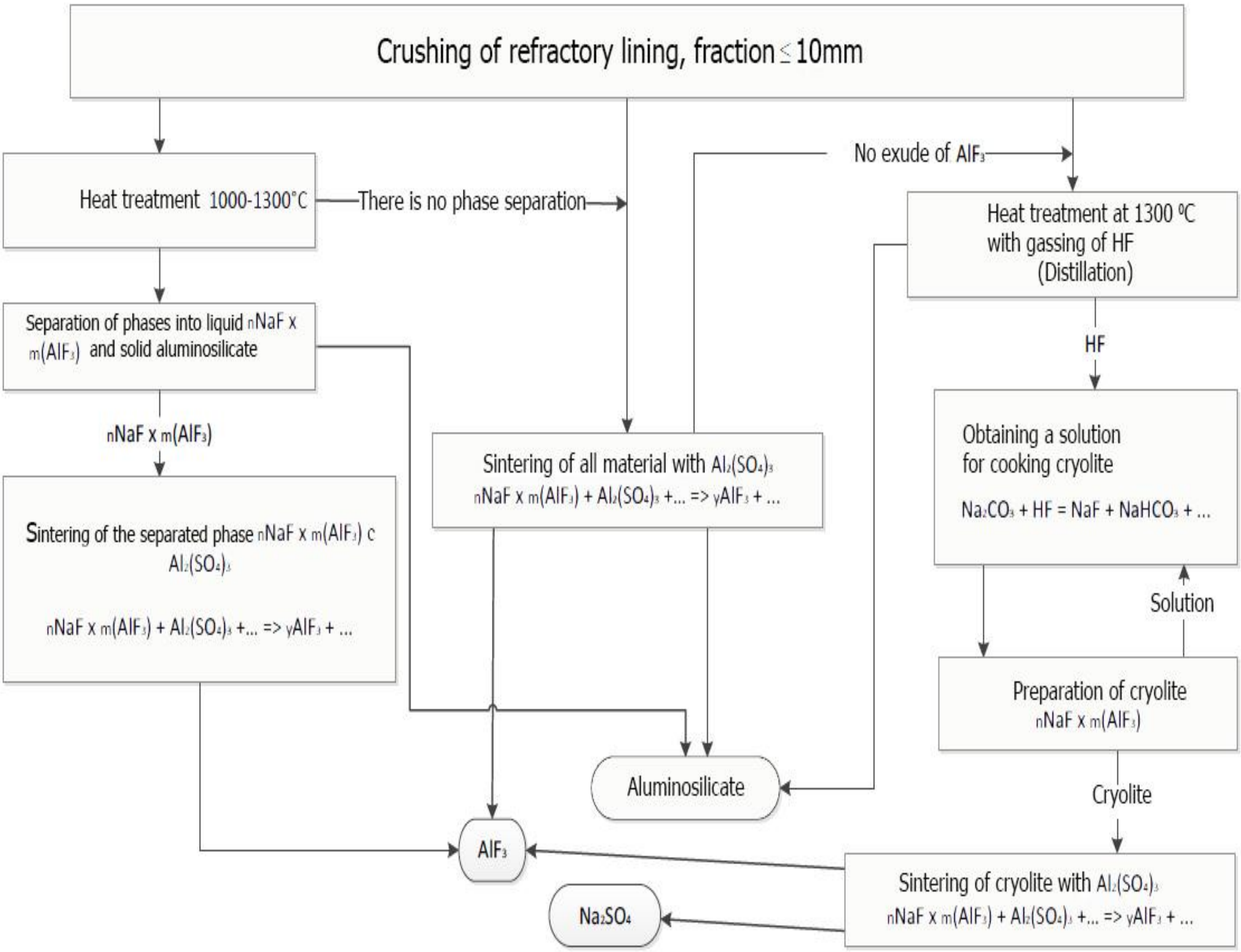

Figure 6: Structural scheme of thermal emission of fluorosols from an aluminosilicate matrix

Diagrams of the technological line of processing of refractory part of spent lining

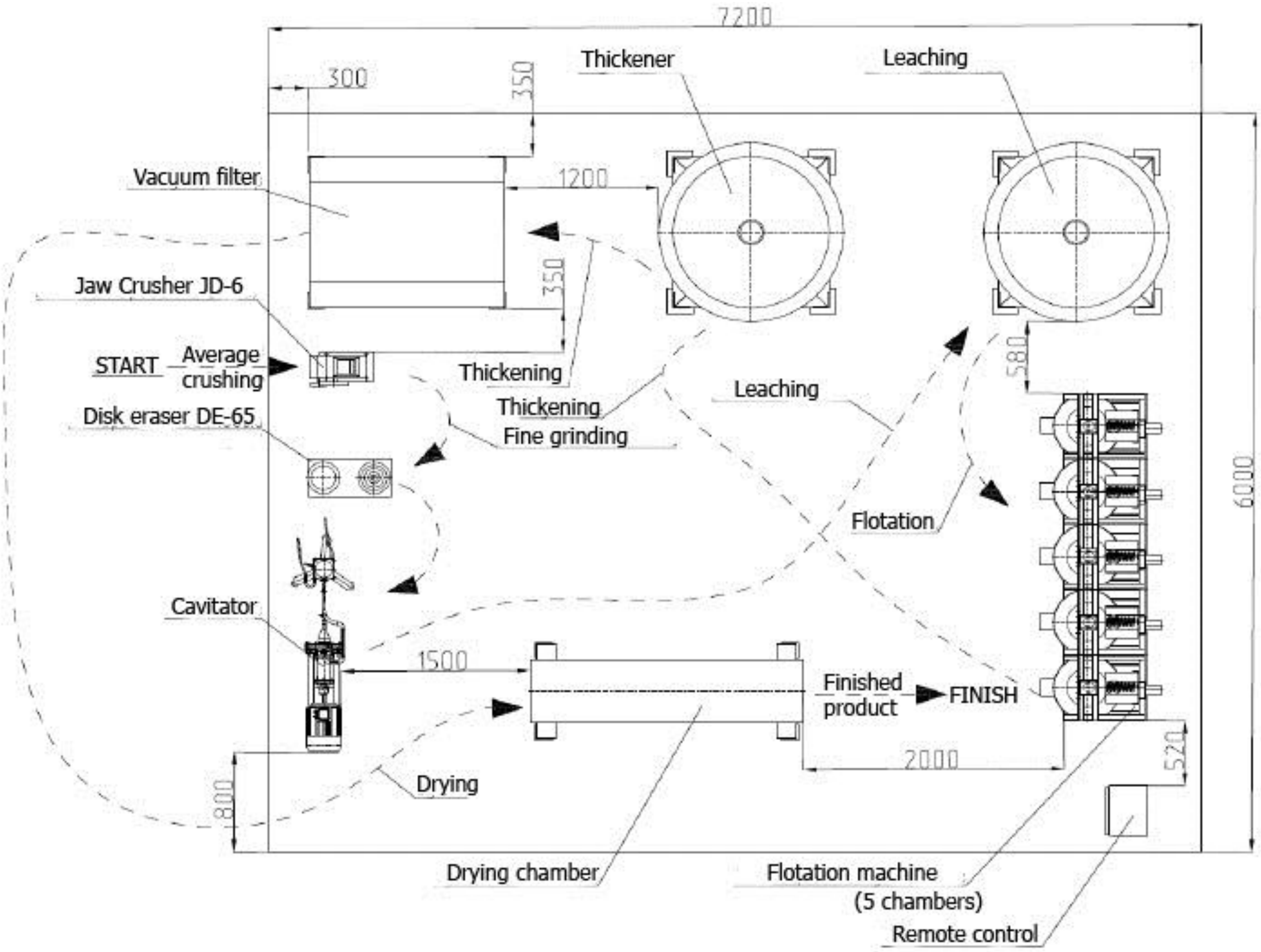

Figure 7: General outline of the equipment used.

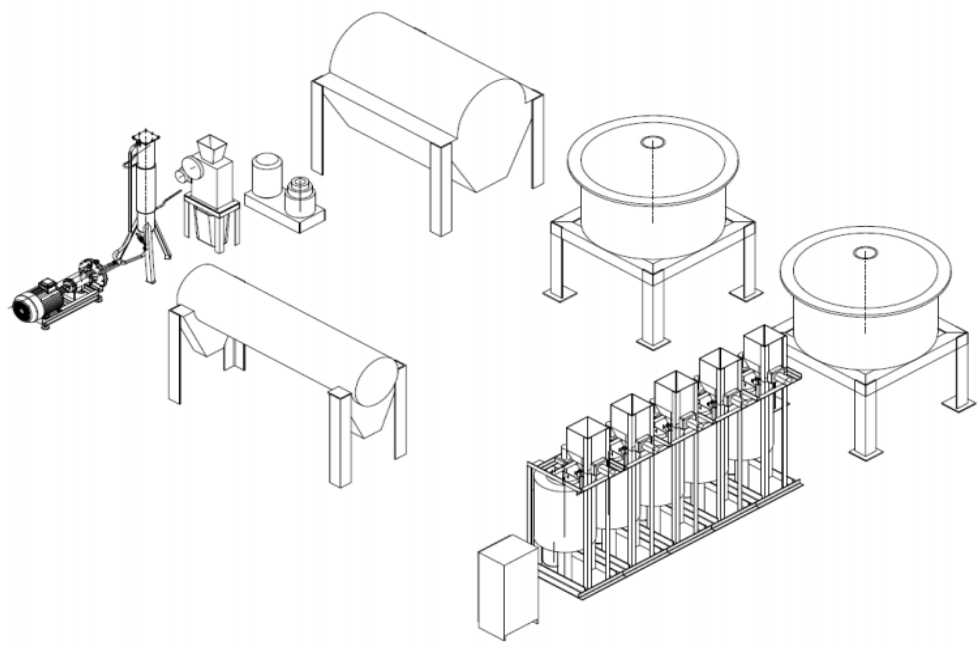

Figure 8: General view of the technological line.

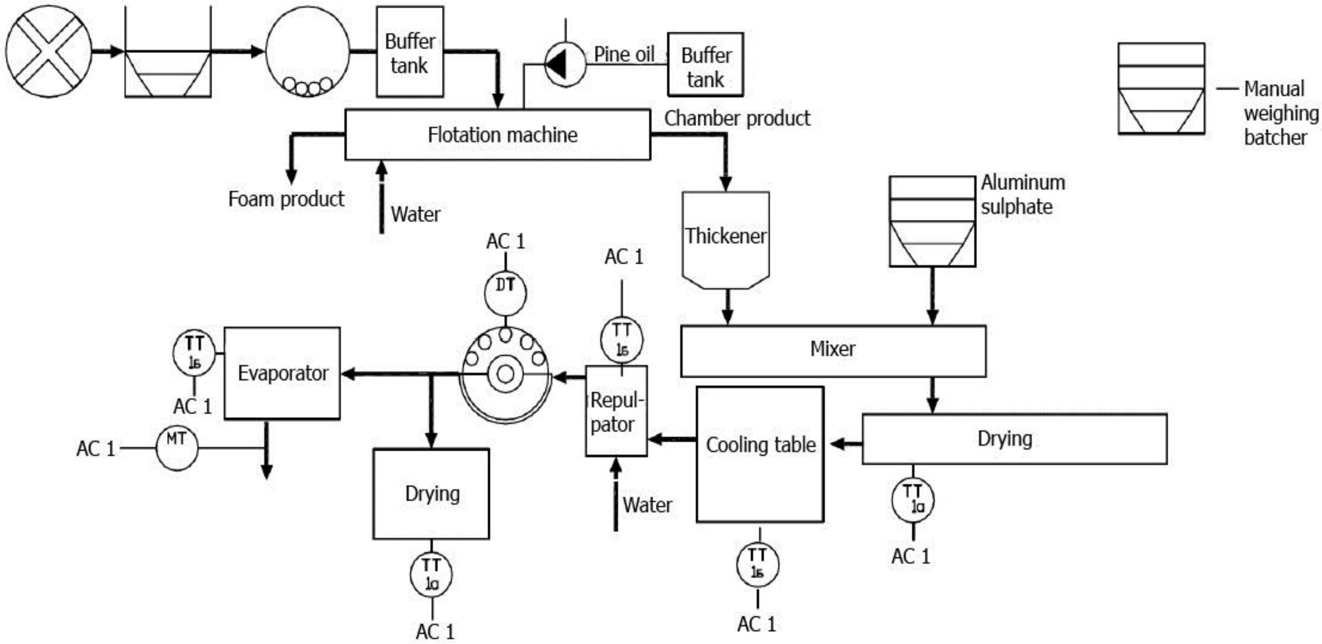

Figure 9: Instrument-technological scheme for processing of refractory part of spent lining.

Conducting research. Analysis of the samples of the spent lining

The most characteristic analyzes are given in Tables 2 and 3, with samples of cell No. 1634 with a service life of 70.4 months, selected on 02.06.2016. The samples are close to those previously studied. On the main significant components - fluorine, sodium and aluminum - the differences are within the previously established intervals. In fact, the SL of each cell has an individual composition, which is especially reflected in the content of aluminum, silicon magnesium and iron.

The carbonaceous part contains, by mass% C-65.0; F-9.3; Na-9.2; Mg = 0.1; Al-4.0; Si- 0.83; Ca -4.45; Fe - 0.85; K - 0.6. Characteristic features are: elevated carbon content and reduced aluminum and magnesium, but overall the sample is representative.

Refractory part in appearance and composition is divided into three parts: the layer under the blocks-lens and the reacted brick, the whole fireclay brick, the thermal insulation is diatomite. The layer under the blocks is formed by an electrolyte that penetrated through the hearth and dissolved part of the fireclay bricks. Contains sodium, aluminum, fluorine and silicon. The second part - fireclay bricks. A significant part of the brick is undisturbed and contains an insignificant amount of fluorine 0.2-1.5%. This is due to the resistance of chamotte to fluorine vapor. The third part is diatomite containing about 7% fluorine, which is due to the porous structure of the diatomite and its high specific surface area.

Table 2: Analysis of spent lining samples by scanning electron microscopy

Sample	C	O	F	Na	Mg	Al	Si	K	Ca	Ti	Fe	Total	Sample description
SLN704	0.80	53.90		0.68	6.68	20.78	15,76	0.15		0,48	0,79	100	Crushed fireclay bricks, chamotte second layer
SLN712	2.60	38.60	10.2	14.76	0.15	14.77	15.97	0.82	1.34	0.26	0.50	100	Layer under the blocks, the reacted chamotte or lens
SLN713	2.45	53.38		3.41		14.59	24.10	0.23		0.72	1.12	100	Refractory, second layer
SLN714	1.34	45.58	7.81	1.75	7.89	3.57	22.72	2.41	0.26	0.25	6.41	100	Diatomite, butt
SLN716	5.28	41.90	11.54	2.93	8.38	3.79	19.60	2.09	0.15		4.35	100	Diatomite, third layer
SLN718	3.36	44.39		1.34		10.18	17.44	0.09		0.83	22.37	100	Butt brick
SLN719	2.50	40.39	10.4	13.67		13.90	16.51	0.99	0.71	0.42	0.51	100	End of fireclay brick 3, brow
SLN722	2.16	50.28	4.80	5.04		12.13	23.41	0.34	0.27	0.56	1.01	100	Center brick under the lens, chamotte

Table 3: Results of X-ray fluorescence analysis of spent lining samples

Sample	C	F	Na	Mg	Al	Si	Ca	Fe	K	Sample description
SLR700		1.30	3.60	0.23	16.50	26.10	0.27	0.78	0.44	A mixture of the refractory part of the SL (SLN704 + SLN713 + SLN718 + SLN722 25% each)
SLN 716		6.90	3.00	8.40	4.50	22.40	0.47	7.20	3.00	Diatomite
SL900	65.00	9.30	9.20	0.10	4.00	0.83	4.45	0.85	0.60	Cores of the carbon part of the spent lining
SL950		0.20	2.20	0.30	16.50	26.90	0.68	1.90	0.44	A mixture of crushed refractory bricks
SLN 712	2.80	12.8	19.10	0.14	16.00	19.50	0.90	1.50	0.70	Layer under the blocks, the reacted chamotte or lens
SLN 719	3.20	20.6	17.20	0.12	16.30	16.80	0.70	0.70	0.90	End face reacted chamotte or lens from the end
SLR900		8.5	8.42	0.87	14.38	18.21	0.55	1.2	0.55	A mixture of refractory bricks and lenses

Pyrolytic methods of processing of carbon part of SL

Two thermal methods of reworking were studied - smelting of electrolyte and sintering of the carbon part with aluminum sulfate.

1. Electrolyte smelting

A successful experience of smelting from coal foam in an induction furnace suggests the possibility of a similar process for a carbon lining, but in a heating furnace it was not possible to obtain positive results. After mastering the induction furnace, the research will continue.

2. Sintering of the carbon part with aluminum sulfate at temperatures up to 700 ° C

Previous studies have been carried out on the processing of sodium fluoride and cryolite in aluminum fluoride during sintering with aluminum sulfate at a temperature of 500-700 ° C in accordance with the reactions:

Initially, the required amount of aluminum sulphate was determined to bind all the sodium to the sulfate. It was found that the excess aluminum sulphate should be 10-20% of the stoichiometry according to the reactions 1-3.

The processing conditions for the carbon part of the SL are listed in Table 4, the analysis of the initial reagents and products in Table 5. The proposed process flow diagram in Figure 1.

Table 4: Parameters of the processed carbon part by sintering with aluminum sulphate under laboratory conditions.

№	Name	Characteristic
1	The amount of lining SL 900	100 g
2	The amount of aluminum sulfate $Al_2(SO_4)_3$ * I8H_2O	60 g
3	Grinding degree of lining	- 0,2 mm
4	Sintering temperature	600 - 700°C
5	S: L in leaching	3:1
6	Leaching temperature	60°C

Table 5: Analysis of initial SL and products of processing.

№	Name	Analysis, wt. %					Phase composition
		C	F	Al	Na	SO4	
1	Initial SL	65,0	9,3	4,0	9,2	2,1	C, NaF, Na3AlF6, Na5AbFi4, AI2O3
2	Carbon sediment	82,0	2,2	1,7	2,4	3,3	C, AI2O3, Na2SO4, Na5Al3Fi4
3	Fluorine-alumina mixture	4,0	48,3	35,6	3,7	4,2	AIF3, Na5AbFi4, AI2O3

In accordance with the scheme, the carbon part is crushed and grinded to size 0.2 mm and dosed for mixing, where aluminum sulfate also enters. It is allowed to supply aluminum sulfate in the form of a pulp or solution. The mixture is fed to a furnace where it is sintered at a temperature of 600-700 ° C for an hour, cooled and fed to leaching with water to dissolve sodium. The pulp after the leaching enters the thickening. As a result of leaching, sodium sulphate passes into the solution and a small amount of fluorine and aluminum (aluminum fluoride and cryolite are sparingly soluble) solution is processed in the factory scheme for obtaining fluorosols and removing sulfates. The sediment is fed to the flotation, where the separation of carbon and the fluorine-alumina mixture takes place, which is filtered, dried and returned to the production of aluminum. The fluorine-alumina mixture contains aluminum fluoride, cryolite and chiolite (low-modulus cryolite). Carbon sediment enters the combustion process using a new technology.

Thus, the sintering scheme of the carbon part of the lining with aluminum sulphate is promising. Nevertheless, it needs to be improved in terms of obtaining a better product for the content of carbon, sodium and sulfur. Also, industrial tests are required.

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