Ways of Solving the Ecological Problem of Alluminium Smelting Hard Waste Disposal

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***Abstract*—Chemical composition and main physical-chemical characteristics (apparent density, electrical resistivity, thermal conductivity, compression strength) carbon cathode block samples of spent lining for aluminium electrolysis unit produced by OJSC "RUSAL Krasnoyarsk"; it is shown that to increase the bath service life it is necessary to form a crust to decrease alumina-cryolite melts penetration into electrolysis carbon cathode blocks which will reduce environmental impact.**

Keywords—aluminum smelting; ecology; industrial wastes; carbon lining

I. INTRODUCTION

Metallurgical industry is an integral part of Russian economy which develops constantly via technological process refinement, rich raw material sources, and practical fulfillment of complex objects [1]. Aluminium industry is one of the largest in Russian non-ferrous metallurgy; "RUSAL" activity is aimed at extraction of bauxite, alumina refining, and primary aluminum production, as well as powders and alloys on its basis. Company emploees together with scientists improve electrolysis technologies of alumina-cryolite melts for achieving high technical and economical indexes [2, 3], expansion of the raw material base [4, 5] and environmental improvement [6-9].

Alumina cryolite melts electrolysis is a main industrial process of primary aluminum production [10]. Alum earth is a source of aluminum, it is received from bauxitic and nephelinic raw material; medium for electrolysis is cryolite with plenty of aluminium fluoride (for achieving values of cryolite ratio 2.2÷2.4). Carbon is target material. Anode assembly for current supply to the melted zone may be equipped with prebaked anode, or anode formation is simultaneous with aluminum electrochemical reduction on the cathode [10], that is electrolysis is carried out on baths with c Soderberg anode (self-baking anode). One of the drawbacks of this method of primary aluminum production is big waste. Nowadays one of the main kinds of solid raw materials in aluminum production is spent lining. It contains carbon and graphite cathode blocks, side blocks, (4 class of hazard), chammote filing and chammote brick, dry barrier mix, socle bricks and others. Besides electrolyte components and metal aluminum penetrated into the carbon bottom, spent lining contains cyanide elements. Spent lining is damped on special polygons contaminating earth, as with rain it penetrates into the earth, water impacting the environment and living beings.

One of the ways to solve this ecological problem is increasing sell life which is determined by degree of destruction of carbon cathode blocks. The main reactions of cathode destruction are: surface reactions, chemical reactions in lining material, reactions with firebricks and insulation [11]. During cryolite-alumina melts electrolysis, cryolite consisting of cryolite, alum earth, calcium fluoride and magnesium, and small parts of some other elements, getting into the melt with alum earth and carbone anode ash, penetrates into carbone cathode blocks through interblock space. Carbon and graphite lining destruction is due to sodium penetration from electrolyte and its free ions, resulting in its widening caused by caused by constant electrolyte impact on bottom materials in view of non-wettability of the bottom with aluminum and pressure of the metal moving bed on cathode blocks surface. Formation of sodium and carbon interface connections is accompanied with volume increase that can result in local pressure increase and cracks formation. The degree of destruction depends on the amount of the absorbed sodium [11]. Penetration of this alkali metal into graphite layers and other carbon containing parts of the bottom nowadays is considered as diffusive movement of electrolyte with constant concentration [11-13]. One of the negative consequences of bottom coal matrix widening due to sodium penetration is microcracks development on the surface of cathode blocks when electrolyzer starts. After electrolyte penetration into the structure of cathode and side blocks there is consequent sodium penetration into cathode [12, 13]. One of the tasks of the after-start period is electrolyzer operating space formation (Fig. 1, [14]). Electrolyzer bottom should be covered with crust in the seam "side-anode" that will reduce electrolyte penetration in this zone into the final lining.

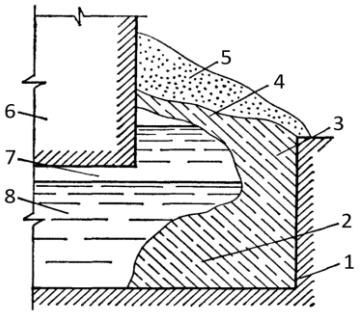


Fig. 1. Electrolyzer operating space scheme: 1 – lining; 2 – bottom crust; 3 – side scull; 4 – electrolytic crust; 5 – alumina filling; 6 – anode; 7 – electrolyte; 8 – aluminum.

The purpose of our research was studying chemical composition and main physical-mechanical characteristics of electrolyze carbone cathode block with Soderberg anode.

II. Methods and Materials

As the object of studies we chose carbone cathode block №8 of electrolyze cathode lining with Soderberg anode of S-8BM(E) type of OJSC "RUSAL Krasnoyarsk" RUSAL branch (Krasnoyarsk). Bath life is 14 months. In cathode assembly carbone cathode blocks of Novosibirsk electrode plant (NovEP), a part of "Energoprom company". This block dimensions are (mm): width is 550, length is 3660, and height is 380. Final lining selection from the upper layer was after cleaning the surface from dust, aluminum and electrolyte rests. Center marks of their carbon cathode blocks were drilled with a device of LLC "Cedima" (Russia).

We chose center marks from two zones of a block. Zone 1 is upper part of the carbone cathode block near electrolysis axial axis (center), zone 2 is upper side of the carbone cathode block in the zone of anode projection. Center marks from carbone cathode and interblock spaces are in Fig. 2.

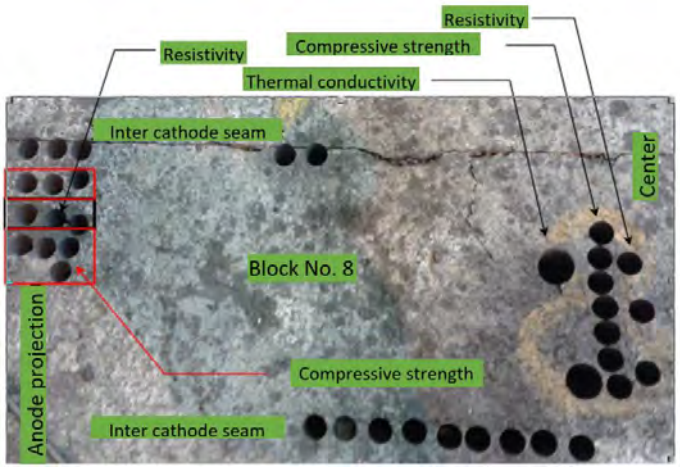


Fig. 2. Center marks from carbone cathode and interblock spaces with characteristics determined in these samples.

The exterior of the blocks for study is in Fig. 3.

For sample chemical composition analytical treatment the sample was ground with a jaw crusher JC10 and prepared for analysis with a disk grinder DG 65. The lining samples were analyzed with electron microscope Hitachi TM 3000, with X-Ray sensor SDD XFlash 430H. The samples were scanned with the electron microscope; the scanned area was 8 mm in diameter, the scanned depth was 1 mkm.

a

b

Fig. 3. Samples' exterior, from electrolyzer carbon cathode blocks: a – center; b – anode projection zone.

X-ray diffraction analysis (X-ray phase) analysis of the averaged sample of different center marks of the carbone cathode block №8 was done with diffractometer D8 ADVANCE Bruker (Germany), with Gebel mirror and detector VANTEC-1 PSD. Step-by-step shooting is done in angle range 2θ from 5 to 70°, with Cu_{α}-rays. Experimental conditions of the analysis are the following: 40 kW, 40 mA, layout – 1 s, step size – 0.02º 2θ. X-ray pattern estimation is done with diffractometer software. For phase identification powder pattern base was used PDF-2.

Carbon block sample stress test was done with a compression testing machine C040PN116 according to GOST R ISO 18515-2014 "Carbonic materials for aluminum smelting. Carbon cathode blocks and backed anodes. Compression strength test". Packed density measuring was done with the method of sizing according to GOST R ISO 12985-1-2014 "Carbonic materials for aluminum smelting. Carbon cathode blocks and backed anodes. Part 1. Packed density measuring with sizing". Method is in measuring geometric dimensions and oven-dried samples mass and calculated as sample mass to its volume. According to GOST

R ISO 11713-2014 “Carbonic materials for aluminum smelting. Carbon cathode blocks and backed anodes. When determining electric resistivity at ambient temperature electrical resistivity (ρ) of carbon cathode blocks was measured: through the sample of the specific cross section steady flow of direct current flew, voltage loss was measured between the sensors and ρ was calculated. Thermal conductivity was measured with a method of the dynamic λ–substitution calorimeter at the device IT-λ-400A, whose operation is based on the monotonous sample heating and temperature fixation.

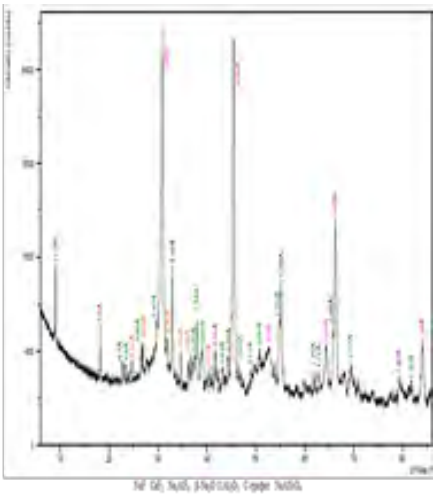


Fig 4. The results of X-ray structure analysis in the studied samples.

III. Results

By X-ray structure analysis in the studied samples of carbon cathode lining were determined the following phases: NaF (sodium fluoride), Na_3AlF_6 (cryolith), $NaAlSiO_4$ (nepheline), C (graphite), $Na_2O{\cdot}11Al_2O_3$ (sodium polialuminate) (Fig. 4).

According to previous research conducted by the authors the carbon part of the spent linen also contains $K_{1,44}Al_{10,88}O_{17,23}$ (potassium aluminate), CaF_2 (fluorite), $Na_5Al_3F_{14}$ (chiolite), Al (aluminum), $Fe(Fe1.24Ti0.61)O_4$ (titanomagnetite) [15]. Chemical composition of the spent coal lining for every electrolyzer is individual and depends on its service length, type and capacity of the bottom, electrolysis technological process, bottom assembly quality and start. Also, the spent cathode lining samples may contain NaCN and Na_4[Fe(CN) (sodium cyanide), AlN (aluminium nitride), Al_4C_3 (aluminium carbide), Al_3Fe (aluminide iron), hydroxide and carbonate of alkaline, alkaline earth metals and other components [16].

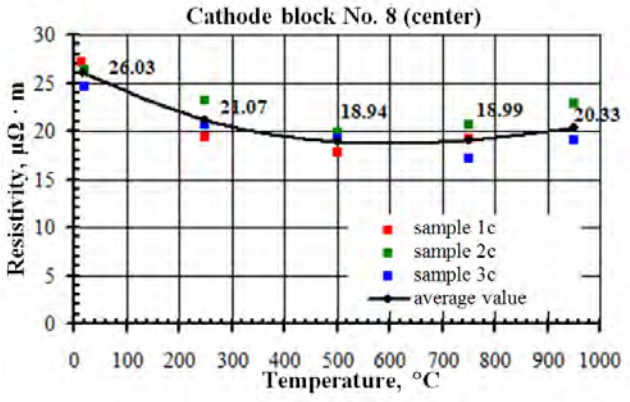
Carbon cathode blocks with electron microscopy scanning (Fig. 5) showed that the sample is heterogeneous by particle size and contains micro inclusions. There are well-developed fluoride crystals, aligned with aluminum carbide. There are also developed crystals of aluminium oxide.

Fig. 5. The surface of the center mark averaged sample from carbone cathode blocks center marks (scanning microscopy).

Value analysis of the apparent density of carbone cathode block samples along length and height showed that sodium saturation degree is different. So, average apparent density for samples from the block central part in the upper part of the central mark was 2.15 g/sm^3; at the depth 180-200 mm inwards the block is 1.94 g/sm^3. For carbon cathode block samples from anode projection zone is 2.1 g/sm^3 (upper part) and 2.06 g/sm^3 (at the depth 180-200 mm). The mean value of the apparent density of the original carbone cathode block produced by NovEP (before electrolyze start) is 1.54–1.59 g/sm^3.

The dependencies in Fig. 6 show that the values ρ of carbone cathode blocks samples of the bath used in electrolyze change with temperature increase. Test results of carbone cathode blocks on determining apparent density and electrical resistivity are in Table I.

As data in Table I show, ρ from samples of different parts of the spent carbone cathode block have close values. With test temperature increase ρ of samples from anode projection zone decreases smoothly and reaches 18.8 mkOm·m at 950°C (mean value of the three samples). The mean value ρ for three samples from the central part of carbon cathode block at the same test temperature was 20.33 mkOm·m. Changing nature of the dependence ρ at temperature increase for samples from the central part of the carbone cathode block can be caused by physico-chemical changes inside the samples during heating.



a

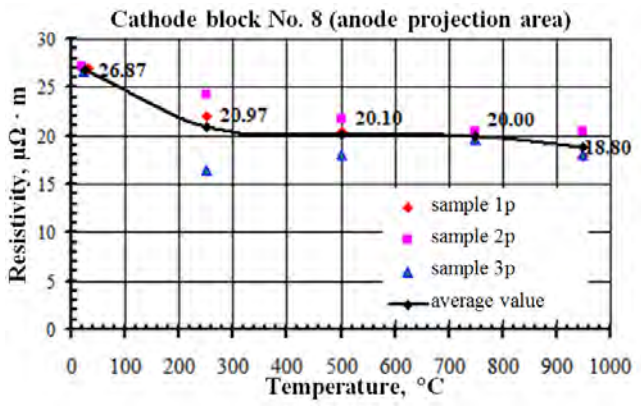


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Fig. 6. Results of measuring electrical resistivity of carbone cathode samples: а – center; б – anode projection zone.

TABLE I. TEST RESULTS OF CARBONE CATHODE BLOCKS ON DETERMINING APARENT DENSITY AND ELECTRIC RESISTIVITY

Material	Test temperature, °C		Electric resistivity, mkOm·m	Apparent density before and after the test, g/sm^3
Cathode block (center)	Sample 1	15.9	27.2	2.07/1.96
		250	19.4	
		500	17.81	
		750	19.2	
		950	19.1	
	Sample 2	19,3	26,3	2.09/2.04
		250	23,1	
		500	19,8	
		750	20,6	
		950	22,9	
	Sample 3	19.0	24.6	2.09/1.98
		250	20.7	
		500	19.2	
		750	17.16	
		950	19.0	
	Average	18.0	26.03	–
		250	21.07	
		500	18.94	
		750	18.99	
		950	20.33	
Cathode block (anode projection area)	Sample 1	31.7	26.9	2.26/1.98
		250	22.1	
		500	20.5	
		750	19.9	
		950	17.8	
	Sample 2	20.4	27.1	2.07/1.96
		250	24.3	
		500	21.7	
		750	20.5	
		950	20.5	
	Sample 3	22.3	26.6	2,07/1,94
		250	16.5	
		500	18.1	
		750	19.6	
		950	18.1	
	Average	24.8	26.87	–
		250	20.97	
		500	20.10	
		750	20.00	
		950	18.80	

We studied heat-physical characteristics of carbone cathode samples from the central part. The exterior of the samples before and after the test is in Fig. 7.

Test for determining thermal conductivity at standard temperature 20°C of the three samples (coded as 11.2, 12.1, 12.2 in Fig. 7) of the carbone cathode block showed that thermal conductivity in 14 months of electrolysis utilization did not change significantly comparing thermal conductivity of carbon cathode block by NovEP as sample for comparing: at temperature 20°C (thermal conductivity coefficient of all the cathode blocks samples is in range 9.0÷12.3 Wt/m·K).

With test temperature increase (to 950.7-955.0°C) sample thermal conductivity also increases (Table II). Differing from pure carbon materials thermal conductivity coefficient at the initial stage of heating (less than 300-400°C) changes disproportionally to the temperature increase, and there is slow change of this parameter.

a

b

Fig. 7. Exterior of carbone cathode block samples from electrolyzer: a – before thermal conductivity test; b – after the test.

After temperature 700°C there is a significant increase in thermal conductivity, which is caused by material structuring. Slow thermal conductivity increase of the electrolyzer carbone cathode block samples can be explained by other components – electrolyte components with different thermal conductivity coefficient values.

Compression strength tests of the carbone cathode blocks were conducted at different temperatures 20, 500, 700, 800, 900 and 950°C (Fig. 8).

TABLE II. RESULTS OF DETERMINING THERMAL CONDUCTIVITY COEFFICIENT AND CARBONE CATHODE BLOCK SAMPLES APPARENT DENSITY

Material	Test temperature, °C		Thermal conductivity, Wt/mK	Apparent density before/after test, g/sm^3
Initial cathode block (NovEP)	20.0		9.0÷12.3	1.94
Cathode block (center)	Sample 11 - 2	178.9	14.77	1.98/1.93
		314.3	15.21	
		502.1	14.76	
		700.3	17.02	
		889.4	20.52	
		955.0	21.30	
	Sample 12-1	151,3	10.02	2.06/1.95
		306.9	11.58	
		502.3	11.66	
		705.2	14.54	
		901.5	22.36	
		952.1	23.00	
	Sample 12-2	136.1	7.14	2.11/2.03
		305.2	8.36	
		502.7	9.45	
		704.9	12.33	
		901.7	18.78	
		950.7	22.01	

Compression test of the samples from different parts of the carbone cathode block decreases after electrolyzer utilization with increasing test temperature. Data in Fig. 8 show that cathode assembly sample strength from the utilized bath is higher at temperature 20°C, than the strength of the initial carbon block sample 1.76 times. It can be caused by denser structure and other components of carbone cathode block electrolyte. At test temperature 950°C sample strength from different parts of carbone cathode block is 1.3-1.4 times less than initial block strength produced by NovEp.

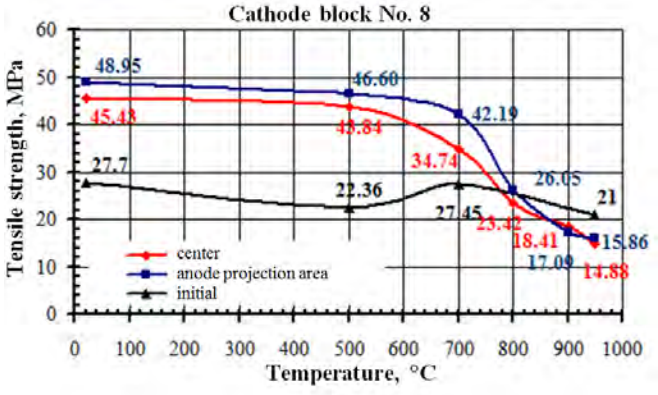

Fig. 8. Test results on temperature influence on the strength of different carbone cathode blocks samples.

Sample strength decrease at high temperature is caused by trace constituents devolatilizing from the cathode block and destruction of the structure entity of the carbon material.

Tests at different temperatures of physico-chemical characteristics of carbone cathode block of the central part and from anode electrolyzer anode projection showed worsening of some properties due to penetration of electrolyte components penetration into carbon matrix, mostly sodium salts. But protecting crust along the perimeter of cathode increases the cell life that is less bottom destruction due to electrolyte components penetration.

Correctly utilized electrolyzer must have a protective crust at the bottom but it is not always possible at the beginning of utilization of the bath. Most manufactures think that electrolyte saturation and sodium penetration into the cathode lining is inevitable. Electrolyzer is started at high cryolite ratio (2.9-3.0), low alum earth concentration and high temperatures [11]. According to commercial operation in the course of time there appear sediments on the bottom of electrolysis, and crusts flow under anode projection that results in less penetration of electrolyte components into the bottom. Electrolysis service life dependence on crust length (according to PC "RUSAL Krasnoyarsk") is in Table III.

TABLE III. RESULTS OF DETERMINING THERMAL CONDUCTIVITY COEFFICIENT AND APPARENT DENSITY OF THE CARBONE CATHODE BLOCK

Parameter	Electrolyzer S-8Bm(E)	
Service time, months.	6-12	55-60
Crust average length, sm	71	111

Crust average thickness will depend on thermal conductivity coefficient between it and electrolyte. As it values are 30-50% higher in zones with high speed of electrolyte flow the thickness of crust at the part of cathode block from anode projection is higher.

IV. CONCLUSION

During primary aluminum production in alumina cryolite melts electrolysis carbon cathode lining is saturated with electrolysis, mostly sodium fluoride, and metallic aluminum, aluminium carbide, alum earth and other contaminating elements.

We studied samples of cathode electrolyze block S-8BM(E) PC "RUSAL Krasnoyarsk" from the central part and from anode projection. Carbon blocks saturation with constituting components impacts main physico-chemical characteristics. It has been determined that apparent density of the lining samples (from both sides of carbone cathode block) at temperature increase decreases. Studying temperature impact on electric resistivity of the studied samples from different zones of carbone cathode blocks insignificant difference has been determined in this criterion. Thermal conductivity values of carbone cathode block at ambient temperature before utilization and after 14 months of bath utilization do not differ. Slow thermal conductivity increase of the studied electrolyzer spent carbone cathode block was caused by other components – electrolyte components which saturated pores of carbon containing bottom. Compression strength of the samples from anode projection zone before the test is higher than this parameter of samples from the central part of carbone cathode block (48.95 MPa versus 45.45 MPa), that evidences less saturation of this samples with electrolyte (lining). In the course of electrolyzer service crust flow under anode projection, that results in less penetration of electrolyte components into the bottom. So, increasing electrolyzer

service life we can decrease the volume of carbon linen, containing contaminating electrolyte components and electrolyze products, that reduces volumes of industrial wastes of primary aluminum production, and consequently reduces contamination of the environment close to aluminum producing enterprises.

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