Carbon Cathode Block Materials: A History of Advancements

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Abstract

History of carbon cathode materials is a history of upgrading and advancements. There are different philosophies of applications of different grades and compositions of cathode carbon blocks. From the point of view of materials science and processing of carbon cathode materials, there are some questions to be defined.

- Volume effect transformations in course of processing and service. In graphitic blocks, the anthracite in service slowly transforms to carbon with volume decrease and the porosity of blocks should increase; this may open way to enhanced bath flow through the pores.
- From scientific point of view, the degree of graphitization of the synthetic graphite in cathode blocks and its influence on performance is interesting.
- Fracture properties of carbon cathode blocks might be improved, since carbon cathode blocks have elasto-plastic fracture behavior. Yet, it is doubtful that this research will contribute to better models of cathode life prediction.
- Intercalated sodium may move in the lattice of cathode carbon block. The comparison of the velocities of the movement of sodium in the cathode carbon block towards refractory and of the movement of cryolite in the permeable pores of the block are still unknown.
- Clarification for the mechanism of sodium swelling of the carbon cathode block is of scientific interest.
- The problem of the minimization of the cryolite flow through the permeable pores of the carbon cathode blocks is of practical interest.

Keywords: Carbon cathode materials, alumina reduction, volume change of cathode carbon, permeable pores in cathode carbon.

1. The History of Application and Advancement of Carbon Cathode Materials

The reduction cell is lined with carbon cathode blocks. The carbon on bottom has two functions:

- To be the vessel of the metallurgical device, where certain levels of the bath and the metal are maintained;
- To conduct electricity which is required for the electrochemical reaction of reduction of aluminium along all the surface of the liquid aluminium.

Permanent improvements of the cathode are taking place from the early beginning of Hall-Héroult process. The material for the first cathode consisted from metallurgical and petroleum coke and pitch, and it was not shaped – it was rammed to the bottom in the form of ramming mix [1]. The first prebaked cathode blocks were installed in the reduction cell in 1920 [1]. The first steel collector bars were installed to prebaked carbon cathode blocks by casting of cast iron in 1927.

Since that time continuous improvement and advancement of the properties and characteristics of carbon cathode materials is taking place. The dimensions of carbon cathode blocks have increased, the shape has changed a little bit, the composition has changed, the properties have improved.

In the earlier days the carbon cathode blocks were split, having the length 1 – 1.2 m and 1.8 – 2.2 m (Figure 1). Nowadays the full-length blocks are up to 3.8 m long and up to 0.7 m wide. The shape of the slot may be different (Figure 2). Now the carbon cathode block is a rather heavy construction, sometimes exceeding one tonne.

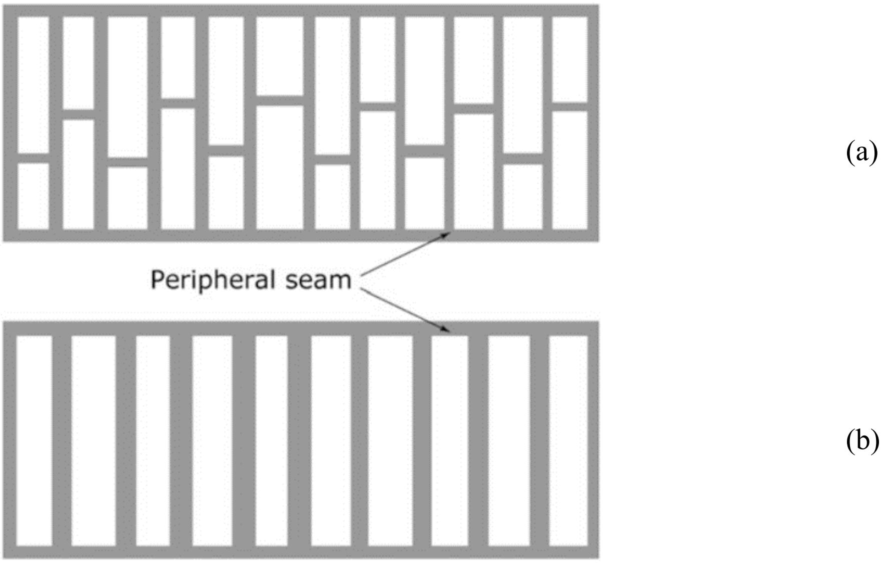

Figure 1. Scheme of cell with split cathode carbon blocks (a) and with full-length cathode carbon blocks (b).

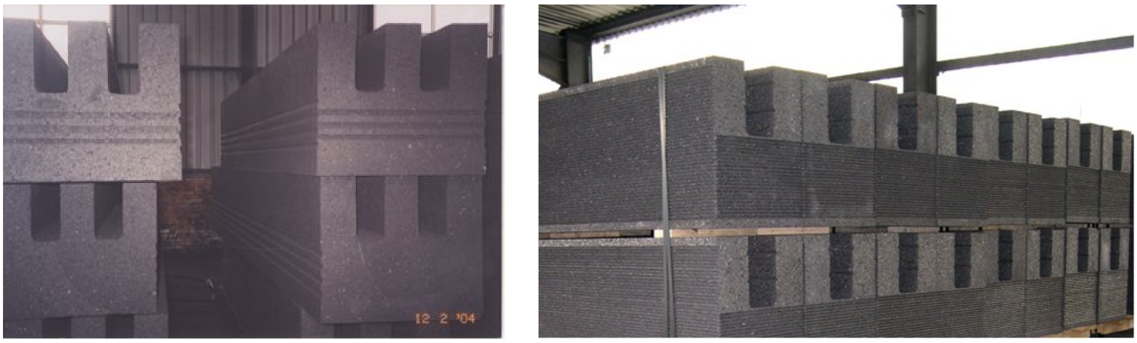

Figure 2. Carbon cathode blocks.

Cathode blocks are shaped by extrusion and by vibro-pressing (vacuum pumping out is sometimes applied to both processes). Extrusion enhances productivity, but vibro-pressing confers the ability to obtain shapes with a lower porosity and higher apparent density. Another advantage of vibro-pressing is the lower amount of pitch (organic binder for shaping) involved. Extrusion requires 20 – 25 % pitch, while vibro-pressing requires 15 – 20 %. During heat treatment, the pitch converts to coke, and in vibro-pressed blocks, there is 6 – 8 % coke, while in extruded blocks, there is 11 – 13 % coke [2]. The porosity of extruded blocks is always 5 – 6 % higher, comparing with vibro-pressed blocks.

In the beginning, carbon cathodes were made from petroleum and metallurgical coke, pitch and anthracite. Anthracite based blocks were used for a relatively long time. There is gas calcined and electrically calcined anthracite. The gas calcination proceeds at 1200 – 1350 °C, the electro calcination proceeds at higher temperature. Electrically calcined anthracite is less homogeneous, but the major part of anthracite goes through temperatures, exceeding 1200 – 1350 °C. It is considered, that 5 – 15 % of electrically calcined anthracite is graphitized and has low electrical resistivity.

In cathode blocks with 30 % graphite, grains of graphite do not form a continuous matrix. In blocks with 60, 80, or 100 % graphite, they form a matrix, and its quality is important. The balance between the grain size composition of graphite and anthracite is a question that needs to be resolved because it is possible to use only large grains of graphite or only medium and fine fractions. It is possible to vary the real density, ash content and electrical conductivity of graphite and anthracite within certain limits. There are several grades of carbon cathode bottom blocks with different characteristics. All producers of carbon cathode blocks have standard grades, containing 30 %, 50 %, 70 – 80 % and 100 % of graphite. The carbon cathode block "100 % graphite" is shaped from graphite and 15 – 20 % or 20 – 25 % of coal tar pitch and is fired at 1200 °C. Consequently, the composition of the fired block is 88 – 93 % of graphite and 7 – 12 % of coke [2].

The graphitic and graphitized blocks are used in order to decrease the electric resistivity and the energy losses. There are the graphitized blocks from isotropic coke and graphitic blocks from the needle-like coke, also there are the graphitic blocks with impregnation. The well-known disadvantage of graphitized blocks is wear (Figure 3). The history of titanium diboride coatings of carbon cathode blocks to reduce the wear is at least 30 years old.

Figure 3. Wear of graphitized cathode blocks.

The carbon cathode should keep the molten bath and aluminium without leakages, it should have high electric conductivity, and should keep its dimensions and properties. There are different philosophies of application of different grades and compositions of carbon cathode blocks. Various compositions of carbon blocks with different additives were tested, there were trials of carbon cathode blocks with different geometry, with different current density and with various coatings.

Finally, the problem to choose the type and the grade of carbon cathode block is a compromise between the characteristics of blocks and the desired performance of the cells [3,4]. The specific design of the cell should be also taken into account. This problem depends on local prices for electricity, type of the cell, LME price, etc. According to [3] the cathode voltage drop in 300 kA cells was 220 mV in case of graphitized blocks, while in case of the blocks with 75 % of graphite it was near 300 mV. According to [3] for the specific conditions of smelter the application of 75 % blocks was the best economic choice.

The optimal design of the reduction cell is a hot topic, and in at least 15 – 20 years the designers of the cells will have to solve the problems of application of carbon cathode blocks. Most probably it will be necessary to change the concept, if inert anode technology succeeds.

2. Questions of the Materials Science and Processing of Carbon Cathode Materials

From the point of view of material science and processing of carbon cathode materials there are some questions to be defined:

2.1. Volume Changes in Processing and Service

In cathode blocks, containing anthracite and graphite, the anthracite in service slowly transforms to graphite and shrinks, because the density of graphite is higher than the density of anthracite, the grain of graphite occupies smaller space than the anthracite grain. The porosity of blocks increases, allowing bath flow through the pores.

Table 1. Density of the cathode carbon block components.

	Density (g/cm^3)
Tar pitch	1.30 – 1.33
Petroleum coke	2.00 – 2.05
Gas calcined anthracite (GCA)	1.70 – 1.75
Electrically calcined anthracite (ECA)	1.80 – 1.86
Graphite	2.16 – 2.26

Graphitization decreases the volume, because the density of synthetic graphite is 2.15 – 2.25 g/cm^3 while the density of anthracite is 1.70 – 1.86 g/cm^3.

$$\frac{\Delta V}{V} = 77 - 83\ \% \qquad (1)$$

The pressing mix for extrusion contains 20 – 25 % of the binder (coal tar pitch) and the pressing mix for vibro-pressing contains 15 – 20 % of the binder. The grain size compositions of the pressing mix give minimal shrinkage, because the matrix is formed by the coarse grains and medium grains. Pitch transformation to coke decreases the volume by 63 – 65 % [2]. The growth of the porosity in 100 % graphitic block due the carbonization of the binder will be 5 – 7 % for vibro-pressed carbon block and 8 – 9 % for the extruded block.

The growth of porosity during graphitization of the coke (due to the transformation of coke to graphite) is 4 – 8 %, that will result in total increase 12 – 18 % (together with the graphitization of the pitch. The porosity of the graphitized blocks is always bigger than the porosity of the baked carbon block. This is the reason for the impregnation (with following additional firing) of the graphitized blocks with pitch.

During the reduction process the anthracite slowly transforms to graphite [1]. The mechanism of graphitization is unknown. The anthracitic block contains 25 % of graphite after one year in reduction, and the process of graphitization does not stop. The mechanism of graphitization at temperature below 1000 °C still needs to be determined.

There should be a small increase of porosity of baked carbon cathode blocks due to slow graphitization of coke binder and due to graphitization of anthracite. The growth of porosity due to graphitization of the carbon binder may be 1.4 – 5 %, and due to graphitization of anthracite up to 7 % (for cathode block with 30 % of graphite after 2 years). There is no information, how and in which way will the pore size distribution change. We can only suppose, that the pores will become bigger, and the cryolite flow through the pores will increase (this aspect of graphitization of anthracite might have some practical interest). The electrical resistivity of carbon cathode blocks decreases with age in service [1, 2, 5, 6], so the graphitization process in reduction has some positive feature.

2.2. Degree of Graphitization of the Synthetic Graphite in Cathode Blocks

From scientific point of view, the degree of graphitization of the synthetic graphite in cathode blocks and its influence on performance is interesting.

Carbon specialists estimate the degree of graphitization of carbon materials as the ratio of the difference between lattice parameters of non-ordered structure of a given substance to difference between lattice parameters of non-ordered structure and graphite single crystal [7].

$$\gamma = \frac{0.334 - c/2}{0.344 - 0.335} \tag{2}$$

where:
0.344 Interlayer spacing of the fully non-graphitized carbon, nm;
0.335 Interlayer spacing of the ideal graphite crystallite, nm;
c/2 Interlayer spacing derived from XRD, nm.

We did not manage to find the estimation of the degree of graphitization of carbon cathode blocks (containing graphite and anthracite and graphitized carbon). This characteristic is of interest for graphitized carbon blocks and “semi-graphitized carbon cathode blocks” [8], treated at 2200 – 2400 °C.

2.3. Fracture Mechanics

The fracture mechanics theory of carbon cathode blocks should be improved, as in reality carbon cathode blocks demonstrate elastic-plastic fracture behavior. Yet, we doubt, that this research will give much to the prediction of service life.

Although there are papers on the determination of fracture toughness and the energy of fracture of carbon cathode blocks, there are no deep investigations on fracture mechanics. It is accepted, that the material of carbon cathode blocks is elastic, and it is possible to analyze the fracture behavior of cathode block as a brittle material. Generally speaking, fracture behavior of carbon cathode blocks is elastic-plastic [9]. According to [9], the fracture toughness of carbon cathode block is 0.15 $\text{MPa}\cdot\text{m}^{0.5}$. Allard [10] published the values 0.3 – 1 $\text{MPa}\cdot\text{m}^{0.5}$ for semi graphitic blocks with the tendency to decrease in case of graphitized blocks.

The strength of carbon cathode blocks does not decrease at high temperatures. There is no information on the critical strain for the initiation of a crack and the critical strain for the growth of the crack. The probability of successful application of the slow crack growth model to the forecast of the service life of the reduction cell is low. There is no good method for the determination of the wear and there is no model that allows forecasting the wear of carbon cathode blocks in service.

2.4. The Intercalation of Sodium

The intercalated sodium may move in the lattice of carbon cathode block [11, 12, 13]. The practical approach to the comparison of the velocities of the movement of sodium in the carbon cathode block to refractory and of the movement of the cryolite in the permeable pores of the block [1] is waiting for a solution.

It is considered [1], that in the process of reduction sodium enters the space between the layers of carbon atoms according to reaction:

$$Al + 3NaF \text{ (in electrolyte)} = 3Na \text{ (in carbon)} + AlF_3 \text{ (in electrolyte)} \qquad (3)$$

The authors of [1] state that the Gibbs energy ΔG for this reaction at 1000 °C is positive, yet they consider, that the reaction proceeds, and gives intercalation compounds of the donor type. Probably, there are other possibilities for the formation of these intercalation compounds (for example, the direct penetration of sodium ion between the layers of carbon), and generally speaking, the equilibria should move the reaction to the formation of the starting products.

Sodium ion in the intercalation compounds should move in the electric field to the negative potential (to collector bar), and the movement of the sodium ion is possible between the layers of carbon atoms, penetrating the grain borders and pores between anthracite and graphite grains. Yet, the movement of the bath in the permeable pores in cathode blocks due to the gravity and the capillary forces should be taken into account.

The adjustment of the problem of the velocity of movement of sodium ion in different carbon materials is waiting for the solution, as well as the adjustment of the velocity of the bath flow in the permeable pores of the block. In addition, we would like to pay attention to the fact, that the irreversible losses of cryolite at the start-up of the reduction cell may be up to 15 tonnes.

2.5. Sodium Swelling

The clarification for the mechanism of sodium swelling of the carbon cathode block has scientific interest. There are two standards of the sodium swelling test ISO/WD 15379-2:2015 without pressure [14] and ISO/WD 15379-1:2015 with pressure [15]. In both, negative electrical potential is applied to the test sample of the cathode carbon block that is dipped in cryolite and aluminium in the vessel while the vessel is in the furnace.

The test sample is a cathode in an electrolytic cell. In the standard for testing without pressure, the change in the dimensions of the test sample is recorded (Figure 4) from the start of the electrolysis process in this cell. In the standard with pressure, the change of dimensions is recorded on the compressed test sample. The differences in the values of sodium swelling with and without pressure are considerable: There is no direct correlation between the values of swelling with and without pressure; the average difference in values is approximately 0.1 – 0.15 %.

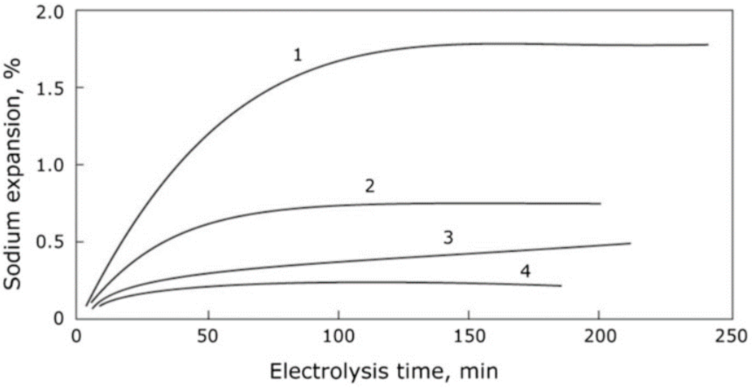

Figure 4. Sodium expansion of carbon materials according to [2]: 1 - cathode block with 30 % anthracite, 2 – cathode block with 100 % graphite, 3, 4 – graphitized blocks.

The kinetics of sodium intercalation in a carbon lattice is not taken into account. The same may be said about the rate of capillary movement of the melt in permeable pores in carbon. Yet it is possible to suppose, that the molten electrolyte fills in all the pores of the sample within 200 minutes and sodium intercalates the grains of carbon material. The comparison of the rate of expansion with the rate of infiltration of electrolyte in the sample would be interesting to study.

In cathode blocks with 30 % graphite, the linear expansion due to sodium swelling may be up to 0.7 %, which corresponds to 30 mm for a block 3.5 m in length. The linear expansion for the cathode block with 100 % of graphite is up to 24 mm, for the graphitized blocks – up to 3.5 – 7 mm. The strain and micro cracking may take place due to this expansion, and the block may also bend. This may lead to the appearance of cracks, through which cryolite (and then aluminium) penetrates to the bottom of the cathode.

Yet the question has scientific interest, because the problem of the strain growth in the blocks at the start-up is solved by the compensation of mechanical strains.

2.6. Porosity and Pore Size Dimensions

The problem of the minimization of the cryolite flow through the permeable pores of the carbon cathode blocks is of practical interest.

Porosity is one of the characteristics in the specification for the carbon cathode blocks. The specialists in the processing of carbon cathode blocks maintain the porosity below a certain level. The problem is solved by the certain grain size proportions with the help of the equations of optimal grain size compositions (Equations 4 – 7) [2, 16, 17, 18]. Equation (4) is the Andreasen equation where n = 0.3 – 0.5. Equation (5) is the Fuller equation. Equation (6) is the Bolomey (Kasheev-Strelov) equation where α = 0.1 – 0.3. Equation (7) is the Dinger-Funk equation.

$$Q_i = 100\left(\frac{d_i}{d_{max}}\right)^n \tag{4}$$

$$Q_i = 100\left(\frac{d_i}{d_{max}}\right)^{0.5} \tag{5}$$

$$Q_i = 100\left[\alpha + (1-\alpha)\left(\frac{d_i}{d_{max}}\right)^n\right] \tag{6}$$

$$Q_i = 100\frac{d_i^n - d_{\min}^n}{d_{\max}^n - d_{\min}^n} \tag{7}$$

where:

Q_i	Amount of a certain grain fraction,
d_i	Volume-weighted diameter of the grain fraction,
d_{max}, d_{min}	Maximum and minimum grain size dimensions, respectively,
n	Coefficient of shape (0.3 - 0.6), and
α	Coefficient that accounts for additional quantities of fine fractions.

The best density of the two fractional mix is 86 %, and for the three fractional mix – 94 %. The example of three fractional mix: fraction 8 – 10 mm, 80 %; fraction 0.5 – 1 mm, 5 %; fraction < 0.075 mm, 15 %.

Table 2. Properties of cathode carbon blocks.

Composition (horizontal) Properties (vertical)	**Graphitic, GCA + 30 % graphite**	**Graphitic, ECA + 30 % graphite**	**Ggraphi-tic, ECA + 50 % graphite**	**Graphitic, 100 % graphite baked at 1200 C**	**Graphitized**	**Graphi-tized impre-gnated**
Real density, g/cm^3	1.94 – 1.97	1.94 – 2.00	2.01 – 2.03	2.09 – 2.16	2.21 – 2.24	2.19 – 2.24
Apparent density, g/cm^3	1.59 – 1.62	1.54 – 1.63	1.56 – 1.63	1.59 – 1.64	1.62 – 1.63	1.72 – 1.73
Open porosity, %	14 - 19	15 - 19	16 - 20	18 - 22	21 - 23	13 - 17
Total porosity, %	18 - 22	20 - 23	20 - 23	24 - 25	26 - 28	20 - 22
Electrical resistivity normal to direction of pressing, at 20 °C, μΩm	56/43	30/40	25/32	18/25	11/13	10/12,5
Electrical resistivity normal to direction of pressing, at 1000 °C, μΩm	-	22/30	18/26	16/20	10/12	10/12
Thermal conductivity normal to direction of pressing, at 20 °C, W/mK	8/6	14/10	19/14	30/22	125/100	125/100
Thermal conductivity normal to direction of pressing, at 1000 °C, W/mK	-	13/12	14/13	22/18	50/40	50/40
Cold crushing strength normal to direction of pressing, MPa	24/22	28/28	27/27	26/25	20/26	30/35
Flexural strength normal to direction of pressing, MPa	9/6	12/9	12/9	12/9	13/10	17/14
Elastic modulus normal to direction of pressing, GPa	11	10/7	9/7	8/6	7/5	9.5/8
Sodium swelling (ISO/WD 15379-1), %	0.7 - 0.9	0.4	0.35	0.25	0.1	0.1
Linear coefficient of thermal expansion normal to direction of pressing, 20 - 520 °C, 10^{-6}/K	2.1/2.8	2.9/3.5	3.0/3.5	2.9/3.4	2.9/3	2.9/3.4
Ash, not more than %	3	2	1.6	1.2	0.9	0.8

In reality it is rather difficult to make a homogenous mix with 15 % of fine fraction since 80 % of coarse fraction does not allow to receive the smooth surface of the edges and the corners. There may appear problems with the shaping of the mix. In reality the people at carbon plants decrease the amount of coarse fraction and increase the amount of medium fraction.

It is possible to choose several variants of fraction compositions, that will allow to receive the material with porosity 14 – 16 %. The pore size distribution in these materials will differ. But for the customers in aluminium industry it will be one and the same material.

To some extent, the equations of optimal grain size compositions and the problem of minimal pore size – are competitors. In order to produce minimal porosity in coarse grained material, the space between the coarse grains should be filled with small amount of fine fraction, that does not form a continuous phase.

In order to produce small pore size in coarse grained materials, the fine grains should be the continuous phase, consequently, the volume of fine fraction should be big (fine pores may appear also at firing at tear off of fine grains from big grains at carbonization). Figure 5 is an example of the result of the grain size composition correction [2].

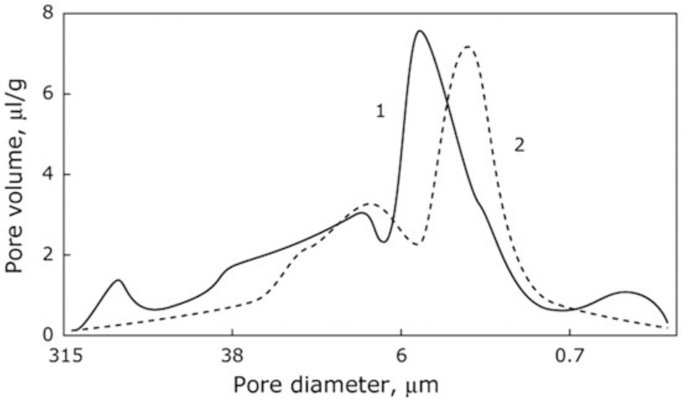

Figure 5. Pore size distribution in different carbon cathode blocks with porosity 16 – 17 % before (1) and after (2) the correction of the grain size composition [2] (the amount of the fine fraction was increased up to 40 %).

Generally speaking, the closed porosity of carbon cathode blocks is 4 – 5 %, the number of dead-end pores is small, and almost all open porosity is a permeable porosity. The rational limitation for the pore size dimension in carbon cathode block may be 25 µm [18]. The question of minimization of pore size dimensions may be solved by optimization of grain size compositions and the use of special additives.

The minimization of the bath flow through the permeable pores of carbon cathode blocks has practical interest. The same may be said about the ramming paste.

3. Conclusions

From the point of view of materials science, there are some questions to be defined in processing of carbon cathode materials for aluminium reduction cells:

- Volume changes in processing and service: In graphitic blocks, the anthracite in service slowly transforms to graphite with volume decrease and the porosity of blocks increases; this may open way to enhanced bath flow through the pores.
- The graphitization of the synthetic graphite in cathode blocks and its influence on performance is still not well understood.
- Fracture mechanics of carbon cathode blocks should be further elaborated, since carbon cathode blocks have elasto-plastic fracture behavior. Yet, it is doubtful that this research will contribute to better models of cathode life prediction.
- The movement of sodium in the cathode carbon block towards refractories and the movement of cryolite in the permeable pores of the block requires further quantitative research.
- Clarification for the mechanism of sodium swelling of the carbon cathode block is of scientific interest.
- The problem of the minimization of the cryolite flow through the permeable pores of the carbon cathode blocks is of practical interest. The question be solved by optimization of grain size compositions and the use of special additives.

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