A New Lining Material for Aluminum Electrolysis Cells that Can be Recycled

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Abstract

The paper discusses several technical, environmental and economic problems related to lining materials used in aluminum reduction cells, including the possibility to re-cycle them. The paper suggests that lignite semi-coke be used instead of conventional thermal insulation materials and refractory bricks. It also discusses the method of preparation of such a material and the results of laboratory studies of the properties of the material. The paper describes the equipment and technology used to apply this new lining material; it discusses original compacting equipment that can be used for un-shaped refractory materials. Also, the barrier layer properties are given. Moreover, the authors describe the concept of the cell that uses the new lining material, including the results of industrial pilot tests of such a cell. Furthermore, the paper discusses the results of an autopsy of an 887-day-old cell, in which lignite semi-coke was used. It was found out that 80% of the new lining material can be re-used, which improves both the environmental safety and economic efficiency of the process of aluminum production.

Keywords: Cell lining materials; electrolysis cells; lignite semi-coke for cell lining; cell lining material recycling.

1. Introduction

The world's amount of SPL in the existing dumps is several tens of millions of tonnes and it increases by 1.7 million tonnes annually [1]. About 30 % of this material is spent aluminosilicate refractory and insulating materials. A significant number of publications cover different methods to dispose and recycle such materials [2 - 5]. However, so far, the value of the regenerated product has not exceeded the cost of processing, and there is no cost-effective and environmentally friendly solution of this problem, yet.

One of the possible solutions is the use of lignite semi-coke as an insulation and, partially, refractory material, including its subsequent recycling. At an industrial level, lignite semi-coke is produced by the oxidizing carbonization of low-ash, low-sulfur coal in the boiler, including fluidized bed combustion at temperatures of 700 -8 00 °C [6]. This allows generating flammable gases and a solid product with a low volatile content. This paper contains the results of studying the possibility of using lignite semi-coke as a lining material of the cathode in the aluminum reduction cell.

2. Experimental

With the help of optical microscopy, electron microscopy, and integrated thermal analyses, lignite semi-coke was investigated; both in its initial state and after 30 months of cell operation. An EVO 50 Carl Zeiss electron microscope (Germany) and an INCA 350 energy-analyzer (UK) were used. The diffraction pattern was recorded with a PW1800 Philips X-ray diffractometer. Phase identification and quantitative X-ray phase (diffraction) analyses of the samples taken were made with the help of an information retrieval system for X-ray phase identification [7] and a database of X-ray references of inorganic phases and minerals [8], including 115 thousand standards. The content of cyanides was determined in a specialized environmental lab (TsLATI) as per the methodology used by the State Environmental Monitoring Authority (PND F 16.1:2:2.2:2.3:3.70-10), by means of a photometric method with the use of pyridine and barbituric acid [9].

The integrated thermal analysis of the samples was conducted by means of using STA 449 Jupiter (NETZSCH), a thermal analyzer that simultaneously measures mass changes (TG) and heat flows (differential scanning calorimetry) and is combined with QMS 403 Aeolos (NETZSCH), a quadrupole mass spectrometer that analyzes gases released during the process of heating samples. Samples were heated from 40 °C to 1 000 ° C, at a rate of 10 °C/min, in the air, as per a temperature program. The quadrupole mass spectrometer (electron ionization) was connected to the STA 449 Jupiter via a gas line that feeds gases at a constant temperature of 230 °C. The data obtained by using the mass spectrometer were combined, on a software basis, with the data from the STA 449 Jupiter. In order to estimate the thermal conductivity of un-shaped materials, a method of non-stationary heat control was used, as per GOST 30256-94 by means of using a MIT-1 cylindrical probe. Thermal properties (at different temperatures) were determined by using LFA 457 (NETZSCH) (a laser flash method). For the studies, semi-coke samples were used. They were placed in a special cell, which excluded any access of oxygen. Chemical resistance was determined both to sodium and to the combined effect of aluminum, sodium and the bath. Research on the combined effect of the above aggressive components was carried out according to the methodology proposed by Tabereaux [10].

2.1. Laboratory testing

Lignite semi-coke was used as a test material. Semi-coke was produced as per the TERMOKOKS-KS technology, which provides for partial gasification of coal in a fluidized bed at temperatures of 750 – 800 °C in order to remove moisture and volatiles. The product of pyrolysis of the Berezovsky MK-1 lignite – the semi-coke – has a dull gray or blackish color and a highly porous structure. The studies showed that more than 90 % of the mass of the initial lignite semi-coke was in a substantially amorphous state. The semi-coke's characteristics are given in Tables 1 - 3.

Table 1. Granulometry of lignite semi-coke.

Parameter	Value
Granulometry (%) by class (mm):	
> 1	10.5
1 - 0.315	51.1
0.315 - 0.2	16.1
0.2 - 0.1	16.7
0.1 - 0.063	1.1
0.063 - 0.056	1.8
< 0.056	2.7

Table 2. Technical properties of sample of lignite semi-coke.

Parameter	Value
Moisture (%)	3.7
Ash (%)	9.9
VMC (%)	6.0

Table 3. Elemental composition of lignite semi-coke.

Parameter	Value
Elemental composition, as dry and ash-free (%):	
C^{daf}	94.05
H^{daf}	1.20
N^{daf}	1.32
O^{daf}	3.20
S^{daf}	0.23

Analyses of micrographs of the initial lignite semi-coke showed that, in terms of morphology (structure, porosity and specific surface area), the semi-coke particles have significant differences. According to the above, the particles were classified in several groups: Group 1 – large, monolithic particles with sufficiently clear boundaries (Figure 1, a); Group 2 – a better developed specific surface area, particles were represented by agglomerates with a layered structure (Figure 1, b). Also, "loose" particles were observed (Figure 1, c). And Figure 1, d shows regular-habit particles with a regular-habit pore system. The observed differences are probably due to different conditions of high temperature treatment of lignite particles in a fluidized bed. The studies of the porous structure showed that the area of closed pores varied from 17 to 32 %, and the total porosity varied in the range of 50 – 65 %. The optimal density of heat-insulating layers (made of unshaped materials) was determined based on meeting the conflicting requirements for the thermal conductivity and admissible deformation coefficient. At a density of the initial lignite semi-coke of 510 to 650 kg/m^3, the thermal conductivity was in the range of 0.112 to 0.133 W/(mK).

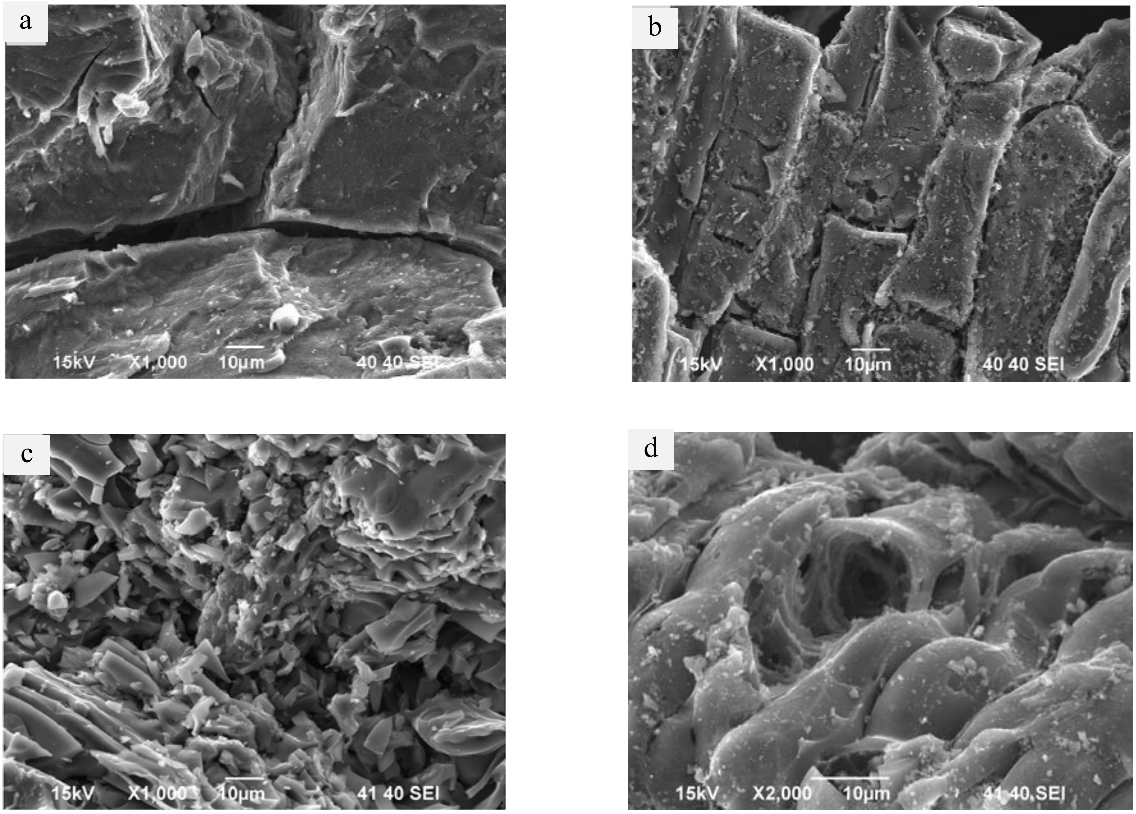

Figure 1. SEM photos of the initial lignite semi-coke, zoomed in x1000 (a, b, c) and x2000 (d).

In order to evaluate the chemical resistance of lignite semi-coke, and its appropriateness for use as a lining material, tests were run to check its resistance to sodium and the combined effect of sodium and fluorides. Ampoules with metallic sodium and samples of lignite semi-coke were placed in a hermetically sealable container with a tube, through which air was being evacuated from the working chamber until the pressure became 0.1 - 10 Pa. After that, the tube was welded, the sodium ampoules were broken without de-sealing the chamber and the container with the samples and molten metal was placed in a two-section electric furnace. The amount of metal introduced into the container was determined based on the difference between the mass of the sodium ampoules and their fragments.

It was found out that the sodium content in the semi-coke samples was increasing monotonically with time – from 0.02 % (at 2 hours) to 0.0774 % (at a retention time of up to 24 hours) (Figure 2). A digital camera was used to evaluate the spreading rate of the bath over the surface of the semi-coke previously compacted to 670 kg/m^3, and the change in the contact angles of the bath. The spreading rate was low, and the contact angles reached the equilibrium (~ 60 degrees) after 80 to 90 seconds. However, the rate of wetting of semi-coke with the bath doubled from 5 to 10 degrees/min for a semi-coke sample treated with sodium within 20 hours at 1 227 K at a vapor pressure of 121.59 kPa.

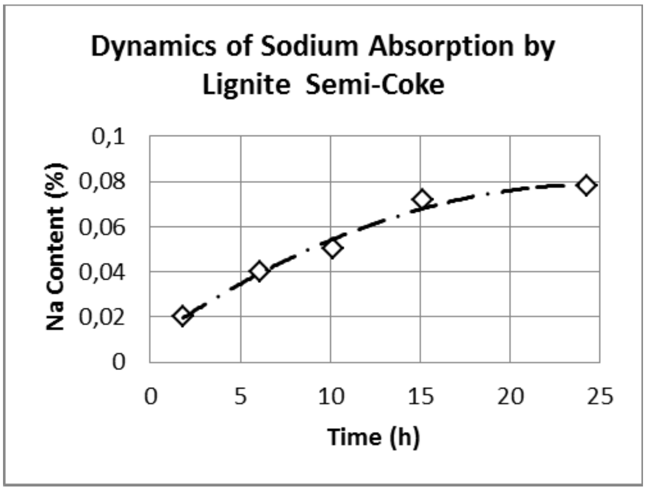

Figure 2. Dynamics of sodium absorption by lignite semi-coke.

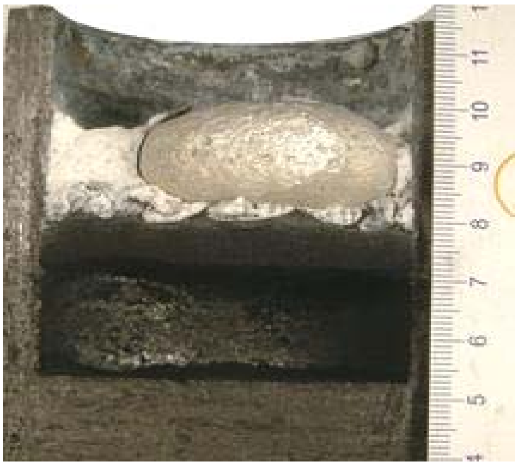

Figure 3. View of cells with digital camera after the test for cryolite.

During tests for resistance to cryolite, it was found out that, within 24 hours, the lignite semi-coke compacted to 740 kg/m^3 started to have a monolithic white crust, the depth of which was ~ 7 % of the initial sample height. The lower layer, the height of which was ~ 22 %, had poor impregnation and could be easily destroyed. The amount of the bath that penetrated the sample was 19.76 grams, where 1 g accrues to poor impregnation. The lower part of lignite semi-coke, with a height of more than 70 %, almost retained its properties; and after cutting the crucible, it freely spilled out of the crucible (Figure 3). The XRD analysis showed that carbon in a highly impregnated material was represented by graphitized carbon but it remained amorphous carbon in the poorly impregnated and lower parts.

After testing the combined barrier mixture (consisting of 12 % lignite semi-coke and the PSh-1 aluminosilicate powder) for resistance to cryolite, three zones could be distinguished. The top layer (~ 15 – 16 % of the total sample's height) became of a light color and turned into a solid monolith. The intermediate layer, a poorly impregnated zone, is located under the upper zone, and is 28 – 29 % thick. The lower zone with a thickness of 55 – 56 % was barely exposed to interaction, and it easily spilled out after cutting the crucible. A sample from the lower layer barely transformed and was close, in terms of chemical composition, to the initial material. The mullite content was at a level of 70 % wt. The average sodium content in the lower layer of the sample was approximately ~ 0.7 %. This indicates that atomic sodium penetrated the carbon-filled chamotte material due to gas diffusion processes. The Na content in the upper and medium layers was 15.1 % and 5.4 % respectively. The drastic decrease in the sodium concentration, when going from the area of inter-phase contact and deep into the carbon-chamotte material, indicates a high resistance and chemical inertness of the latter, given the characteristics of its structure (in comparison with compact materials). Further formation of nepheline and albite phases slowed down the process of degradation and carbon graphitization, as evidenced by the results of chemical and X-ray analyses of the PSh-1 sample doped with 12 % wt. of lignite semi-coke. The results of the quantitative X-ray diffraction analysis (on conversion to ‘elemental composition’) are in good agreement with the data of the above chemical analyses. In the upper part of the sample, carbon was in the form of graphite, the content of which reduced down to ~ 6 % due to the dilution of the sample with cryolite. Traces of mullite and nepheline were visible, but there were no specific albite lines. More than a half of the middle part of the sample consisted of nepheline and albite. There was a high content of mullite (26.8 %).

2.2. Experimental studies in an industrial cell

The behavior of un-shaped materials was investigated in two PB cells operating at 175 kA. In one of the cells (Cell A), a combined barrier material (CDBM), containing lignite semi-coke, was investigated. In another cell (Cell B), lignite semi-coke was primarily used as an insulation material. The refractory lining of Cell A consisted of 2 layers of insulation, two layers of chamotte bricks and a barrier layer made of a combined mixture of lignite semi-coke and chamotte powder (CDBM). The Cell B lining consisted of a layer of insulation, made with the use of lignite semi-coke and an upper layer of an aluminosilicate dry barrier mixture. The cell design characteristics are given in Table 4; the physical and chemical properties and the grain size distribution of CDBM are shown in Table 5.

Table 4. Cell design characteristics.

Type of cell	A	B
Life time (days)	2 331	887
Apparent porosity of carbon blocks (%)	18.3	
Type of DBM	CDBM	DBM E-50
Type of refractory	Firebrick	Lignite semi-coke
Type of insulation	Vermiculite	Lignite semi-coke

Table 5. Physical and chemical properties and grain size distribution of CDBM.

Parameter	Value
Al_2O_3 Mass fraction on a calcined basis (%)	30 - 35
SiO_2 mass fraction on a calcined basis (%)	60 - 62
Semi-coke mass fraction (%)	25 - 30
Apparent density (kg/m^3)	1 300
Granulometry distribution (GSD) (%):	
3 - 1 mm	38.2
1 - 0.5 mm	14.6
0.5 - 0.1 mm	9.0
0.1 - 0.063 mm	14.6
Less than 0.063 mm	23.6

During the first two years, the temperature of the bottom of Cell A was lower by 15 - 20 °C than that of the reference cathode. Cell A was in operation for 2 331 days and was shut down because of a local temperature rise in the bottom, and iron in aluminum. The autopsy results showed that it was due to the contact of aluminum with the shell at the downstream end, but not due to aluminum penetration into the zone below the cathode. Horizontal cracking of the cathode blocks along the back side of the cell was observed. It began after a multi-day emergency down-time. This led to an increased infiltration of fluorides and a rise in the local temperature of the bottom. During 6 years of operation, CDBM was completely impregnated by fluorides, but the insulation was in good condition (Figure 4) and provided for the required heat balance of the cell. The thickness of CDBM increased (in terms of height) only by 40 mm (Figure 5), resulting in a minimum deformation of the collector bars. The content of cyanides right under the blocks in CDBM was ~ 0.4 %.

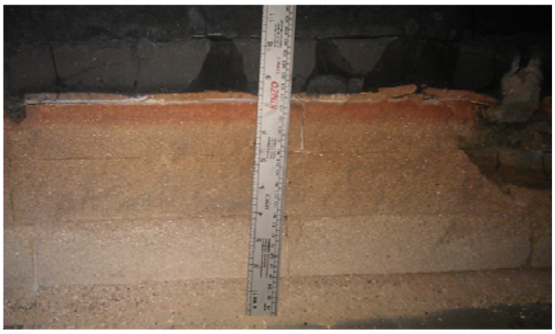

Figure 4. Condition of Insulation and Refractory Bricks, Cathode of Cell A.

Figure 5. Condition of CDBM after 2,331 days of operation, Cathode of Cell A.

Cell B was the first cell, in which only un-shaped materials were used under the cathode – an aluminosilicate dry barrier mixture and lignite semi-coke. The average density of lignite semi-coke was ~ 700 kg/m^3. Above the semi-coke, there was a high-density dry barrier mixture (E-50). The porosity of the dry barrier mixture compacted by the specially developed equipment and as per the special technology [7], was 17 - 19 %.

After 889 days, the cell was shut down for a scheduled assessment of the state of the lining materials. The autopsy showed the lignite semi-coke transformed into a three-layer material. Above and below, it was powder-like. In the middle, it had a binded monolithic structure with a dark oily hue. The same material in the peripheral zone can be characterized as monolithic, in terms of structure, and more durable from a mechanical point of view. The thickness of the monolithic material was minimal at the center and increased as it approached the periphery of the cathode. Its re-use without further treatment was impossible. Its total quantity was ~ 20 %.

The material composition analysis of the lignite semi-coke taken from the central and peripheral (at a distance of a quarter of the length of the block from the cathode side) areas showed that its major part (up to 75 – 80 % of the total weight) retained its initial properties, and consisted mainly of carbon ~ 95 %, including carbon in the form of graphite – 6.25 % (Table 6). Compounds such as calcite, calcium oxide and silica were found. In the peripheral zone, 11.15 % of monolithic sodium carbonate was formed. The total carbon content was 81.73 %; the amount of carbon in the form of graphite was 5.13 %. Cyanides were not detected in the central zone in either XRD or XRF scans. The cyanide concentration, determined by an independent photometrical method, was 0.12 % in the center and 0.43 % in the peripheral zone. The calcium oxide and carbonate content, both in the central and peripheral zones, was approximately equal. There were no fluorides in the lower part of the lining. The upper monolithic zone consisted primarily of sodium carbonate (Table 7), the sodium carbonate content was higher in the peripheral portion than in the center (59.4 and 58.5 % respectively). The concentration of cyanides in this area, determined by a photometric method, was 4.3 %. There were no fluorides both in the middle and lower parts of the lining.

Table 6. X-Ray Diffraction analysis of material composition of lower lining layers of Cell B.

Formula	Mineral Name	Center	Periphery
C	Carbon	88.7	76.6
C	Graphite	6.25	5.13
CaO	Lime	1.13	3.04
Na_2CO_3	Gregoryite, syn	0	1.15
Na_2CO_3		0	10.3
$CaCO_3$	Calcite	2.06	2.57
$CaMg_{0.7}Fe_{0.3}(CO_3)_2$	Dolomite	0	0.28
NaCN		0	0.76
SiO_2	Quartz	1.75	0

Table 7. X-Ray Diffraction analysis of material composition of middle lining layers of Cell B.

Formula	Mineral Name	Center	Periphery
C	Carbon	33.1	31.5
C	Graphite	0.96	1.96
CaO	Lime	4.41	6.32
Na_2CO_3	Gregoryite, syn	3.48	5.4
Na_2CO_3		25.9	0
Na_2CO_3	Natrite	30.1	54
$CaMg_{0.7}Fe_{0.3}(CO_3)_2$	Dolomite	1.85	0.67

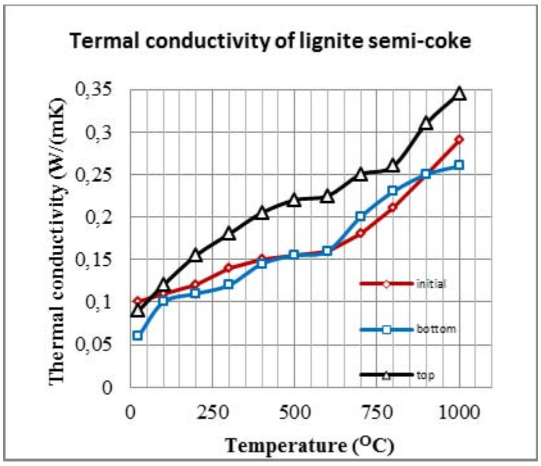

Figure 6. Thermal conductivity of lignite semi-coke.

The upper zone was powder-like. According to the X-ray analysis, the powder (Table 8) consisted primarily of carbon (56.43 %); 2.53 % was represented by graphite. The distinctive elements found in the upper zone were sodium fluoride, the concentration of which was 4.9 %, and a high content of calcium compounds, the content of which reached 16.8 %. In the upper zone, cyanate in the amount of 1.83 % was found. The sodium cyanide content was 5.2 % (photometric method).

The thermal properties of the lining materials after 30 months of operation were studied right on site by using the MIT-1 equipment. The study showed that the thermal conductivity of the main material – the lower layer – was equal to 0.09 W/(mK); for the monolithic middle layer, the thermal conductivity coefficient increased up to 0.5 W/(mK); and for the upper layer, it was 0.13 W/(mK). The coefficients of thermal conductivity of the initial semi-coke, and the spent semi-coke from the lower and upper parts of the lining, defined by LFA 457 at different temperatures, are shown in Figure 6.

Table 8. X-Ray Diffraction analysis of material composition of upper lining layers of Cell B.

Formula	**Mineral Name**	**Upper**
C	Carbon	53.9
C	Graphite	2.53
CaO	Lime	13.8
NaF	Villiaumite, syn	4.9
$CaCO_3$	Calcite	2.97
NaCN		7.38
NaOCN		1.83
MgO	Periclase	3.93
SiO_2	Quartz	2.52
$Ca_{8.68} Na_{0.62} (Al_6O_{18})$		5.25
Fe	Iron	0.91

The integrated thermal analysis of a semi-coke sample taken from the middle layer of the lining of cell B showed that (Figure 7), the mass of the sample, when heated to 200°C, was decreasing due to the loss of the adsorbed moisture, which was 1.4 %. At 249.7 °C, there was a slight exothermic effect. Then, at a temperature of 315.8 °C, there was another, but a more significant exoeffect. In the same temperature range, the sample mass increased by 2.8 %. In the temperature range of 350 to 600 °C, the sample mass continued to increase (another 2.5 %). At higher temperatures, the intensive burning and the reduction of the sample mass were taking place. They were accompanied by the release of the following gases: CO_2, NO and NO_2.

3. **Discussion**

The studies have shown that the use of the product of pyrolysis of lignite (semi-coke) as an insulating and, partially, refractory material for the cell's cathode is motivated by such properties as low thermal conductivity, high chemical stability (both with respect to sodium and the combined effect of fluorides, aluminum and sodium).

According to the studies by Oye [4] regarding sodium absorption by commercial cathode materials, the gas-calcined anthracite filler, containing 30 % of graphite, absorbs 5 % of sodium; the graphite filler material, calcined at 1 200 °C, contained 1.5 % Na; the petroleum coke, heat-treated at 2 300 °C, had 0.3 % sodium. The studies have shown lignite semi-coke adsorbs 4 times less atomic sodium than high-temperature petroleum coke. This is confirmed by the studies conducted earlier by M. Rapoport [12]. It was shown that non-graphitic carbon and carbon that cannot be subject to homogeneous thermal graphitization – coal of the lowest metamorphic degree and semi-coke from such coal – had a large amount of strong cross bonds that impede the mobility of carbon flat layers, and, hence, the penetration of sodium into the interlayer space. However, it should be noted that the spread of the melt over the surface of the powder-like lignite semi-coke can be not so much due to the material resistivity but due to the formation of a low melting phase due to the interaction of the mineral component of the lignite semi-coke, represented mainly by calcium oxide, with the components of the molten bath. The monolithic material is located in the space between the 850 °C isotherm (which corresponds to the liquidus temperature of sodium carbonate) and the 540 °C isotherm (condensation temperature of sodium during operation of the pit). In the lower layers, powder-like lignite semi-coke changes its properties just slightly and can therefore be subjected to recycling without any additional processing.

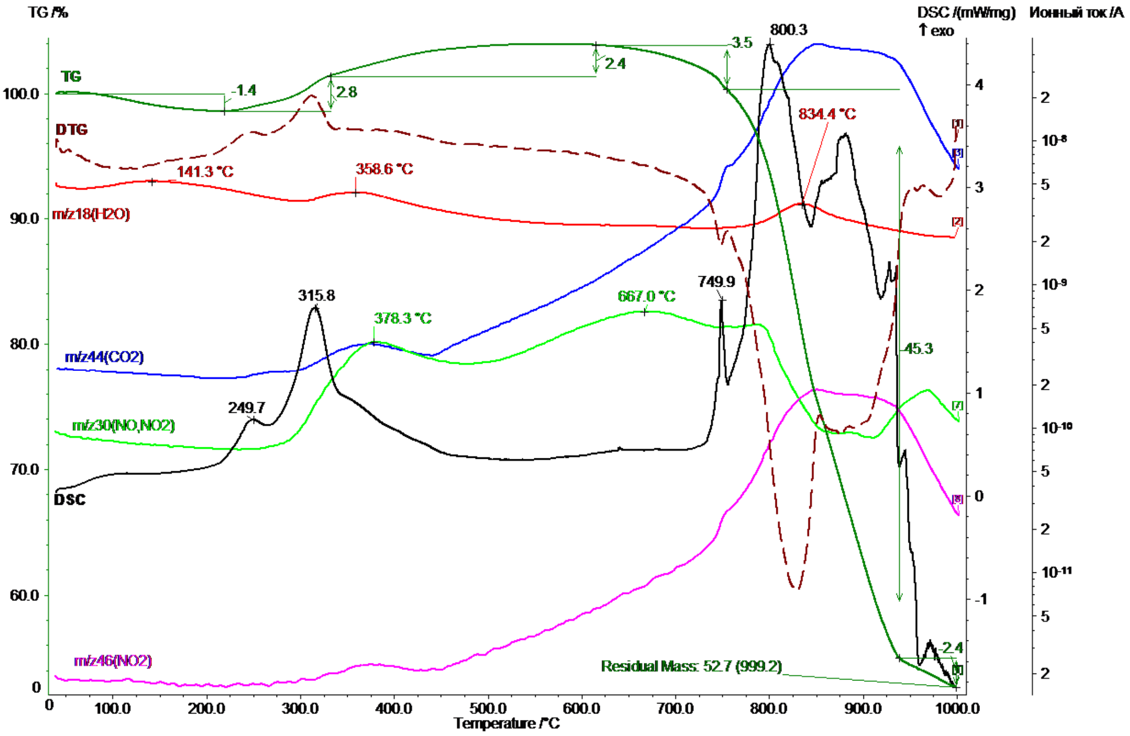

Figure 6. Results of Differential Thermal Analysis of semi-coke sample.

One of the key issues that may limit the use of lignite semi-coke as a lining material is the formation of cyanides inside such a material. The studies have shown that cyanides are in a dispersed state inside semi-coke. They have a high chemical activity and can be oxidized (if oxygen is available) at low temperatures to produce heat as per the following reaction:

$$2NaCN+3O_2 = Na_2CO_3+CO+2NO \quad \Delta H^{o}_{500\,K} = -873 \quad kJ \qquad (1)$$

Probably, the occurrence of the above reaction can explain the exothermic effect at a temperature of 315.8 °C, which was identified by means of the integrated thermal analysis. The increase in the mass of the sample up to 5.3 % is due to an increase in the mass of condensed reaction products relative to the mass of reacted chemical compounds. The evolution of nitrogen oxides observed during the differential thermal analysis is also due to reaction (1). Therefore, the non-recyclable part of the lignite semi-coke, represented mainly by sodium carbonate, can be burned at temperatures above 600 °C, including complete destruction of cyanides. Ballasting of the upper layers of semi-coke with chamotte powder will provide for a low level of cyanides, which was confirmed by the results of the autopsy of Cell A. The thermodynamic analysis shows that sodium, which enters the mixture of semi-coke and aluminosilicate, will, first, react with the formation of albite and nepheline, and only after nepheline decomposition, including the formation of sodium aluminate, the formation of sodium cyanide will begin. The cyanide level, by the end of the cell life, can be minimized by means of optimizing the dimensions of the respective layers.

In contrast to the existing processes, the proposed approach is simple and accessible; given the low cost and the possibility of recycling, this approach is also highly efficient from an economic point of view. Using a new un-shaped material – the lignite semi-coke – opens the door to the mechanization and automation of the process of assembling and disassembling cathodes, including a significant reduction in labor costs and time, and, in the meantime, the improvement of the quality of the process of lining. This allows a highly efficient use of the material.

4. Conclusions

1. It has been shown that lignite semi-coke may be used as a lining material for the under-cathode area of the cell.
2. It has been found that, after 889 days of operation, up to 80 % of the initial semi-coke used as a lining material may be subjected to recycling, and the remaining part may be burned at temperatures above 600 ° C.
3. The autopsy of the 2 331-day-old cell shows that the mixture of lignite semi-coke and powder-like aluminosilicate provides for quite a low (0.4 %) level of cyanides in the spent monolithic material.
4. The technology, which uses lignite semi-coke, allows having an economic effect by virtue of the following: reduction of the cost of lining materials; reduction of labor costs during installation; reduction of the amount of waste; and the reduction of fees for the storage of waste (possibility to recycle).

5. Acknowledgements

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6. References

1. Morten Sørlie and Harald Øye, Cathodes in Aluminium Electrolysis, (3rd Ed., Aluminium-Verlag GmbH, Düsseldorf, 2010), 662.
2. D.G. Brooks et al., Thermal Treatment of Spent Potliner in a Rotary Kiln, *Light Metals* 1992, 283-287.
3. Wangxing Li, and Xiping Chen, Running Results of the SPL Detoxifying Pilot Plant in Chalco, *Light Metals* 2006, 219-225.
4. E. Sturm, J. Prepeneit, M Sahling. Economic and environmental aspects of an effective diffusion barrier, *Light Metals*, 2002, 433-437.
5. Bruna Meireless and Henrique Santos, Economic and Environmental Alternative for Destination of Spent Pot Lining from Primary Aluminum Production, Light Metals 2014, 565-570.
6. S. Islamov, About the new concept of use of coal, *Coal,* 2007, 5, 67-69.
7. Igor Yakimov, et al., RETRIEVE - a system for XRPD phase and structure analysis, *Z. Kristallogr. Suppl.* 2009, 30, 209-214.
8. http://www.icdd.com.
9. http://meganorm.ru.
10. C. Allaire et al., An improved corrosion test for potlining refractories, *Light Metals*, 2001, 245-249.
11. Canadian Patent CA 2,556,317. Method and apparatus for forming seamless lining layers of aluminum reduction cells. A.V. Proshkin et al., An Open to Public Insp.: 2007/02/17.
12. M. Rapoport , Carbon and graphite interlayer compounds and their value in the aluminum industry. *CNII*, M., 1967, 67.