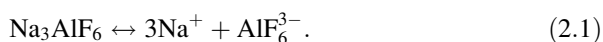


Chapter 2

Refractories and Carbon Cathode Materials for Aluminum Reduction Cells

2.1 Aspects of Aluminum Reduction

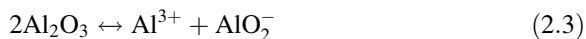
During the industrial reduction process, molten cryolite dissociates:



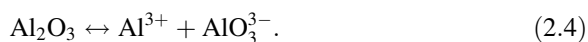
The AlF_6^{3-} ion is also partly dissociated:



Alumina dissolves in cryolite and dissociates:



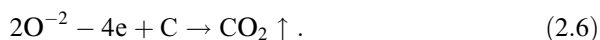
or



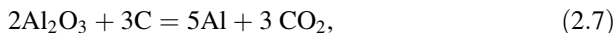
The ions of aluminum discharge on the cathode,



and oxygen ions discharge on the carbon anode and interact with carbon:



Finally, the composition of anode gases is 20–40% CO and 60–80% CO₂. In a simplified view, all cathode and anode reactions may be shown as



The melts of aluminum and of electrolyte are nonmiscible liquids. The density of liquid aluminum is 2.3 g/cm³, while the density of liquid bath is kept around 2.1 g/cm³, so in a reduction cell, the melt of electrolyte sits above the molten aluminum. Actually, the surface of molten aluminum on the bottom of a reduction pot appears to be the cathode in the reduction process. Usually, the depth of molten aluminum is 15–40 cm, and the depth of electrolyte is 15–25 cm.

In an industrial process, the electrolyte (the bath) has three main functions:

1. It conducts the electrical current between the anode and the cathode.
2. It dissolves alumina.
3. It provides a physical barrier between the aluminum forming on the cathode and the carbon dioxide/oxide that appears on the anode.

In a Hall–Heroult process, the electrolyte is cryolite, Na₃AlF₆ (3NaF · AlF₃), with dissolved alumina and additives (up to 16–18%) of aluminum fluorite, calcium fluorite, magnesium fluorite, and sometimes other fluorites [1–4]. The melting point of pure cryolite is 1010 °C (Fig. 2.1), but the temperature of the electrolyte may be reduced either by adding fluorides or by varying the ratio of sodium fluoride (NaF) to aluminum fluoride (AlF₃). In pure cryolite, Na₃AlF₆ (3NaF · AlF₃), the cryolite ratio (CR) is 3. Both variants—additives or a variation of the CR—decrease the melting point of the bath to 930–960 °C. The temperature of the process is 950–965 °C, and the freezing point is about 950 °C.

Different CRs and additives in different ways influence the basic technical and economic characteristics of the reduction process, improving one characteristic and decreasing another. Currently, it is impossible to describe the optimal composition of electrolyte, and the situation with smelters depends on various local circumstances, including raw materials, energy costs, and the design of cells, among other factors.

The anodes are in the molten electrolyte; the interpolar space between the anode and cathode is 4–6 cm. Normally, the depth of the level of aluminum at the bottom of the reduction cell (after tapping) is 25–35 cm, and the depth of the level of electrolyte is 15–25 cm. Above the melt of electrolyte on the border with air is crusted frozen electrolyte covered with alumina. Some frozen electrolyte forms the ledge on the side lining.

The tapping of aluminum is done once a day (we discuss the lining of the ladle in Chap. 3); the amount of aluminum on the bottom of the cell should be sufficient for the normal operation of the cell. A ladle with aluminum, tapped from the cells, is moved to the cast house. Usually, the dross is taken from the surface of liquid aluminum before weighing and pouring in the holding furnace for making alloys.

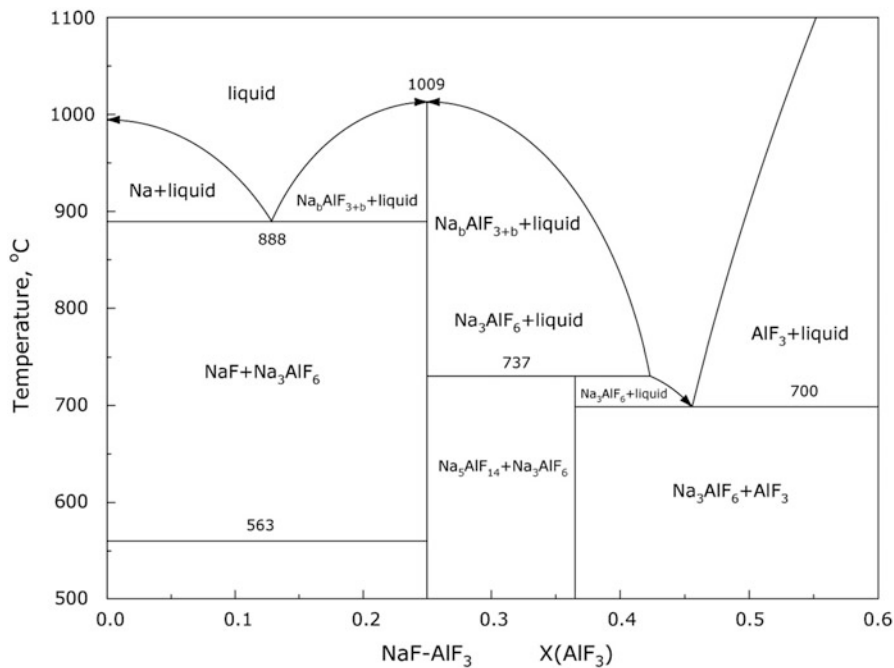


Fig. 2.1 NaF-AlF₃ diagram [1–4]

An important issue for the refractory specialist is that the level of molten aluminum (and, consequently, the level of electrolyte above the level of molten aluminum) in the reduction cell varies throughout the day—after tapping, it is low, and it increases slowly throughout the day.

The amount of aluminum during the reduction process is calculated according to Faraday's law:

$$M = 0.3354 \times I \times t, \quad (2.9)$$

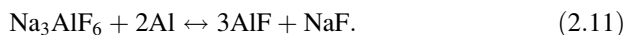
where M is the amount of aluminum, 0.3354 is the electrochemical coefficient for aluminum (g/A-h), I is the current (A), and t is the time.

In practice, the amount of aluminum is lower. There are reverse reactions (which also take place and require energy), and there are current leakages in the cell itself and in the busbar system and shell.

Here are some examples of so-called reversed reactions, which result in the appearance of unstable transient nonstoichiometric substances:



or



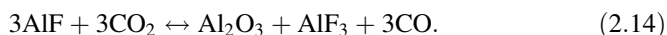
Aluminum subfluoride (AlF_2) is not stable and transforms into aluminum fluoride and highly dispersed aluminum, which easily oxidizes:



Aluminum subfluoride may also oxidize by oxygen:



and by carbon dioxide under anodes:



In the course of these reactions, the received aluminum may transform back into alumina. Also, reverse electrochemical reactions consume energy.

Current efficiency is a function of the cell.

The reduction process is controlled by several parameters:

- Energy consumption: 13,000–14,000 kW/t Al
- Alumina consumption: approximately 1920 kg/t Al
- Carbon consumption: up to 425–550 kg/t Al [the theoretical consumption according to reaction (2.7) is 338 kg/t and 667 kg/t according to reaction (2.8)]
- Current efficiency: up to 95% for reduction cells with baked anodes and up to 90% for reduction cells with a Soderberg anode

As a rule, the parameters on cells with 60 months' service and longer are lower. One more very important parameter that is not directly included in the parameters of reduction is the service life of reduction cells. The best-known parameters as of this publication are

- Energy consumption: around 12,000–132,000 kW/t Al;
- Current efficiency: up to 96%.

Currently, the trend is to decrease the current in order to attain lower energy consumption.

This book is addressed to refractory producers and specialists in cell lining and design and in the reduction process. Carbon consumption and alumina consumption in a reduction are in no way influenced by the quality of refractory materials or the design of cells. The quality of refractory materials and the design of cells influence service life directly. Regarding energy consumption and current efficiency, there is no direct link between the quality of refractory and the carbon cathode materials on current efficiency, but indirectly the design of cells (which takes into account the materials) may exert some influence on energy consumption.

There is no direct link between the quality of cathode lining materials and the current efficiency of the reduction process. However, rather indirectly there may be a link between the design of reduction cells made with high-quality cathode lining materials and current efficiency.

In terms of each part of the reduction cell and the materials for these parts, we will comment on the possible links between material quality and design and energy consumption, current efficiency, and service life.

Also, we list some instabilities of existing reduction technology that are usually not connected with the quality of cathode materials but may seriously influence the service life of cells:

- Poor quality of alumina, which leads to the formation of sludge on the cathode surface
- Poor quality of anodes (as a result of the poor quality of coke or pitch or deviations in anode technology), which may lead to overheating of cells
- Overheating of electrolyte
- Freezing of electrolyte as a sludge, operating cells with insufficient electrolyte, and others

The cathode current density is $0.7\text{--}0.85\text{ A/cm}^2$. The voltage in the reduction pot is $4.1\text{--}4.5\text{ V}$, and the trend is to decrease the voltage to $3.7\text{--}4\text{ V}$.

Reduction pots may be divided into small (with a current of $100\text{--}200\text{ kA}$), medium (with a current of $200\text{--}300\text{ kA}$), and super powerful (with a current of $300\text{--}500\text{ kA}$).

Reduction shops are long buildings, usually approximately $25\text{--}28\text{ m}$ wide and up to 1.6 km long. Usually, reduction pots with cells below 200 kA are placed lengthwise in two rows, while cells of 200 kA or higher are normally placed in one row. Between the cells there should be sufficient space to move industrial vehicles.

A reduction cell (electrolytic cell, reduction pot) is a high-temperature device used to produce aluminum by electrolysis (reduction). It is a shallow bath tank ($0.6\text{--}0.8\text{ m}$ deep), filled with melts of aluminum and electrolyte (bath). Reduction cells are $10\text{--}15\text{ m}$ long and $3\text{--}5\text{ m}$ wide.

Reduction cells are lined with carbon cathode bottom blocks and side lining. The voltage on cathode blocks is supplied by steel collector bars and a system of busbars. Below the cathode blocks are the refractory layer and the heat insulation layer. Figure 2.2 contains a schematic of a reduction cell with baked anodes.

Although reduction cells with a Soderberg anode are still in operation, their characteristics (technical and ecological) are lower compared with reduction cells with baked anodes. There is no principal difference in the construction of a cathode, a refractory lining, and a steel cradle between reduction cells with baked anodes and those with a Soderberg anode.

The service life of a reduction cell is one of its main technical and economic characteristics. Reduction cells are rather costly devices, and the cost of the

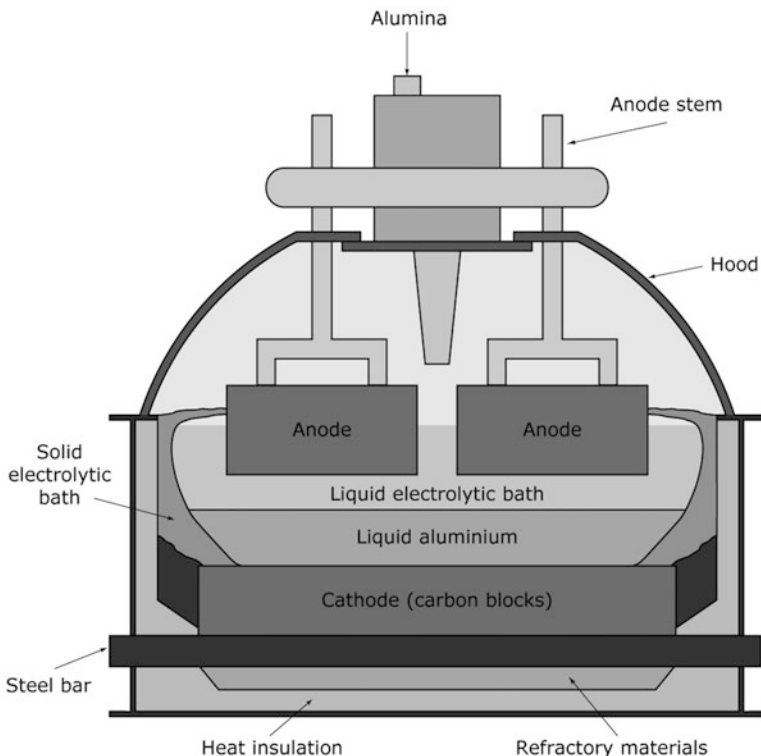


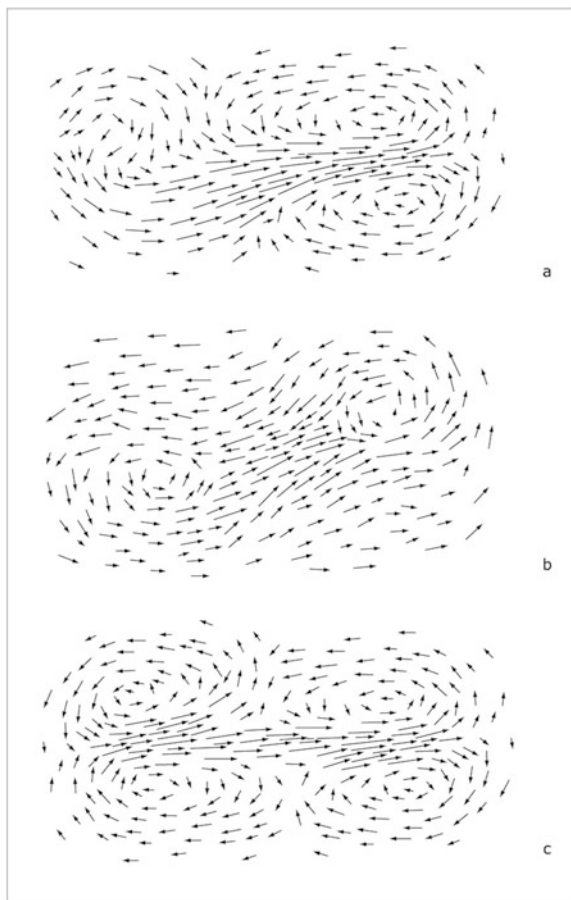
Fig. 2.2 Reduction cell (cross section)

aluminum produced depends on the service life of the reduction cells. The service life of modern reduction cells should be around 10 years, or 120 months. Some reduction cells operate for up to 120 months or even longer. However, the average service life of a reduction pot is currently 60–72 months. Sudden shutdowns during startup in the first year of service are a headache for the plant managers yet rarely happen.

There are around 30 typical constructions of reduction cells (not including variants and subvariants of typical constructions). Generally speaking, these constructions are not optimal, and producers have devoted considerable sums of money to the modernization of existing constructions and R&D on new constructions. If we consider that new reduction cell constructions are adopted for installation after 6–7 years of trial service, the problem of functional depreciation of reduction cell constructions (obsolescence) will exist for at least 20 years. We consider the target for the service life of Hall–Heroult reduction cells to be 10–12 years (120–144 months).

One more issue that should be kept in mind by refractory producers is the constant movement of molten aluminum and electrolyte in cells. As stated earlier,

Fig. 2.3 Examples of velocity fields of molten aluminum and electrolyte in reduction cells



the depth of molten metal in cells is 24–35 cm and the level of electrolyte is 18–22 cm. A reduction cell of 15×4 m with a direct current of 440,000 A may be considered a large rod with direct current. Inside this rod one will always find fluctuations of the magnetic field, which result in the constant movement of the melt at a speed of 1.5–9 cm/s up to 15–30 cm/s. Figure 2.3 shows examples of velocity fields in reduction cells.

The history of reduction cell designs goes back more than 100 years, but certain features have remained in all designs, for example, a considerable amount of heat is dissipated through the side walls of cells and electrolyte freezes on the side lining, protecting the lining materials (Fig. 2.4). The normal thickness of a side ledge is 3–5 cm, but it varies along the height to 8–12 cm. This frozen electrolyte plays a positive role in that it protects materials. It dissolves upon overheating of a cell or may be destroyed by the movement of molten aluminum and the electrolyte circulating in the cell (Fig. 2.3) under the influence of magnetic forces.

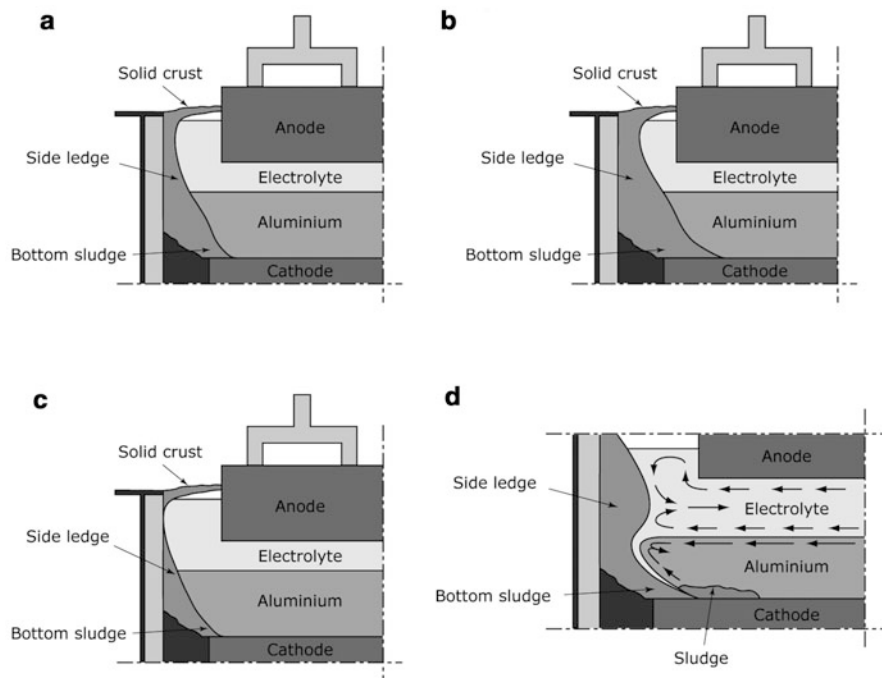


Fig. 2.4 Cross section of side lining showing frozen electrolyte in the form of side ledge and sludge: (a) in normal operation; (b) side ledge is increased, low energy supply; bottom sludge is excessive; (c) cell is overheated, part of side ledge is dissolved; (d) normal operation; *arrows* show movement of aluminium and electrolyte in cell

Electrolyte frozen on the bottom (called sludge) plays a negative role because it decreases the surface of the cathode. Probably the main issue that refractory producers with a significant experience in production and supply of refractories for ferrous metallurgy and other industries do not understand is that the reduction cell is a high-temperature metallurgical device that is heated up owing to the electrochemical reaction of the reduction of aluminum. This processing of this reaction requires very strict temperature conditions, and consequently, the heat balance of the reduction cell is sufficiently more complex compared to conventional high-temperature metallurgical devices. A 10° to 15° temperature increase above the required temperature will increase the probability of deviations in reduction processing (e.g., anode effect), while freezing the electrolyte on the edges of blocks will decrease the surface of the cathode, where the said electrochemical reaction takes place, and hence the productivity of the cell, while the difference between the freezing point of the electrolyte and the working temperature is only 15° – 20° . This comment may be of help to producers of refractories for their activity in the aluminum industry.

The current energy is used for the electrochemical reaction of aluminum reduction, and this is the key issue of the reduction process. But current energy is also spent in the carbon cathode block, in the collector bar, and in the contact between collector bar and carbon cathode block. It is additionally spent in the electrolyte, in the layer of aluminum, owing to the carbon oxide bubbles under the anode, and in various contacts in the anode system.

Hence, not all energy from a current is used for direct purposes. The value of energy is obtained by multiplying the current by the voltage. What follows is a diagram of the energy and voltage balance of a reduction cell. In pale yellow are cells of the table depicting the factors of voltage balance, subject to change over time. In green are the cells of the table depicting the factors of voltage balance that to some extent may be improved by the quality of the cathode materials and cell design.

The aging of cathode materials leads to an increased cathode voltage drop and, consequently, to increased energy consumption. Those in charge of the reduction process will have maintenance devices to keep the process going, yet this set of devices is not big. They are somewhat dependent on many process factors, including the quality of alumina and of the anodes (and the coke for the anodes), but to a large extent they are dependent on the quality of the cathode lining materials. The perfect heat balance of a cell is probably a key factor in a proper reduction process as well as for a long cell service life (Fig. 2.5).

The classical heat balance of a reduction cell has not changed significantly in 100 years (Fig. 2.6a). The side lining has no or almost no heat insulation, while the bottom has good thermal insulation. The infiltration of electrolyte through carbon cathode blocks to the refractory layer increases the thermal conductivity of refractories, but the infiltration increases the thermal conductivity of the heat insulation layer dramatically. Heat flow through the bottom increases.

Approximately 50% of heat is dissipated through the side wall (including the busbar and flange), and approximately 50% is dissipated through the bottom and upper parts. Previously it was believed that the more heat that goes through the side part of a reduction cell, the better. For instance, heat flow through a side wall forms a side ledge, which prevents the side lining materials from deteriorating; additionally, the increased energy dissipation promotes extra amperage [4]. However, considerations of energy economy led to a search for variants to decrease thermal losses (Fig. 2.6b). Little has been achieved, but as of this publication, in 2015, energy consumption below 13,000 kWh/t Al is a reality, and there are plans to reduce it to 12,000 kWh/t Al and even further, to 10,000 kWh/t.

From 1970 to 2010 the trend toward better productivity, current efficiency, and energy consumption was to increase the cathode current density (together with an increase in cell amperage). Increases in current density require very accurate maintenance and might be the cause of magnetic instability. Changes in energy prices and other circumstances drive the trend toward increasing the amperage and productivity of cells without increasing the current density. The dimensions of cells will likely increase, but current density will remain at a level of 0.7–0.8 A/cm².

external voltage drop	0.15 v	
cathode voltage drop (including the voltage drop in cathode block, the voltage drop on the contact of carbon block with busbar and the voltage drop in the busbar)	0.2-0.37 v	Heat losses 6,375 kWh/1 kgAl, voltage drop 2,032 v
anode voltage drop (including the voltage drop in anode, the voltage drop on the contact of anode with rod and the voltage drop in the rod and clamp)	0.35-0.5 v	
bubble induced voltage drop under anode	0.17-0.25 v	
electrolyte voltage drop	1.34 - 1.5 v	The energy to produce Al 6,331 kWh/1 kgAl (taking into account overvoltage), voltage 2,018 v
alumina decomposition voltage	1.756 v	

Fig. 2.5 Simplified diagram of voltage balance for a reduction cell. The data are generalized from [1–4]

As we will discuss subsequently, there is currently no known material that can resist the following materials:

- Molten aluminum
- Molten cryolite
- Gaseous vapors of sodium and fluoride compounds in the presence of oxygen, carbon monoxide, and carbon dioxide

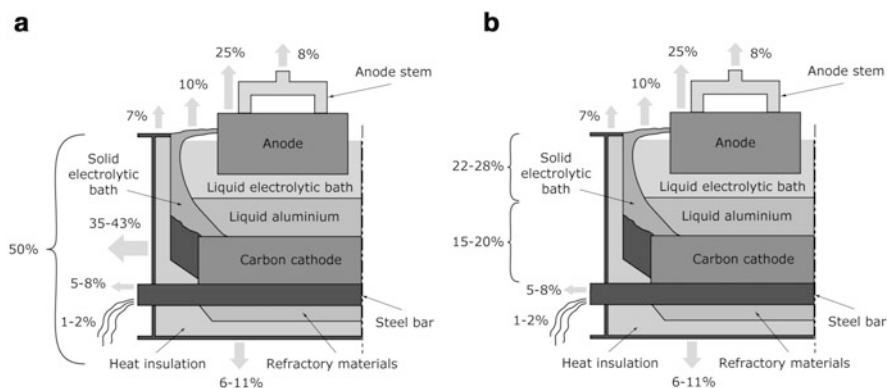


Fig. 2.6 (a, b) Heat balance of Hall–Heroult cell. (a) Classical according to [1, 2]; (b) Updated (Generalized from [3–9])

Even if the idea of the reduction cell without side ledge (with the thermal insulated side walls, sort of adiabatic cell) is realized, the Hall–Heroult reduction process will likely require a significantly greater surface for electrochemical reaction (Sect. 2.5).

2.2 Lining of Reduction Cells; Preheating, Startup, and Operation; Retrofit of Cells and Trends; Main Causes of Failures; Dry Autopsies

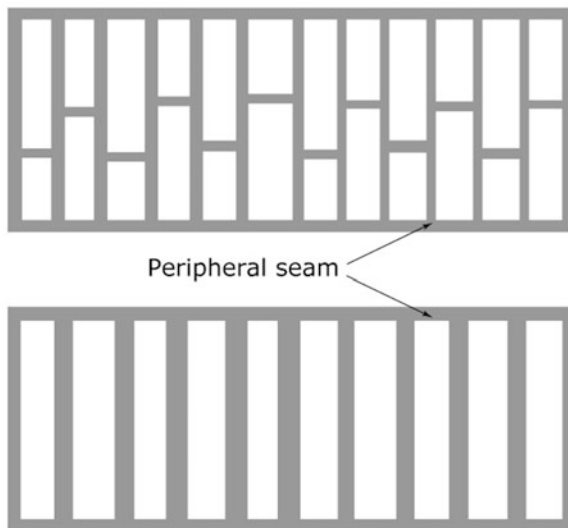
2.2.1 Brief Discussion on Reduction Cell Linings

Reduction cells are lined with carbon cathode blocks and a side lining. The voltage to the cathode is supplied by collector bars. Below the carbon blocks are the layer of refractories and the heat insulation layers (Fig. 2.7). The carbon cathode blocks may be full-length or split. They may be up to 3500–3900 mm in length, 750 mm in width, and 550 mm in height.

Carbon cathode blocks are installed (Fig. 2.8) on the refractory barrier layer. Gaps between blocks are 30–40 mm, while the peripheral seams between the ends of the cathode blocks and the peripheral side linings are up to 150 mm and are filled with carbon ramming paste. Today there are alternatives to the manual ramming of gaps with hand rammers and machined ramming with special devices that are more convenient because they eliminate the “human” factor. The side lining is made of silicon carbide (SiC) blocks or carbon side-wall blocks.

Current is applied to cathode blocks by steel collector bars. Steel collector bars are inserted (“rodded”) into slots of the cathode blocks by cast pig iron using carbonaceous glue or contact paste. The thermal expansion fitting of steel collector bars in slots is no longer done.

Fig. 2.7 Scheme of cell with (a) slit cathode carbon blocks and with full-length (b) carbon cathode blocks



All methods have advantages and disadvantages. Gluing or ramming is simpler, the labor costs are low, and it introduces no cracks. However, the voltage drop is higher than in cast contact, and the increase in the voltage drop will be relatively quick (which promotes additional energy consumption of the reduction cell process).

The slots in the carbon cathode blocks for gluing, ramming, and casting the steel bar differ. Typical slot shapes appear in Fig. 2.8.

Casting with cast iron may introduce cracks (Fig. 2.9). To avoid this potential issue, carbon blocks should be preheated in special furnaces before sealing by cast iron, which is rather costly. However, the electrical resistivity with a cast seal is an order of magnitude lower than that with ramming and gluing [10, 11] and the increase in the voltage drop at service is rather steady (which makes the reduction process more effective from an energy consumption point of view). Labor costs for cast-iron sealing are approximately 50% higher than with ramming and gluing, but all methods are used at smelters (Fig. 2.10).

If the refractory layer is made from bricks, it is impossible to avoid point contacts between the carbon block and the supporting refractory brick layer. Usually, a thin (30–40 mm) powdered bedding refractory layer is used over this layer of brick material in order to avoid gaps between the brick layer and the bottom blocks and to distribute the load more effectively. In the past, this bedding material was granular alumina; later, there were many variants, such as carbon ramming paste and castables (fireclay-based and SiC-based), among others. Perhaps the most typical material of granular bedding is a dry fireclay (alumina silicate) mixture. It may be used as thin pad material, but it may also be used as the refractory barrier layer itself.



Fig. 2.8 Installation of carbon cathode block with sealed steel collector bar in shell

Typically, the refractory layer is made of alumina silicate (most frequently fireclay) bricks or unshaped dry barrier mixtures. The main purpose of the refractory layer is to withstand temperature and to be a barrier to the penetration of liquid fluorides, which reach the refractory layer rather easily through the permeable pores of carbon cathode materials to the refractory layer and then to the heat insulation layers.

The question of joints between bricks is a question of high visibility. Liquid bath can easily penetrate between the gaps of bricks. Some producers prefer to use bricks

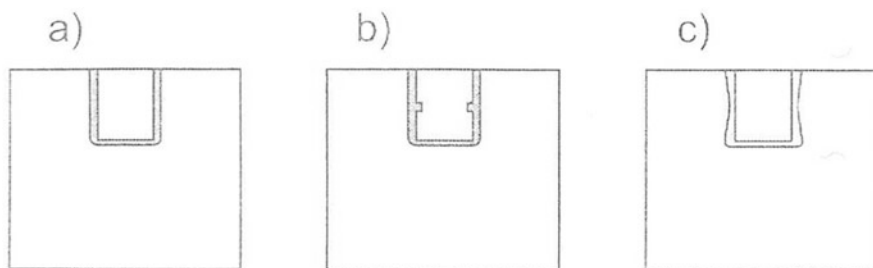


Fig. 2.9 Examples of slot shapes for (a) ramming paste, (b) glue sealing, (c) cast iron sealing

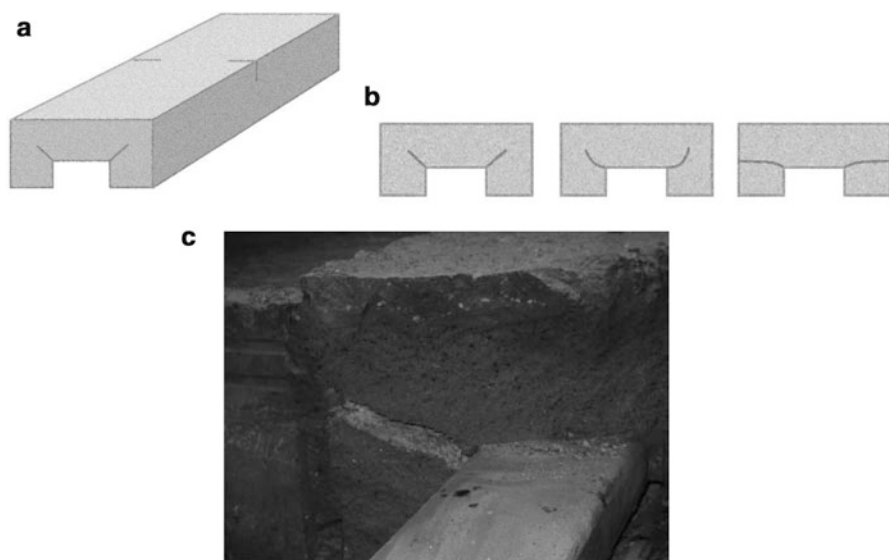


Fig. 2.10 (a, b) Shapes of cracks in carbon cathode block owing to thermal tensions at casting; (c) picture of cracks in block at dry autopsy

with dimensional tolerances that can be achieved only by mechanical grinding. This is not done regularly, but the question of dimensional tolerances in this application is serious, and only highly qualified brick layers perform the lining.

The bottom heat insulation layer of reduction cells is composed of diatomaceous (moler) bricks, vermiculite slabs, perlite bricks, and calcium silicate boards. To smooth the surface of the bottom of the steel cradles, sometimes people use fireclay grit (grain).

Side-wall blocks are protected from the bath and aluminum carbon ramming mix. In modern constructions, this cover is made from a separate baked piece of anthracitic graphitic or graphitic refractory. The construction is called a *combiblock* (Fig. 2.11b). Depending on the construction and design, the height of the cover varies from 0.3 to 0.5 m.

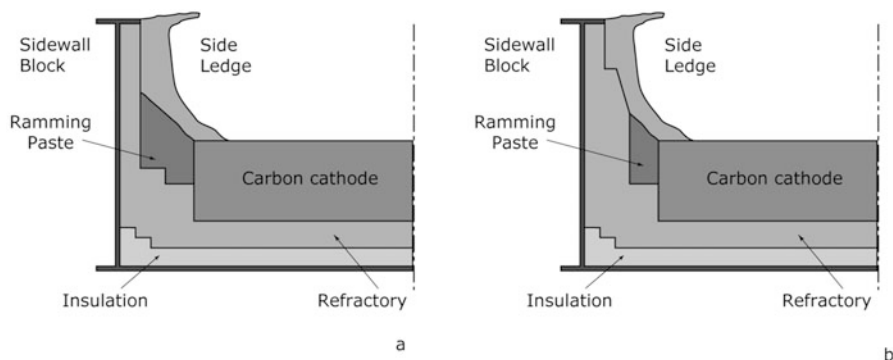


Fig. 2.11 (a, b) Cross section of typical lining

The side-wall blocks from carbon or SiC are placed on a refractory shoulder side line. This side line is above the refractory layers under the cathode bottom blocks. It may be made of bricks or castables, usually together with heat insulation boards. This side line serves two purposes. First, side lining is installed in the refractory side line, and second, it helps to compensate for mechanical tensions due to sodium swelling (and thermal expansion) in carbon bottom blocks. Heat insulation materials are easily deformed owing to tension, but the construction of the refractory lining remains undamaged.

Following the installation of the side lining, the deck top is welded to the steel shell. The gap between the upper part of the side-wall block and the deck top is filled with a ramming mix with a high thermal conductivity. Earlier ramming mixes used included carbon and fireclay-based concrete, but the contemporary variant is SiC-based concrete.

The temperature of the process is 950–965 °C, and the temperature on the upper edge of the carbon bottom block may be considered the same, at least in the center. Near the edges of the cell and in the corners the temperature is usually below the freezing point of electrolyte, which explains why the edges of the carbon cathode blocks are covered with bottom sludge. A temperature of 910–920 °C is close to optimal during a normal reduction process on the border of the bottom edge of the carbon cathode block and the upper part of the refractory barrier layer. Of course, in the side edges of the carbon cathode block, the isotherm 910–920 °C goes in the block (Fig. 2.12). The temperature between the bottom of the refractory layer and the upper layer of the thermal insulation is within a range of 700–750 °C but sometimes may reach 800–850 °C. Usually, during a normal operation, the side lining is covered with a side ledge, so the temperature on the side lining that contacts the bath may be considered to be 900–930 °C, while the temperature of the side wall of the steel cradle is below 200 °C. The temperature of the steel shell in the bottom in normal operation is 80–120 °C, while the temperature of the steel cradle in the bottom before shutdown may reach up to 150 °C, and even

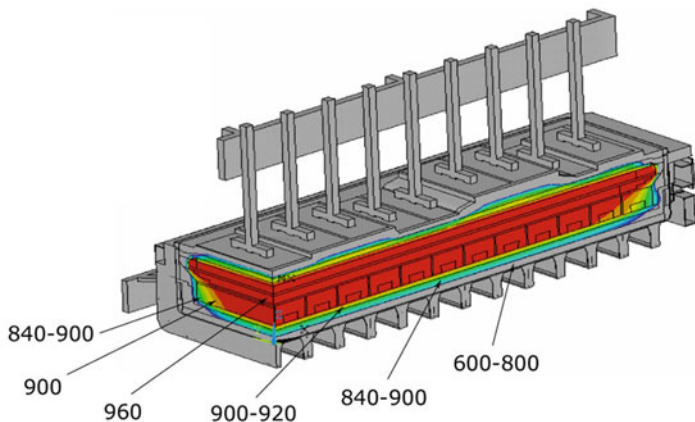


Fig. 2.12 Approximate temperatures in different layers of lining in reduction cell during normal processing

200–300 °C. Hence, the service temperatures of refractories are not very high, especially in comparison with the service temperatures of refractories in ferrous metallurgy.

Usually, the lining repair of a reduction cell is performed in a specialized repair shop; rarely is it done right in the reduction shop. Typically, a thin layer leveling the granulated fireclay grit is placed in the new steel cradle or in the cradle after repair, and then the heat insulation slabs are lined. On the layers of heat insulation the refractory barrier layer is lined (bricks or dry barrier mixtures), the side line is made near the edges, and the cathode bottom blocks are installed. There are no mortars between insulation layers. Bricklayers try to avoid using mortars because excessive water requires evaporation, which is not an easy process. Sometimes mortars are used to line the upper layer of bricks (if the refractory layer is made from bricks). The carbon ore SiC side-wall blocks are installed on the side line after the cathode bottom blocks have been installed.

Probably the most important operation in lining is the ramming of the gaps with a carbon ramming mix. It is usually performed right in the reduction shop, when a new reduction cell is installed in the line, but it may also be performed in the repair shop. This definition is essential in countries with temperatures that are sometimes below zero degrees Celsius; usually, the reduction shop building is not heated, whereas the repair shop building is heated. In such cases, a special tent is usually installed above the cell and hot air is supplied inside the tent.

As mentioned earlier, the construction and design principles of Hall–Heroult reduction cells are a work in progress. Cells that were new 20–30 years ago may require modernization because their efficiency characteristics are not as good as those of newly designed cells. Still, though, from an investment point of view, modernization (retrofit) may be more attractive than the construction of a new smelter or a change in the cell design (which may lead to a multitude of technical

problems, for example, energy supply, change of rectifiers, or the internal logistics of transportation of aluminum at the smelter).

The conventional procedure to increase productivity and efficiency is to retrofit a cell to increase the current. This retrofit, whose purpose is to increase the current and efficiency, is a complex engineering problem. The standard decision to change the grade of a carbon cathode block for a block with increased electrical conductivity is accompanied by an increase in thermal conductivity. An increased quantity of aluminum means increased heat of the electrochemical reaction, which should dissipate. As a rule, a retrofit made to increase production involves not only a change in the grade of the block but also the redesign of the lining of the cell, sometimes including even a change in the length of carbon cathode blocks.

The concept of drained anode will be discussed in the next chapter, together with the question of coatings on carbon cathode blocks. If sometimes a drained cathode is used in industrial practice, the thickness of the level of aluminum and electrolyte will be close to zero; hence, the voltage drop in the cathode will decrease and the energy consumption of the reduction process will dramatically decrease. It is expected that the current efficiency of the drained anode will also increase.

2.2.2 Preheating and Startup of Reduction Cells

It is necessary to preheat a newly lined reduction cell, that is, to heat the lining to the temperature of the service and to prepare the cell for pouring the molten bath without dangerous thermal tensions. During preheating, the ramming paste in the gaps carbonizes. The bottom lining becomes monolithic, and the water from mortars, vermiculite, or calcium silicate slabs is evaporated.

The preheating and startup of reduction cells are described in [10–12]. There are several methods of preheating, some of which are interesting from a retrospective point of view:

1. Preheating during anode bake (for Soderberg anode);
2. Electrical resistance preheating (coke bed, shunted, with full current);
3. Liquid metal preheating;
4. Thermal preheating (with oil burners, with gas burners, with electrical panels);
5. Liquid bath (cold start).

The main methods are preheating with burners and electrical resistance preheating (Table 2.1).

At this time, the two main methods of preheating are electrical resistance preheating and thermal preheating. All other methods just listed are interesting from a historical point of view.

Depending on the method, the preheating lasts from 24 to 72 h. During preheating the carbonization of the ramming paste in gaps takes place, and the cathode becomes monolithic. Ideally, the surface temperature of the cathode bottom should be similar to the temperature of the bath (950–970 °C) that is poured in

Table 2.1 Advantages and disadvantages of preheating methods (Based on [10–12])

Method	Advantages	Disadvantages
Liquid metal preheating	Rapid heating of the surface, relatively rapid settling of vertical gradients, low temperature gradients on the surface, low oxidation of carbon cathode materials, ecologically friendly	Rapid temperature increase of carbon cathode blocks and in ramming paste. Risk of thermal cracking in carbon blocks, risk of shrinkage of the ramming paste and leakages
Resistance electrical preheating	Short time	High temperature gradients during preheating, uneven temperature distribution at the surface of cathode
Thermal preheating	Low temperature difference along the surface and uniformity of the temperature gradient, easily programmed	Require more time. Oxidation of carbon materials from the surface. More complex from the point of operation

the cell, and there should be no local overheatings (above 1000 °C). The surface of the cell is large, and it is almost impossible to achieve uniform heating. It is considered normal if only 10% of the whole surface is lower than required [10–12].

The recommended rate of heating is 30° per hour within the first 11 h of preheating and 10° per hour within the following 60 h, while the temperature step at the highest point (950°–970°) should be at least 1 h.

The cathode should become monolithic after preheating. In reality, it becomes monolithic only sometime after preheating and startup, while changes in the cathode continue to occur within the whole service life cycle.

During preheating, it is necessary to avoid thermal shock cracks and to form the structure of the ramming paste in the gaps and in the peripheral seams (Fig. 2.13). During startup, the liquid bath (electrolyte), specially prepared and taken from other cells, is poured into the cell and the current is switched into the cell. After 1 day, the liquid aluminum (taken from other cells) is poured into the cell, and the process of aluminum reduction begins. The main issue of startup is to avoid overheating or freezing, which may ruin the cathode, and so the cell should be operated in a normal regime.

When the required temperature is obtained and a sufficient temperature exposure takes place, the gas/oil burners are switched off and removed, the anodes are positioned, and the bath (tapped in advance from other cells) is poured into the cell. With electrical resistance heating, the anodes are raised so that coke may be removed and then they are lowered again and the liquid bath is poured. As the liquid bath is poured into the cell (usually three launders, or 10–14 t), the current is switched on at a voltage of 6–8 V. Within a week, the voltage is slowly decreased to 4–4.5 V. The metal (previously tapped from the other cells) is poured in the cell after the so-called soaking period (12–36 h). After this, alumina is added to the bath and the reduction process begins. The early operation process lasts up to 3 months, after which normal operation begins.

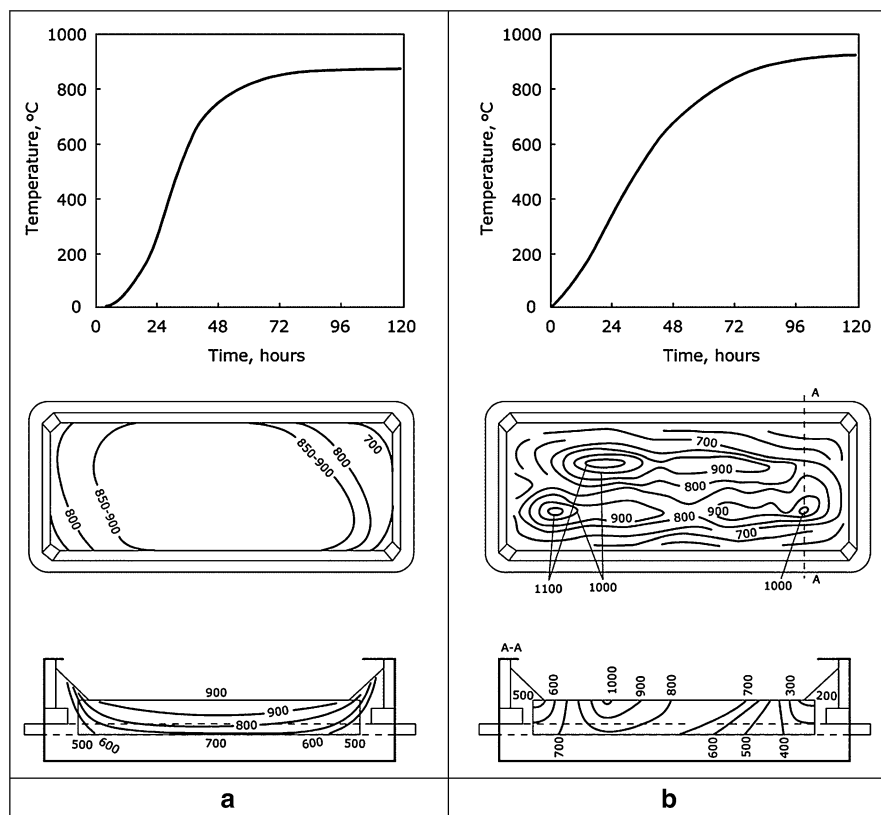


Fig. 2.13 Comparison of (a) resistance electrical preheating and (b) thermal preheating: temperature regimes; temperature gradients at *bottom-front view*, *side view* redrawn from [10]

Probably the most important facts producers of refractories and carbon cathode materials should know about preheating, startup, and early operation are the following:

1. Startup specialists begin the reduction process with a bath that has a CR of about 3 and then steadily reduce it to 2.6–2.8. The consequences are that
 - At the beginning of the process, the temperature of the bath in the cell may be 1000–1020 °C (Fig. 2.1), while in normal operation, it is 950–965 °C.
 - The viscosity of the bath changes; the same may be said of the freezing point and the chemical activity of the bath to refractories.
2. There are data on bath viscosity depending on the CR and the temperature [2, 3, 13], but for simplicity, refractory producers may keep in mind that the viscosity of the bath in a reduction cell is close to the viscosity of water.

3. During startup and the early operation period, the planned losses of cryolite (and aluminum fluoride) are up to 12–18 t/cell. The bath should be refilled by this amount at the startup period and is planned at the smelter. Aluminum and these fluorine salts (bath) appear at first in the cathode block and then reach the refractory barrier layer. In a pessimistic scenario, molten fluorine salts reach the heat insulation layer.

2.2.3 Service Life and the Main Causes for Shutdowns

The modern reduction cell is a rather costly high-temperature device. The cost of reduction cell repairs has a sufficient effect on the production cost of aluminum and smelter operation. Another reason for the special attention plant managers give to the service life of cells is that sudden shutdowns mean unreceived aluminum and problems with operation.

There are many ways to record data on service life and sudden shutdowns, some of which are very sophisticated. Weibull distribution analysis of failures is well accepted on smelters [10]. Probably the most convenient record on any smelter is the record of the service life and the plotting of the number of pots against age (Fig. 2.14). Another record may be the percentage of sudden shutdowns. If there are problems with the service life, such maxima may reveal the specific reasons for the failure.

As of this writing, a service life within 2100–2500 days is considered normal. There are many reasons for reduction cell shutdowns, and it usually is very difficult to identify only one reason. Professor H. Øye [10] has listed the following factors as influences on service life:

- Materials,
- Cell design,
- Construction,
- Preheat,
- Startup,
- Operation.

The value of these factors varies from one smelter to another, and even at only one smelter, the value of these factors may be discussed at length. The undisputable facts [10] are that a poorly designed and constructed cathode cannot work for a long time even if the preheating, startup, and operation were fairly good; and there is no reason to expect good service life from a well-constructed cell if it is made from ambiguous materials and without proper care.

At smelters with a good service life, reduction cells are switched off according to schedule. The main reason for this is economics: The production characteristics of a cell with a considerable service life are low compared with that of a young cell, and it is more economically feasible to change it out for a new, younger cell. However, a

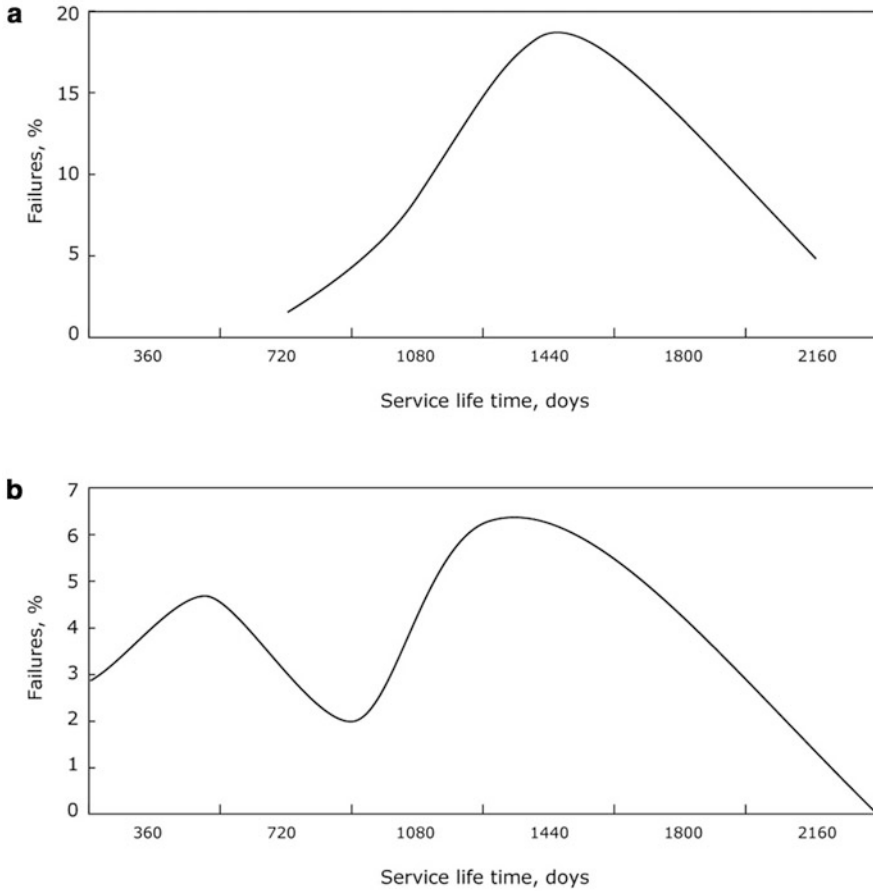


Fig. 2.14 Distribution of cell failures on smelters (**a**, **b**)

certain percentage of sudden shutdowns are due to damage to the bottom or side lining (to be discussed later), damage to the shell (deformation due to sodium swelling, damage to the deck top, melt penetrations, and so forth).

Recall that after preheating, the bottom lining (including cathode bottom block gaps and seams) is a single unit, the cathode bottom. The cause of damage to the cathode bottom and metal leakage may be any of the following:

- Thermal shock due to nonuniform heating and the appearance of cracks;
- Nonuniform shrinkage of ramming paste in gaps and poor bonding (gaps) between blocks and ramming mix owing to a lack of adhesion;
- Stratification of ramming mix and sodium-induced exfoliation of cathode blocks;
- Local overheatings and cracking;

- Mechanical strains in cathode bottom blocks caused by interactions with busbars and cracks;
- Mechanical strains in cathode blocks caused by interactions with shell and lining in the course of sodium swelling;
- Problems with the design (freezing point of electrolyte in heat insulation layer);
- Exfoliation of upper part of carbon cathode blocks;
- Overheating because of problems in reduction technology;
- Bottom heaving;
- Bottom wear;
- Metal penetration in cathode;
- Undetected defects (cracks or holes) in carbon cathode blocks during fabrication or during casting of steel bars;
- Quality of ramming paste;
- Human factor during lining process (especially during ramming);
- Side lining degradation from oxidation;
- Side lining degradation due to lack of a side ledge (either from overheating or from too high a speed of electrolyte in the cell).
- ...

Readers may choose to cite the aforementioned factors affecting service life (materials, cell design, construction, preheat, startup, operation) as the reasons for their own failure. Once molten aluminum leaks into the bottom lining, in the best case, the future service life will be months, but sometimes hours. The iron content in aluminum increases, there may be local overheatings, and the metal may leak into the steel collector bar windows.

A cathode bottom failure may be caused by any of the following factors:

- Leakage of bath or infiltration of bath under carbon blocks and appearance of a “lens” formed as a result of interactions between electrolyte and refractory, with a subsequent rise of the bottom blocks (sometimes followed by cracking of the blocks); in turn, this may be caused by overheating of the bottom lining;
- Cathode wear (up to 10–20 mm/year);
- Holes in blocks;
- Leakage of bath and metal into cracks;
- Leakage of bath into holes and nonuniformities in gaps with subsequent appearance of “lens” with cracking, and so on.

It is not easy to detect the presence of cracks in carbon cathode blocks in an operating cell. It is difficult to fix the leakage of bath and aluminum in a bottom lining. Thus, the reasons for switching off a cell are as follows:

- High iron content in aluminum;
- Temperature of cradle bottom (above 300 °C);
- High temperature of one or several busbars (above 300 °C).

The exfoliation of the surface layers of carbon cathode blocks in early operation is usually not the cause of a switch-off (to be discussed later). This process takes

place because of (1) interactions between carbon and bath and (2) the poor quality of carbon cathode blocks.

The reasons for cathode damage may be the inner cracks and undetectable holes in the carbon blocks and the poor-quality construction of the cathode lining. Sometimes sudden shutdowns of young cells with 1 or 2 years of service life take place. Such shutdowns diminish the service life on the smelter and are extremely undesirable. According to various estimates, this takes place owing to the poor quality of cathode materials, poor construction, or poor startup.

2.2.4 Dry Autopsies

Dry autopsies came into practice relatively recently, in the 1990s. Professor Øye implemented them in the analysis of failure modes [10]. Although rather costly, dry autopsies are a good tool for understanding the reasons for cathode failures in order to take corrective actions in the construction of a cell, to pay special attention to the quality of lining materials, or to take corrective actions in preheating and startup procedures. In current practice, a series of dry autopsies (a different service of the cell) is a standard procedure in the process of designing and implementing a new cell type.

Usually, analysis of the reasons for a cell shutdown, based on dry autopsy results, is state of the art, but a very brief description (mainly from Prof. Øye [10]) may help to remember the necessary actions during the process.

Formulate a dry autopsy plan (the full process is time-consuming and may take up to 2–3 weeks), which includes the collection of all initial information on the cell, the dry autopsy process itself (which may take a long time), analysis of the lining materials received in the course of the dry autopsy, a preliminary report and a final report on the results of the autopsy, and the causes of the failure (in the case of failure) (Fig. 2.15).

Collect all preliminary information (cell design, lining design, lining material specifications, information on producers, information on shell, type of preheating and record, type of startup and record, operational data during reduction process, direct cause of shutdown if one occurred, history of iron and silicon content in aluminum, information on side ledge and bottom sludge, records on temperature, records on cathode voltage drop, information on specific problems if any). Measure the geometry of the shell (length, width, diagonals) and compare it with the drawing (deformations of the sides and bottom), and inspect possible cracks and local deformations of the shell, steel bars, and steel bar windows.

Clean the cell to remove electrolyte, visually inspect the bottom (cracks, holes, heaving, exfoliation, state of joints), and, if it is in perfect condition, decide whether to do the cutting and drilling. If defects are visible, it is necessary to decide where to drill and cut the bottom. A sketch of the preliminary inspection with a drawing of the surface of the cell that marks the visual defects may help in deciding where to

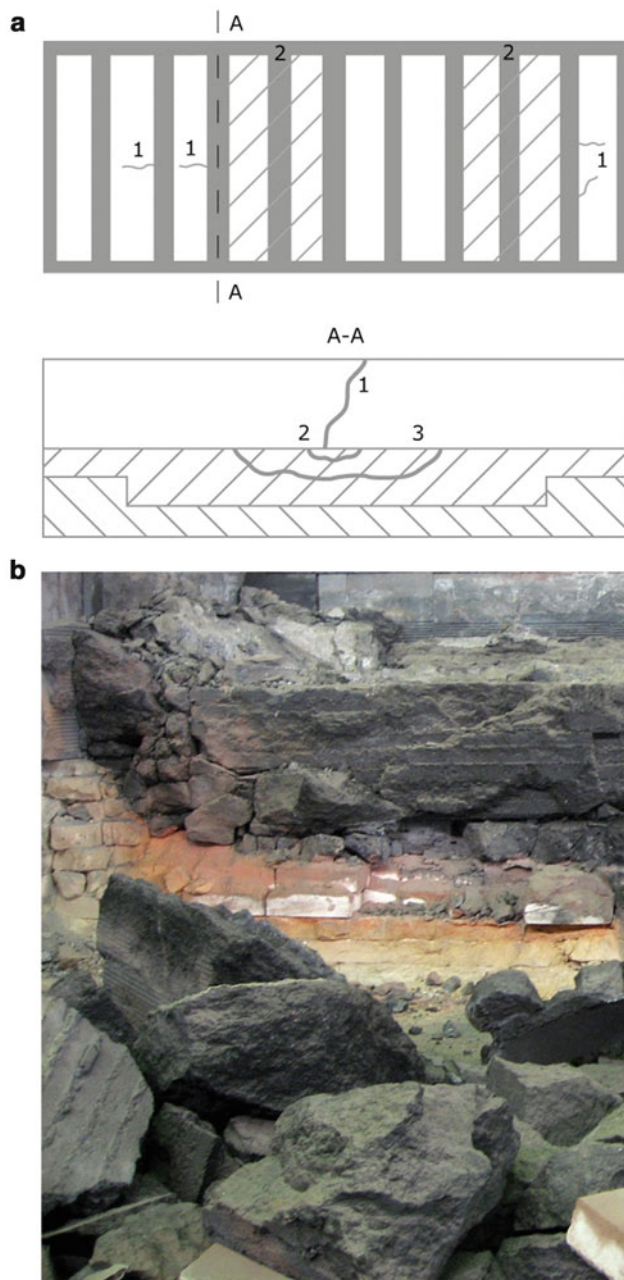


Fig. 2.15 Plan view of (a) reduction cell, cleaned to remove electrolyte and aluminum for dry autopsy. 1—visual cracks in cathode blocks, 2—planned places for trenches; 1—crack in cathode block with traces of aluminum; 2—aluminum under crack; 3—corroded by electrolyte refractory; (b) dry autopsy—cross section of lining from trench



Fig. 2.16 Exfoliated carbon cathode blocks after startup

make a trench (groove). Be cautious and careful here, because the removed cathode block may be the entire cause of the failure. Usually, it is better to make a groove (trench) in the lining near the location(s) of possible damage (cracks or holes) (Fig. 2.16).

After a groove (trench) in the lining is made, careful inspection and recording are done to inspect the trace of liquid metal in the crack in the carbon block and in the refractory, the trace of electrolyte leakage in the carbon block (or in the joints) and in the refractory, the condition of the collector bars (interactions and deformations), and the condition of the refractory layer and the heat insulation layers (chemical interaction and deformations).

Usually, the groove (trench) in the lining is at least 1 m in width, so it is possible to inspect the carbon blocks, collector bars, refractory, and insulation layers on the side opposite to where the damage occurred. This is also important information.

Laboratory analysis of carbon cathode blocks, refractory, and heat insulation layers sometimes may be of considerable help in considering a more serious failure. The dry autopsy report should include the drawings, photos, results of laboratory analysis, conclusions on the direct cause of failure, and causes that might indirectly influence the failure (e.g., the temporary overheating of electrolyte was not the direct cause of the leakage of electrolyte, but it might be the reason for the melting of electrolyte in the existing thin crack in the cathode bottom block), and recommendations for improving the lining, design, construction, and operation.

2.3 Carbon Cathode Bottom Blocks

In this section, we discuss the following characteristics of carbon cathode bottom blocks:

- Types and properties;
- Elements of technology (raw materials, processing);
- Analysis and testing;
- Defects;
- Service (chemical interaction: reactions, mechanical interaction + thermal shock), infiltration.

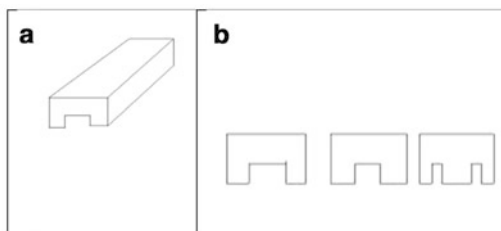
2.3.1 Types and Properties

The bottom of a reduction cell serves two functions: to be the bottom of the high-temperature metallurgical device, with a certain level of molten aluminum and bath, and to be the cathode, on the surface of which the electrochemical reaction of aluminum reduction takes place. The upper level of the bottom is made out of electroconductive carbon blocks (Fig. 2.17a). The shape of the steel collector bar may vary (Fig. 2.17b). Full-length blocks may be 3–3.8 m long. Slit blocks may be 1–2.5 m long. The width of the blocks may vary from 0.3 to 0.7 m (the latter is with two slots), and the height may vary in the range 0.4–0.55 m.

The carbon cathode bottom blocks are the most important part of the cathode construction, and this statement is not an exaggeration. A single crack that reaches the surface of the block at startup may cause a shutdown of the cell within the first months of service. On the other hand, the expected service life of a cell is calculated on the basis of bottom wear. That is why the quality of carbon cathode blocks is given special attention (Fig. 2.18).

We would like to mention the idea that the materials science of carbon cathode bottom blocks is currently in development. Solutions regarding the optimal complex of properties of carbon cathode materials and the optimal structure of carbon cathode materials for the Hall–Heroult process may be given on the basis of knowledge of interactions between carbon materials and cryolite and aluminum within 10–15 years.

Fig. 2.17 (a) Carbon cathode bottom block; (b) shapes of slots



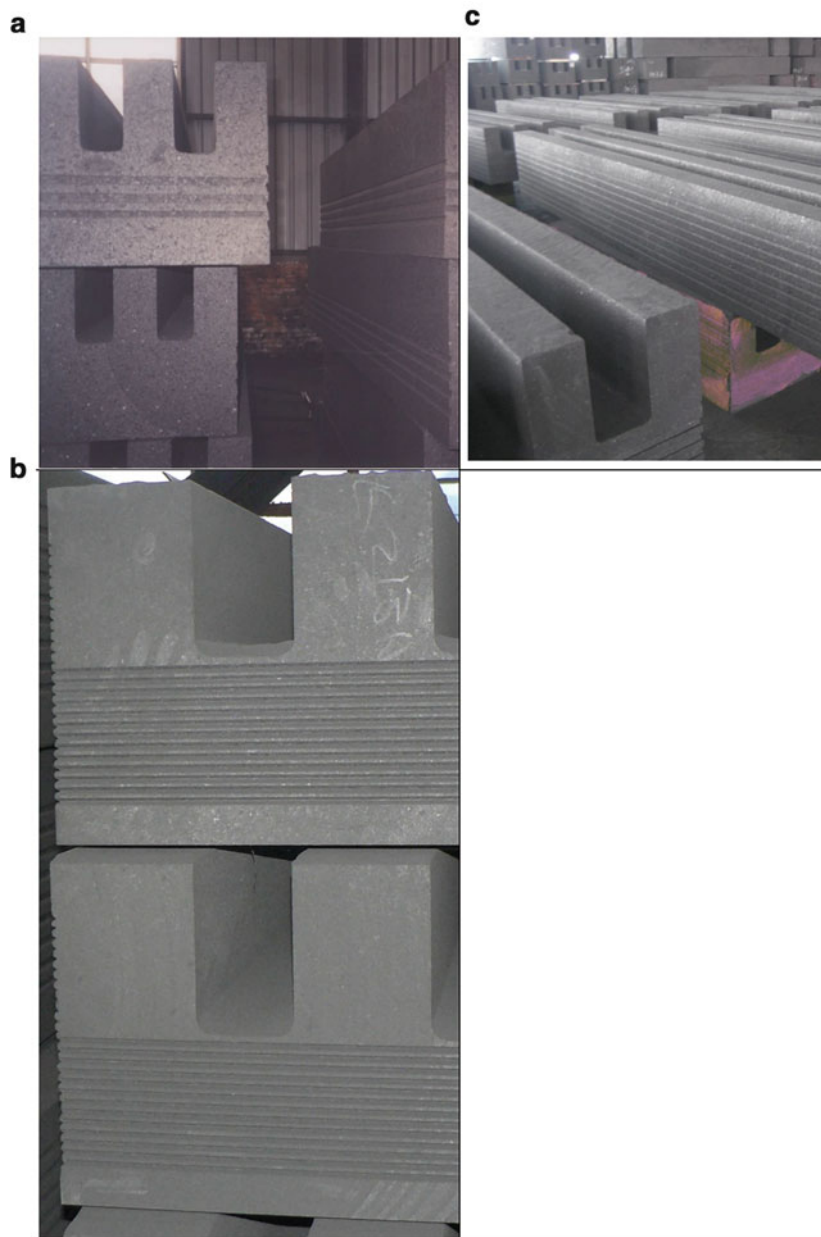


Fig. 2.18 Photos of cathode bottom blocks

One of the current trends in the reduction process regarding carbon cathode blocks is the possible use of carbon bottom blocks with a shaped (ridged) surface (Fig. 2.19). The main advantage of such shaped (ridged) blocks is the decreased turbulence of electrolyte in the cell owing to magnetic forces. It is doubtful that this

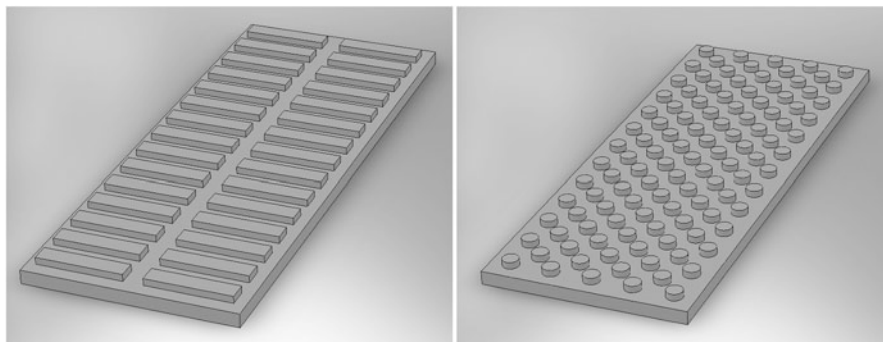


Fig. 2.19 Shaped carbon cathode blocks

shape of blocks would decrease energy consumption, but it could increase the current efficiency. However, the most problematic part of such a setup is the wear resistance of the material of the parts that stick out above the surface.

The materials science approach to carbon cathode blocks is almost the same as the approach to the carbon ramming mix. There are no particular questions—after the preheating, the ramming mix should have the properties of the carbon cathode material, or be close to them. Here are the specific aspects of application:

- After preheating and during startup, the ramming mix should neither exfoliate nor shrink, producing not even minor gaps or cavities in the joints;
- The porosity of the carbon mix after preheating is always higher than the material of the carbon cathode block;
- The pore size distribution in the carbon mix after preheating always differs from the pore size distribution of carbon cathode blocks;
- The ramming mix in the peripheral seams to some extent compensates for the linear thermal expansion of cathode carbon blocks (until it becomes nondeformable owing to carbonization).

2.3.2 Elements of Technology, Raw Materials, and Processing

Within the last 30–40 years, the processing of carbon cathode blocks has become more complex. Many types of cathode carbon blocks have appeared, and it is not easy to understand the different and changing properties of carbon materials.

Initially, carbon cathode blocks were made from anthracite; after some time, synthetic graphite was added to anthracite to achieve better electrical conductivity and have fewer problems with sodium swelling. Today, between 20 and 80% of synthetic graphite is added in the raw mixture for cathode blocks to calcined

anthracite. This line may be extended to 100% of synthetic graphite, when graphite and coal pitch are used for the green mixture, yet the temperature of the heat treatment is around 1200 °C, so in this type of material, the grains of synthetic graphite are surrounded by grains of coke (the coke appears as a result of the carbonization of the pitch).

Although within the age of trials there have been tests with graphite contents of 15, 20, 50, 80, and 100%, currently there are three more or less standard compositions: 30% graphite, 80% graphite, and 100% graphite (graphitic blocks). All these compositions are obtained by mixing raw materials (calcined anthracite and synthetic graphite) with coal pitch, shaping, and firing in a reduction atmosphere at 1200 °C.

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 involved (organic binder for shaping). Extrusion requires 20–25% pitch, while vibro pressing require 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. Note that, although there are some advantages in vibro pressing compared to extrusion, it is possible to obtain good cathode blocks by both processes.

The quality and grain size composition of synthetic graphite exert a significant influence on quality. In semigraphitic blocks (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 significant. 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 (Table 2.2). All producers of carbon cathode blocks have standard grades, yet there are minor differences in properties among the grades of various producers:

With 30% synthetic graphite	} Anthracitic graphitic
With 50% synthetic graphite	
With 70–80% synthetic graphite	

- Graphitic (with 100% graphite, heat treatment at ~1200 °C);
- Graphitized;
- Graphitized and impregnated.

Anthracitic blocks without the addition of graphite are either no longer or rarely used. For super-powerful reduction cells, graphitic and graphitized carbon cathode

Table 2.2 Typical properties of carbon cathode blocks

Composition	Semigraphitic (gas calcined anthracite +30% graphite)	Semigraphitic (electrically calcined anthracite +30% graphite)	Semigraphitic (electrically calcined anthracite +50% graphite)	Graphitic (100% graphite baked at 1200 °C)	Graphitized	Graphitized impregnated
Property						
Real density, g/cm ³	1.94–1.97	1.94–2	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, mKΩ m, normal to direction of pressing at 20 °C	56/43	30/40	25/32	18/25	11/13	10/12.5
Electrical resistivity, mKΩ m, normal to direction of pressing at 1000 °C	–	22/30	18/26	16/20	10/12	10/12
Thermal conductivity, Wt m/K, normal to direction of pressing at 20 °C	8/6	14/10	19/14	30/22	125/100	125/100
thermal conductivity, Wt m/K, normal to direction of pressing at 1000 °C	–	13/12	14/13	22/18	50/40	50/40
Cold crushing strength, MPa, normal to direction of pressing	24/22	28/28	27/27	26/25	20/26	30/35
Flexural strength, MPa, normal to direction of pressing	9/6	12/9	12/9	12/9	13/10	17/14
Elastic modulus, GPa, normal to direction of pressing	11	10/7	9/7	8/6	7/5	9.5/8
Sodium swelling (ISO 15379-1), %	0.7–0.9	0.4	0.35	0.25	0.1	0.1
Thermal coefficient of liner expansion (10 ⁻⁶ , град ⁻⁶), 20–520 °C, normal to direction of pressing	2.1/2.8	2.9/3.5	3/3.5	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

blocks are increasingly being used (although there are constructions of cells with 30–50% graphite in the blocks). We can suppose that in cells with a current below 250 kA, and even below 300 kA, semigraphitic cathode blocks will be used for a long time.

The source of synthetic graphite for anthracitic graphitic and graphitic blocks may be unconditioned graphitized electrodes in the ferrous industry, specially graphitized shapes (that should be crashed and grinded), and scrap material from the mechanical grinding and surfacing of electrodes and graphitized cathode blocks. Usually, there are wastes of green shapes (before the baking furnaces) and unconditioned baked shapes. Producers try to minimize waste and use them as raw materials. From a technological point of view, these wastes are normal raw materials, containing carbon in the form of graphite and anthracite, yet special operations are required to use these wastes in the production cycle. In any case, the ratio of these wastes and normal raw material should be strictly controlled.

Problems may appear when utilizing wastes from the mechanical surfacing of graphite electrodes because problems may arise in mixing with pitch (possibly leading to cavities in the finished product). Usually, graphite with a grain size below 1 mm is either strictly limited or even forbidden for production.

The temporary binder for carbon blocks is coke pitch (Table 2.4). Its coking value is about 50%, which means that if 20% pitch were added to a green mixture of graphite and anthracite, approximately 10% coke will be in the baked cathode block. It is believed that high-temperature pitch (with a high content of hinoline) increases wear resistance; however, it requires a higher mixing temperature.

The leading producers of carbon cathodes pay careful attention to the preparation of raw materials (sewing, weighing), to mixing (the homogeneity of mixing, temperature control), and to shaping (extrusion or vibro pressing), where defects in blocks may be introduced (cavities, cracks, unconsolidated areas). It is only during heat treatment (baking) that these defects may be revealed.

Process control should be performed at each stage. The density of the green shaped block may already be the control parameter. Usually, after shaping, each block should have its own identification number.

The next grade of carbon cathode blocks is graphitized carbon blocks. They are used (together with graphitic) for super-powerful reduction cells. The petroleum coke is mixed with coal pitch and the green shapes are installed in the graphitization furnaces with a temperature between 2500 and 3000 °C with ensuing mechanical grinding. Graphitized blocks are more porous than semigraphitic blocks. The true density of graphite is superior to that of semigraphitic blocks. The true density of graphite is superior to that of coke and anthracite; during graphitization, the inner structure becomes fuller, which is the reason for the larger true density. However, in the case of a constant volume, the porosity of the carbon material increases. To decrease the porosity and increase the wear resistance, there is a process for impregnating graphitized blocks by pitch with subsequent calcining. The advantage of graphitized blocks is their low electrical resistivity (which means lower power consumption) and low sodium swelling (to be described later). However, their disadvantages are a higher price and low wear resistance.

The next step in this process to improve properties (mainly electrical conductivity and sodium swelling) is the application of graphite blocks. Mixtures from petroleum coke are mixed with coal tar pitch, shaped, baked in a reduction atmosphere at 1200 °C, and then placed in graphitization furnaces at temperatures between 2400 and 2800 °C. At such temperatures, coke transforms into graphite. As the process of transformation goes with a negative volume effect, graphite blocks are more porous than anthracitic graphitic ones. Sometimes customers at smelters install graphite blocks in cells impregnated with pitch and bake them one more time. The porosity of such blocks is lower than that of graphite blocks without impregnation. The typical properties of carbon cathode blocks are given in Table 2.2. The principal processing schemes of anthracitic, anthracitic graphitic, graphitic, and graphitized blocks appear in Figs. 2.20 and 2.21.

Raw Materials

Anthracite is a fossil carbonaceous material containing minor amounts of inorganic salts—sodium oxide, potassium oxide, calcium carbonate (carbon specialists call it ash), and organic compounds (called volatiles).

The deposits of anthracite around the world differ, and not all anthracite materials may be used for the production of cathode blocks. The mineralogy of anthracite is not easy, and specialists in carbon define fusenite, inererite, micrinite, and liptinite structures, all differing in the morphology of their structure. Following calcination, the influence of these structures in raw anthracite on properties is not great, so for an aluminum producer, the structures of raw anthracite are interesting only from an educational point of view (Fig. 2.22). The main aim of calcination is to remove the volatile resin, such as organic compounds (10–15%). Not all anthracites may be used after calcination for the production of carbon cathode blocks, and not all anthracites may be calcined in a similar manner. However, the quality of anthracite in a deposit influences the density and ash content of calcined anthracite, so aluminum producers should at least be aware of the deposit of anthracite that is used for the production of carbon cathode blocks.

Sometimes deposits of anthracite may coexist with calcite. The contamination of calcite in carbon cathode blocks (usually, it is small white spots) is considered to be very harmful for service life because calcite may react with electrolyte, leaving cavities, but it may also absorb moisture from air at storage. The reaction of calcite with water moisture coincides with a considerable volume effect, resulting in strains and craterlike cracking of carbon blocks. Anthracite may be contaminated by iron oxide (Fig. 2.23).

Anthracite may be calcined in gas calcining furnaces (Fig. 2.24) and electrically calcining furnaces (Fig. 2.25). The calcining of anthracite in rotating gas calcining furnaces at 1200–1350 °C gives uniform calcination. In electric calciners, the temperature in the arch is 2000–2500 °C. Electric calcination gives less uniformity in properties, but a considerable part of anthracite is subjected to temperatures significantly higher than 1200 °C, which leads to greater changes in the structure of

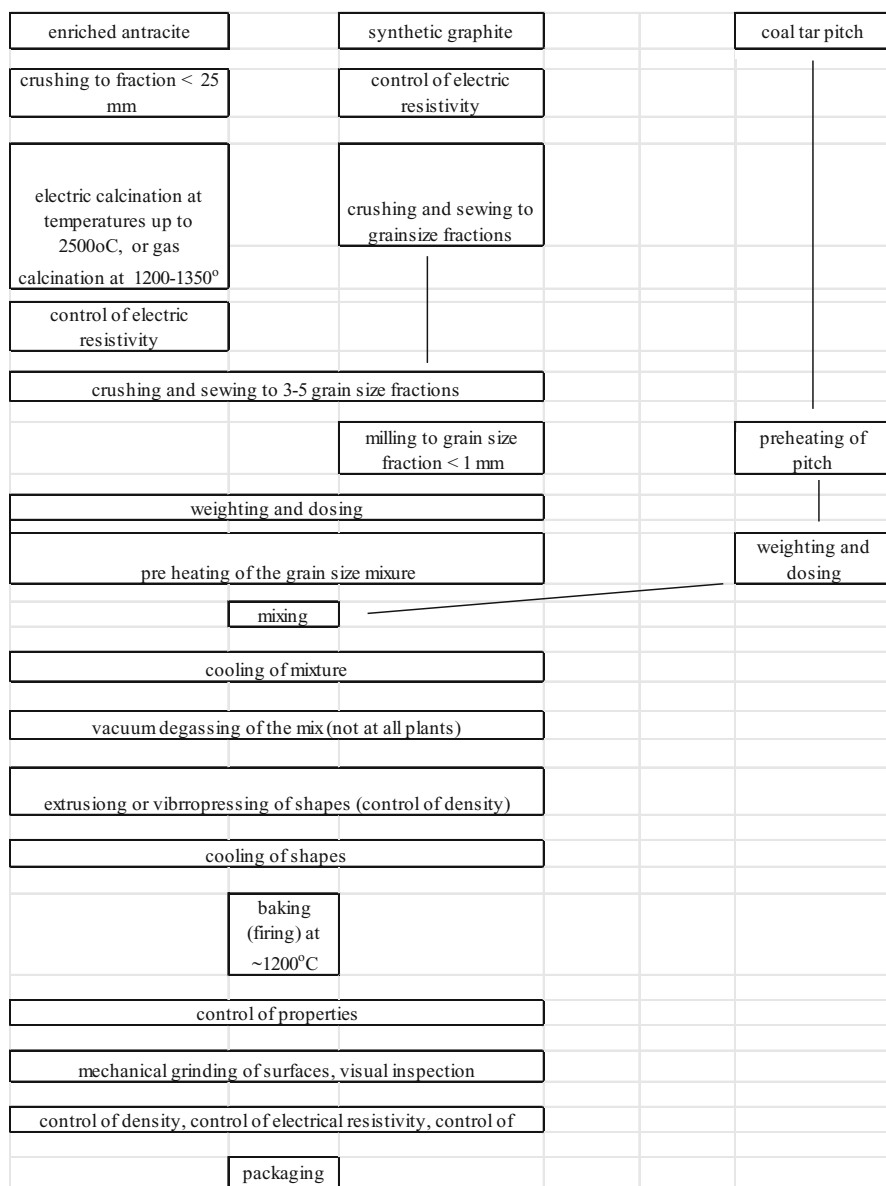


Fig. 2.20 Principal processing scheme of anthracitic graphitic and graphitic carbon cathode bottom blocks

anthracite, and some part (7–15% to 10–25%, depending on the adjusted parameters of calciners) transforms into graphite. Electrically calcined anthracite has a lower electrical resistivity and a higher true density compared to gas-calcined anthracite (Table 2.3).

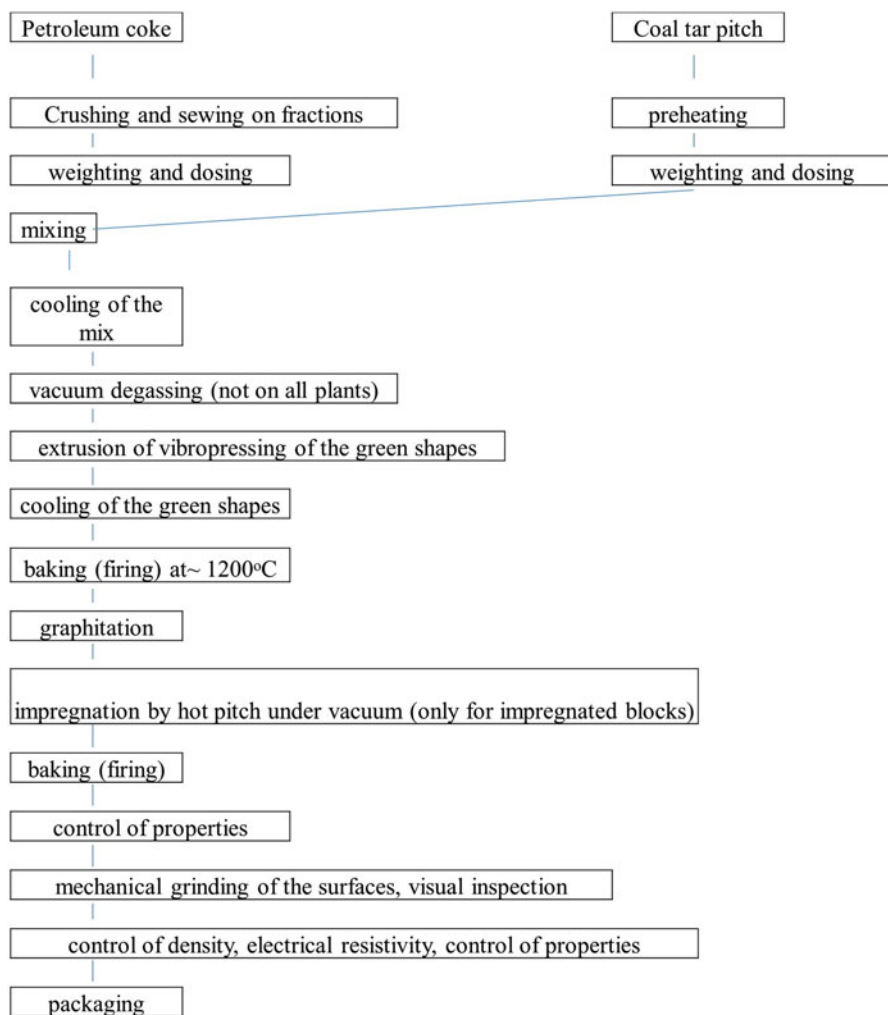


Fig. 2.21 Principal processing scheme of graphitized cathode bottom blocks

Electrically calcined anthracite is considered to be a more advanced raw material for semigraphitic blocks compared to gas-calcined anthracite because it gives a lower electrical resistivity of carbon cathode blocks and a very small (but detectable) decrease in sodium swelling. The reason for this is the higher temperatures of thermal treatment during the electric calcination process. Gas-calcined anthracite is still rather widely used around the world for specific types of bottom blocks, side-wall carbon blocks, and carbon ramming paste. Large pores and cracks



Fig. 2.22 Raw anthracite grains



Fig. 2.23 Raw anthracite grains with contaminations

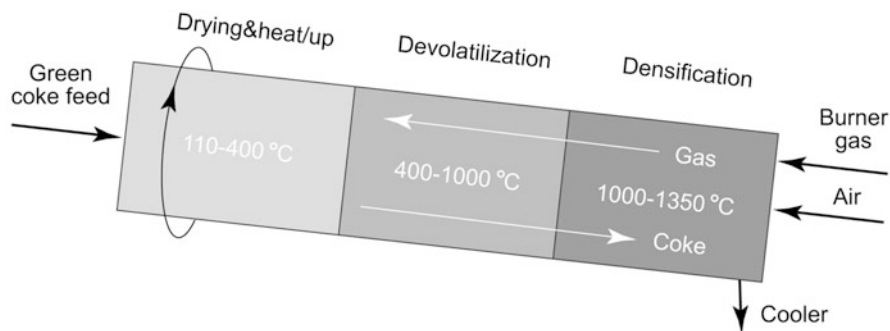


Fig. 2.24 Gas calcination furnace

Fig. 2.25 Electric calcination furnace

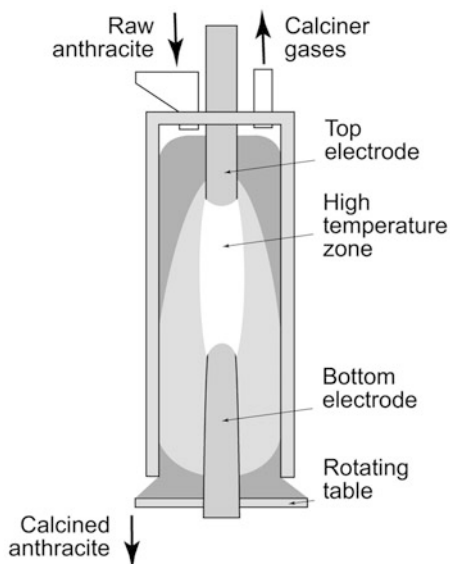


Table 2.3 Typical properties of raw materials for carbon cathode blocks

	True density, g/cm ³	Electrical resistivity, mkΩ m	Ash, %
Electrically calcined anthracite	1.8–1.86	500–650	3–5
Gas-calcined anthracite	1.7–1.75	1000–1100	3–5
Synthetic graphite	2.15–2.25	80–180	0.3–0.5

should not appear during calcination. Carbon cathode blocks, made with gas-calcined anthracite, have higher strength properties (which is not considered to be an advantage).

Natural flake graphite is not used for the production of carbon cathode blocks, mainly because of economics, but also probably because the addition of flake graphite does not significantly increase the properties of carbon cathode blocks (because it takes place with the addition of flake graphite for refractories for ferrous metallurgy).

The raw materials for synthetic graphite are petroleum coke and coal tar pitch. The formed shapes from petroleum coke and pitch are fired in baking furnaces at 1200 °C, and then they are installed in graphitization furnaces (direct or indirect graphitization) with temperatures of 2500–2800 °C. Recall that to receive raw graphite materials for semigraphitic blocks, it is possible to use either specially prepared shapes or scrap material from the production of graphitic cathodes or electrodes.

Synthetic graphite is produced in graphitization furnaces. The green shapes, consisting of calcined petroleum coke and pitch, are baked (fired) in baking furnaces at 1200 °C and placed in graphitization furnaces (direct or indirect graphitization). During this process, the shapes from petroleum coke at temperatures of 2500–3000 °C become graphitized. The shapes from coke may be specially prepared for subsequent crushing but also may be the wastes and unconditioned materials from the production of graphitized electrodes for ferrous metallurgy. The properties of synthetic graphite appear in Table 2.3; they may vary depending on the chemical composition of the coke and the temperature of the graphitization process. Graphitized shapes are crushed, milled, and sewed for grain size fractions.

The properties of coal tar pitch are listed in Table 2.4. Pitch with a higher softening point is considered preferable for the production of carbon cathode blocks because in high-temperature pitch, the coking value is greater and there are fewer volatiles. Yet pitch with a higher softening point requires higher temperatures for preheating and mixing with powdered mix.

Grain size fractions are preheated in mixers (by electric or steam heating) to 95–105 °C, the weight amount of pitch preheated to 140–150 °C is poured into the

Table 2.4 Typical properties of coal tar pitch for production of carbon cathode blocks

Property	Unit	High temperature	Medium temperature
Softening point (ring and rod)	°C	85–90	72–76
Softening point (ring and ball)		–	90–98
Volatiles	%	53–58	<59
Insoluble in toluene	%	<31	26–31
Insoluble in khynoline	%	<12	<10
Ash	%	<0.3	0.3
Water content	%	–	<4.0
Coking value	%	<55	<50
Sulfur	%	<0.5	<0.5
Na ₂ O	%	<0.018	<0.018
Viscosity at 155 °C	sPz	1500–4500	400–1500
Viscosoty at 185 °C	sPz	300–500	100–300

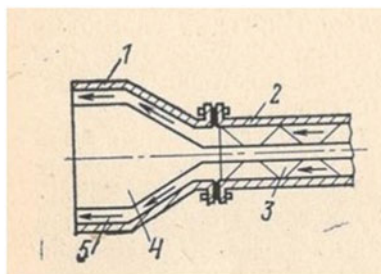
mixer, the mixing process continues for 10–15 min (for temperature homogenization up to 135–145 °C), and then the mix is transported to the press (in a vessel or by a vibro conveyor). The pressing mix is cooled to 100–110 °C and is ready for extrusion or vibro pressing. In intensive mixers, the process of preheating the grain size composition and cooling the mix is significantly quicker.

Occasionally, possible defects originating from raw materials arise in carbon cathode blocks. Of course, there may be problems with coal tar pitch, but pitch itself is not the source of defects if the mixing and shaping were performed correctly. Synthetic graphite varies in ash content and in the degree of graphitization, which finally reveals a different electrical conductivity (which may be adjusted by various technological means). Impurities are rare in graphite (if a magnetic separator is installed). Impurities are possible in calcined anthracite, and they have two origins: natural calcite inclusions or ferrous inclusions owing to calcination (which should be removed by a magnetic separator). Usually, there are wastes from the shaping process (extrusion or vibro pressing), which may actually be normal materials, that are usually implemented in the process one more time. The amount of such wastes should be limited, and they should be carefully preheated and mixed; otherwise, they may also become the source of deviations in properties and in density (possible source of cracks).

The shaping of carbon cathode blocks may be performed by extrusion and by vibro pressing. Both processes have advantages and disadvantages. The possible defects in cathode blocks after extrusion and after vibro pressing also differ.

Usually, an extrusion press has a force (effort) of 3500–6300 t. A pressing mix is cooled to 100–110 °C and then loaded in the drum (container) of the press, which is heated to 110 °C and is prepressed at a pressure of 150–180 atm to eliminate cavities and holes. On some extrusion presses, degassing (vacuuming) is done after prepressing, and then the closing mechanism of the die hole (nozzle) is opened and the shaping process (at a pressure of 50–60 atm) begins. After each 3- to 5-m-long shape passes through the nozzle (Fig. 2.26), the knife cuts off a shape and the closing mechanism closes. The nozzle of the extrusion press is preheated to 110–190 °C, and the temperature in different parts of the nozzle is controlled by thermocouples. Owing to the friction of the pressing mix on the nozzle lining, the velocities of extruded mass in different parts of the nozzle differ (Fig. 2.27). The consequence is the difference in density in different parts of the extruded shape,

Fig. 2.26 Nozzle of extrusion press for shaping a pipe. 1—extrusion drum, 2—extrusion nozzle, 3, 5—fixture, 4—space for pressing mixture



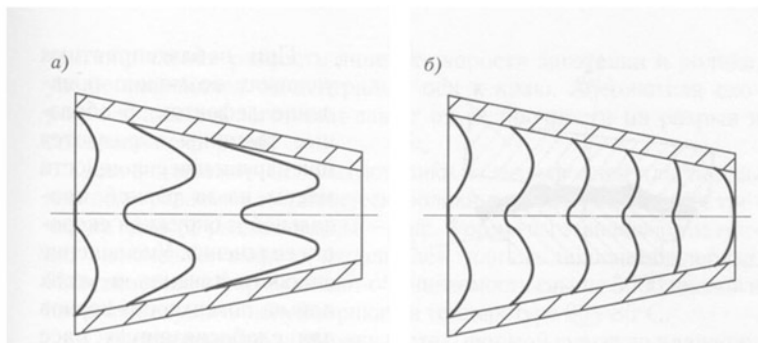


Fig. 2.27 Velocities of extruded mass in different parts of nozzle differ; this may lead to different densities in extruded shape

which may lead to lamination at firing. After the pressing, the shapes are cooled by water and after some aging are transported to the baking furnaces.

A vibro press can produce shapes of carbon cathode blocks having a length of up to 4.1 m and a width of up to 0.75 m at an effort of 120–240 t. The mold of a vibro press is preheated to 100–120 °C, the temperature of the pressing mix is 120–140 °C, and vacuuming is not done on every press. The pressure of the process is 5–7 MPa, the amplitude of vibration is 2–4 mm, the frequency is approximately 25 Hz, and the duration of the pressing cycle is 5–8 min, which allows three to four shapes to be made per hour. Frequently, producers apply vibration without applying pressure, and then the prepressing with pressure takes place, and only then does the final pressing occur (Figs. 2.28 and 2.29). Table 2.5 shows an example of a vibropressing regime. First the vibration is applied without pressure, then the pressure is applied while the frequency is increased and the amplitude is diminished. After the first cycle the pressure is released and the upper punch goes up, then the punch goes down, and increased pressure is applied, while the frequency is increased (comparing with the first cycle) and the amplitude is diminished.

Unfortunately, because of the friction of the pressing mix on the mold during the vibro pressing, the density in the pressed shape also differs (Fig. 2.28), which also might give different densities and even laminations in the fired shape.

Usually, vibro-pressed blocks have an advantage in porosity in comparison with extruded blocks; the difference might be up to 5–7%. Usually, vacuuming decreases porosity by up to 2–3%.

Conventionally, each block is measured in the air and in water and the density determined (Archimedes' method). This value is a good technological parameter for the control of a green shape. Usually, each block is stamped (Fig. 2.30), and the number is used in records.

High-quality carbon cathode blocks may be produced by extrusion and by vibropressing. The productivity of the extrusion process is slightly better than that of vibropressing. Defect-free blocks may be achieved by both methods, though

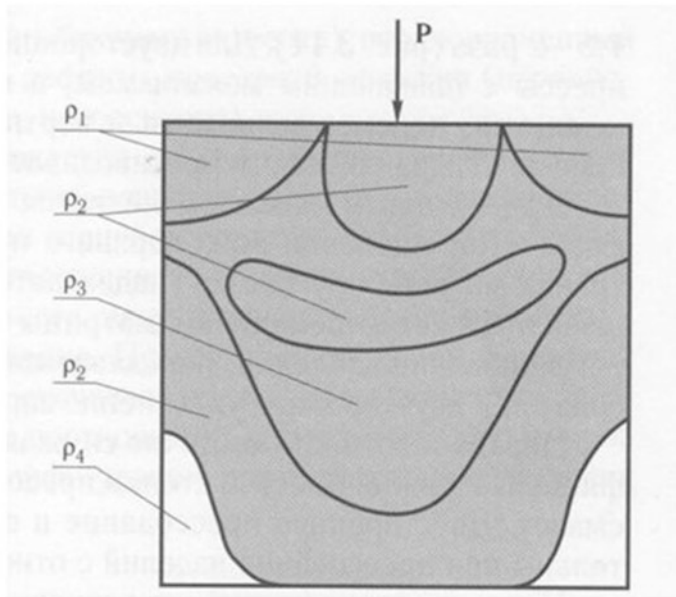


Fig. 2.28 Different densities in vibropressed shape owing to friction of mold and pressing mix

Fig. 2.29 Different regimes of vibropressing—vibration without application of pressure (*above*) and vibropressing with pressure (*below*)

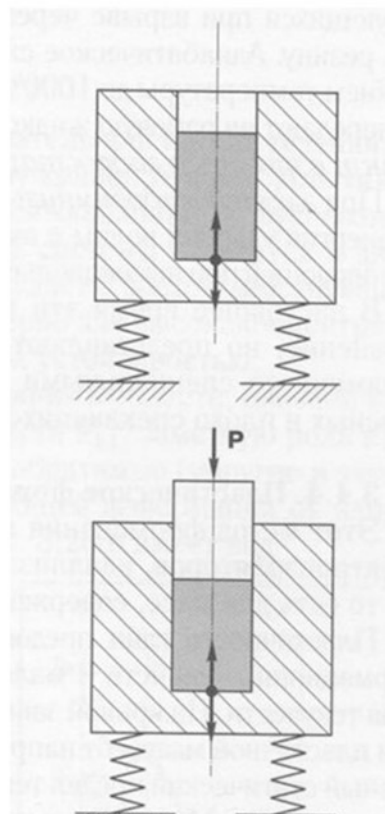


Table 2.5 Example of vibropressing regime of carbon cathode block

Operation	Pressure, MPa	Time, min	Frequency, Hz	Amplitude, mm
Vibration without pressure		1.5–2	27	4
Vibration with pressure	0.34	1	33	2
Pressure is released and upper punch goes up				
Vibration with pressure	0.34	1.5	40	1.5

Fig. 2.30 Stamp on extruded green shape

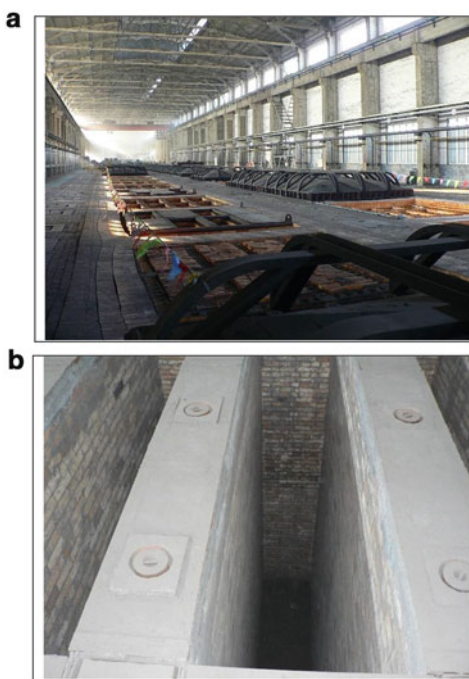
the extrusion process is more sensitive to inhomogeneities in the density of the pressing mix. Yet big cavities in carbon cathode blocks are very rare, which cannot be said of precracks (which are not seen by the naked eye even after baking or graphitization and mechanical finishing but may open during preheating of the reduction cell and during service). As mentioned earlier, extruded blocks have greater porosity, but a good pore size distribution may be achieved in both processes, so this small difference in porosity may not be considered an advantage (in the case of good pore size distribution).

Firing

Carbon cathode blocks are fired (baked) in a chamber ring furnace, where the hot zone moves along the chambers of the furnace while the shapes are located in the chambers, which is not quite conventional in today's refractory industry. Chamber ring furnaces (Fig. 2.31) are used for the firing of carbon cathode blocks for the following reasons:

- The necessity of a long and finely adjusted temperature regime in the reduction atmosphere;
- The necessity of using the filling (which gives a reduction atmosphere but also prevents the deformation of cathode blocks under gravity forces).

Fig. 2.31 Baking furnace:
(a) general view; (b)
chamber



Baking furnaces are operated on natural gas, diesel oil, or generator gas that burns in flues, and the heat is transferred through refractory lining (indirect heating). All zones (preheating, heating, and cooling) move accordingly. The material in the chamber is subjected to all stages of the cycle: loading of shapes, loading of coal filling, preheating, heating, cooling, unloading of filling, and unloading of shapes. Actually, the ring-baking furnace is a counterflow reactor (green shapes are heated by gases, appearing as a result of the burning of the fuel material and the volatiles emerging in the hot zone).

There are open (without cups) (Fig. 2.32a) and closed (with cups) ring-baking (Fig. 2.32b) furnaces (both variants are good). Each chamber consists of five to eight cassettes. A cassette is a rectangular box, between 4.5–7 m high, 3–6 m long, and 0.5–1 m wide (Fig. 2.31). Shapes are placed in the cassettes (both vertical and horizontal loading is accepted), and coal filling is loaded in the cassettes. Thermocouples may be placed in the tops of the chambers, in the flue wall (sometimes the initial part of firing is controlled according to the thermocouples in the flue walls, and the final part of firing takes place according to the thermocouple above the upper part of fired cathodes). A variant of the temperature firing regime appears in Fig. 2.33 (the thermocouple is above the fired cathodes).

Usually, the temperature of fired cathodes is around 1200 °C. A very important characteristic of the ring furnace is the temperature gradient along the height. In good variants, the temperature gradient is within 20°, and this is achieved by perfect

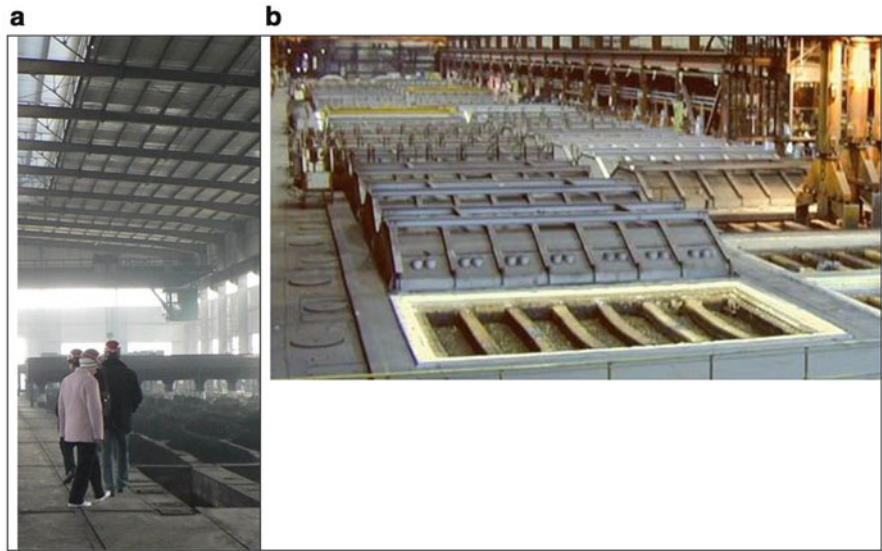


Fig. 2.32 Open (a) and closed (b) ring-baking furnaces

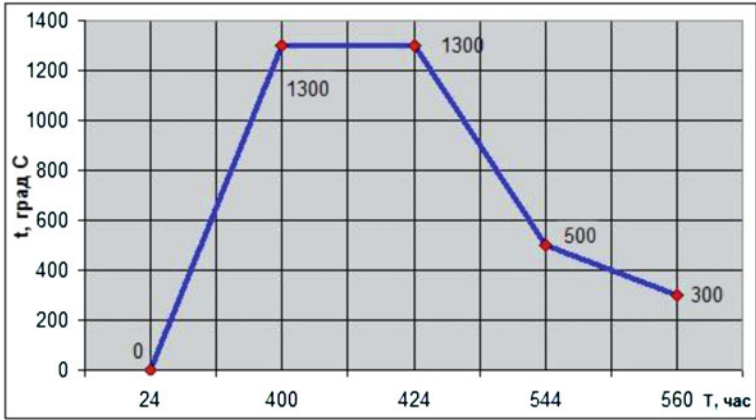


Fig. 2.33 The temperature firing regime of cathode anthracitic graphitic blocks

thermal insulation of walls and correct thermal balance. A slow temperature rise increases the firing time and the energy consumption; too fast a temperature increase may cause cathode shapes to crack. The most critical (for cracking) is a temperature interval of 200–600 °C (when the evaporation of volatiles is intensive). It is felt that the rate of temperature increase there should be below 10 °C per hour [14]. After 600 °C, the rate of temperature increase may be 15–20 °C per hour.

The inhomogeneities of density in green shapes may be revealed as cracks and precracks during firing, which is why the attention given to the temperature regime should always be painstaking. Another possible defect of baking (that may happen in furnaces with temperature gradients) is insufficient firing of part of the block (in case of vertical loading) or the surface of the block (in case of horizontal loading). In service, it may cause the exfoliation of the surface layers of the blocks owing to sodium swelling.

Graphitization

Fired shapes are loaded in graphitization furnaces. In the Acheson process (indirect graphitization), the electroconductive medium is carbon filler, and the shapes are heated as a result of the electroresistivity of the filler. In direct graphitization, the filler is used only to make the reduction atmosphere and to prevent heat losses. The electroconductive media are the shapes of carbon cathode blocks. They are placed lengthwise to the current leads and the movable transformer is switched to the leads, so the hot zone of the furnace is also moving (Figs. 2.34 and 2.35).

In both processes, the percentage of unconditioned shapes due to cracking is considerable (many cracks are revealed after surface finishing of blocks). These unconditioned blocks are used for the production of anthracitic graphitic blocks. In both processes, it is possible to produce good product, but direct graphitization is less costly.

The graphitization furnace of direct graphitization may be up to 50–60 m in length; the so-called green baked shapes are installed by a crane, then they are covered by metallurgical coke (fired coal), and the voltage is switched on. The heating time up to maximum temperature is 48–60 h, the holding time at maximum temperature is about 12–20 h, the cooling is natural, but the total time together with cooling takes up to 30 days.

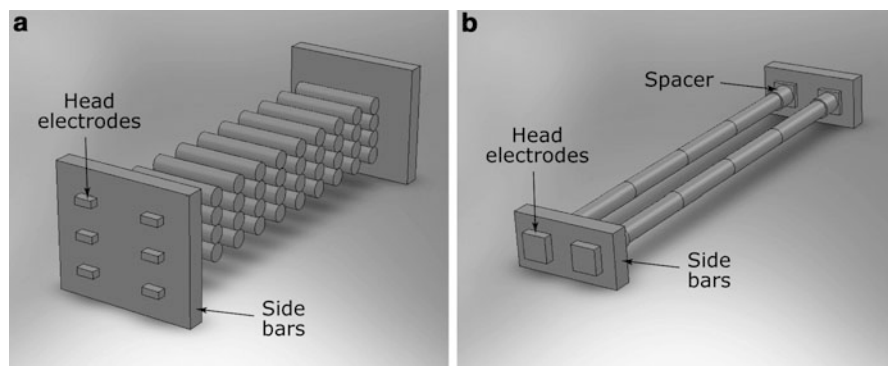


Fig. 2.34 Schematic drawings of (a) indirect (Acheson) and (b) direct graphitization processes



Fig. 2.35 Graphitization furnace for direct graphitization

Table 2.6 Densities of materials in production of carbon cathode blocks

	Density, g/cm ³
Coal tar pitch	1.3–1.33
Petroleum coke	2.0–2.05
Gas-calcined anthracite	1.7–1.75
Electrically calcined anthracite	1.8–1.86
Graphite	2.16–2.26

So-called isotropic coke and anisotropic coke were used for the production of graphitized carbon blocks. Blocks from isotropic coke have a higher strength and wear resistance, while blocks from anisotropic coke have a higher coefficient of expansion. Depending on the shaping method (extrusion or vibropressing), the orientation of the grains from anisotropic coke may differ. The blocks from isotropic coke are more popular.

It is necessary to keep in mind the volume effects and changes in density and porosity at baking and at graphitization.

Coal tar pitch, the binder for shaping carbon cathode blocks, during heat treatment converts to coke. The density of coke is significantly higher (Table 2.6), and the change in volume is 63–65%. Recall that, usually for extrusions 20–22% pitch is used, whereas vibropressing uses 12–15%. The change in volume (and the consequent increase in porosity) owing to the coking of pitch in green shapes will be 5–7% for vibropressed shapes and 8–9% for extruded green shapes.

The density of graphite is significantly higher than that of coke, and in the course of graphitization, the volume change (and the porosity increase) will be 4–8%, and taking into account the graphitization of the pitch 8–12%. In carbon materials there is no shrinkage, and the sintering process in the course of heat treatment leads not to a decrease in porosity, but to an increase.

To reduce the porosity of graphitized blocks, it is possible to impregnate them with coal tar pitch and its compositions. After the graphitization process, carbon shapes are cooled and placed in special vessels with vacuum and controlled temperature. After the air is pumped out, the coal tar pitch compositions fill in

the vessel and infiltrate the carbon shapes. Different organic substances are added to the pitch to reduce the viscosity. The impregnated carbon shapes are dried and fired in previously described baking furnaces, and the pitch in the pores carburizes and transforms into coke. One impregnation with subsequent firing diminishes the porosity to 7–8%, which is a considerable value. The trials on double impregnation showed a significant cost increase of a rather costly production.

Mechanical Milling (Finishing)

Modern blocks are mechanically grinded from all surfaces (including the inner slot surface). The grinding reveals inner defects and gives strict tolerances in dimensions. The quality of mechanical grinding depends not only on the type of equipment, but also on the type of the instrument. A diamond instrument is more expensive, but its service time is longer.

The requirements of aluminum producers for tolerances are rather strict— ± 10 mm in length and ± 3 mm in width and height. The same may be said about the tolerances in normality of surfaces and cavities. Mechanical grinding is done by a carbide hard alloy instrument, but a diamond instrument may also be used.

Depending on the approach to surface finishing, mechanical grinding may be done by a special multiposition milling machine or on a series of machines, beginning with a diamond saw and including a bed-type milling machine, planer-type millers, and so forth.

Mechanical grinding is done in a mechanical shop. It is usually accompanied by visual inspection (because after surface finishing, many defects, such as small cracks and metal or mineral inclusions, are easily seen in good light), by the control of electrical resistivity, sometimes by some nondestructive control for internal defects (e.g., sonic, ultrasonic, electro-impulse, X-ray). Then the blocks are packed (Fig. 2.36).

2.3.3 Defects in Carbon Cathode Blocks

Carbon cathode bottom blocks have large dimensions. Unfortunately, during the fabrication process—during pressing or during baking—defects may appear in carbon cathode blocks: cracks, cavities, impurities, and inclusions. If cracks or cavities are on the surface of blocks, they are more or less clearly seen, and during visual inspection at the producer's or customer's plant in the aluminum industry, blocks with defects are rejected as defective and sorted out. They may be crushed and the crushed material reused for production. The same may be said about metallic or calcite inclusions (Fig. 2.37).

The problem is that not all defects may be seen on the surface. Only one crack in the bottom block—that is, inside the block, not seen on the surface—might be the

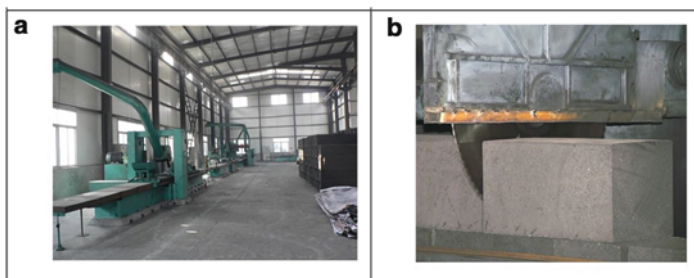


Fig. 2.36 Equipment for mechanical milling (finishing) of carbon cathode blocks

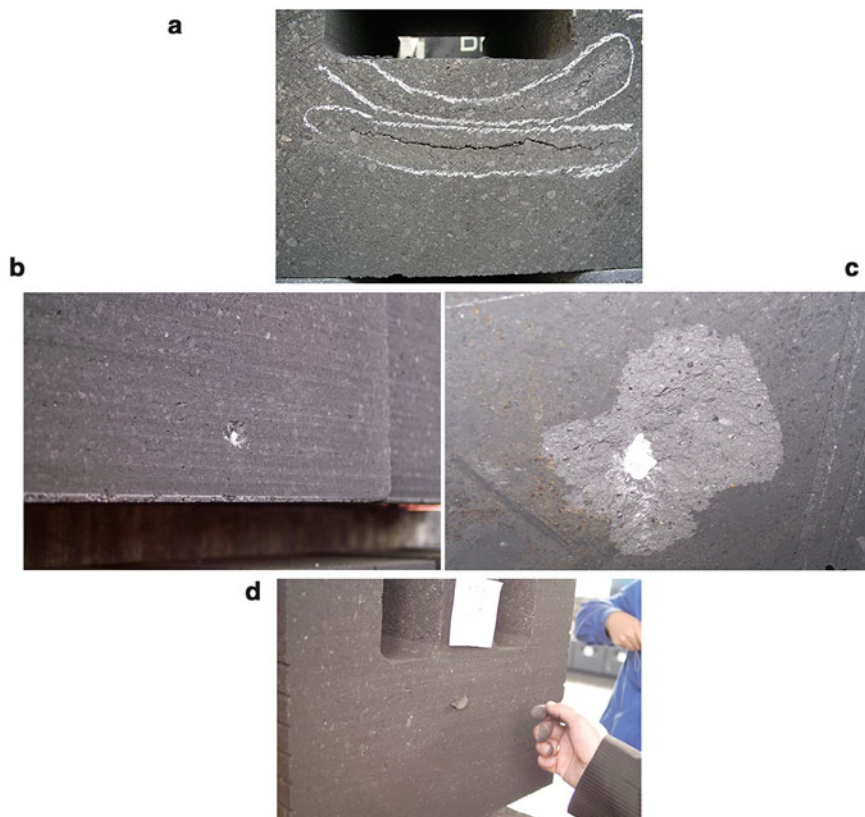


Fig. 2.37 Inner defects in carbon cathode blocks that may be revealed at cutting: (a) inner crack; (b) calcite grain; (c) ferrous contamination (almost undetectable visually, but magnet sticks to it); (d) calcite contamination

cause of a sudden shutdown of a cell during startup or during early service. Unfortunately, such internal defects are not rare and may occasionally appear.

One example of the appearance of such an internal defect may be when graphite grains were not wetted properly by high-temperature pitch, and in the mixer some inhomogeneity appeared in the mix of graphite and pitch; the major part was wetted properly, but probably one tenth of the mix in the mixer was not wetted by pitch to the same condition. Once this ready mix of graphite and pitch was placed in the mold of the extrusion press or vibro press, the pressure (and probably the vacuumation of the mix in the mold was done before the application of pressure) was applied, the pressing in the mold became a solid body, but at unloading, during the elastic relaxation (recovery) of the pressing, the parts of that poorly wetted mix moved in a slightly different way than the rest of the pressing. The strain between the portion of poorly wetted mix and the portion of properly wetted mix revealed the microcrack during baking (firing).

Another reason for the appearance of delaminations (which lead to microcracking) is that, owing to speeded regimes of pressing, air cannot escape from the pressing mix, and some air will be absorbed by liquid pitch (known as overpressing). The air in the pitch will promote high relaxation (after the load is released), causing delaminations (Fig. 2.38).

This possible microcrack, which has a very complex surface, might have dimensions of up to 300–400 mm but still remain undetectable. Even if this microcrack reaches the surface of the block, it will still be almost undetectable because the distances between the surfaces of this crack are 100–300 μm and are not seen visually. This crack may or may not open during the preheating of the cell or startup if tensions in the temperature rise grow (Fig. 2.39).

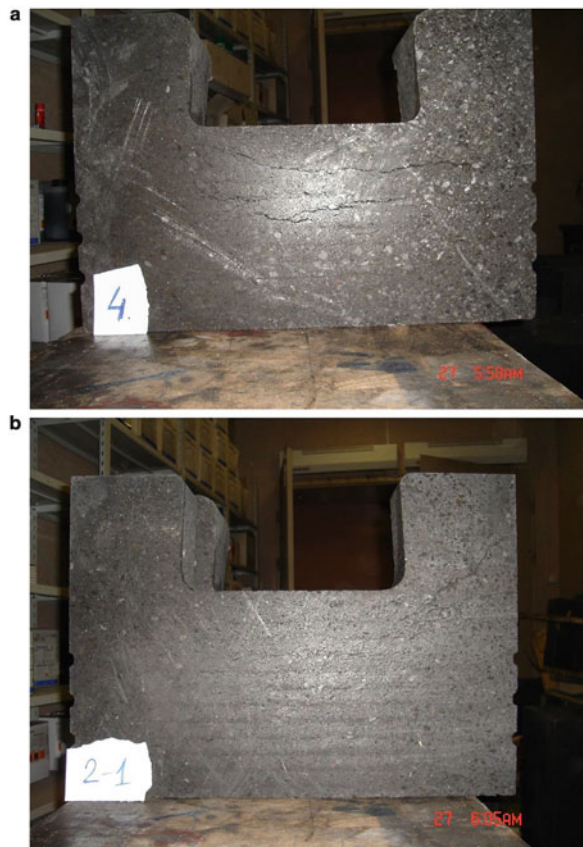
The most dangerous technological defects are as follows:

- Internal cracks that did not reach the surface of the block (strain concentrators for the growth of the crack) and internal cavities, which may be filled in with bath and which are also strain concentrators (the bath may crystallize in such cavities, while the volume effect of the crystallization is positive).
- Poorly premixed parts of blocks, where the porosity may be 1.5–2 times higher than normal. Usually, the dimensions of pores in such parts may exceed the average dimensions of pores by a factor of hundreds. This defect may appear if the pressed shape was considered to be a defect. This “defect” block is usually crushed, and the crushed material is considered to be a common raw material that is added to the mixer. During mixing, this crushed material may become part of the mix or it may retain its own structure.

Fig. 2.38 Delaminations due to overpressing in sample of carbon material, revealed after firing



Fig. 2.39 Picture of two surface cracks: one inside the block, another reaching at one edge the surface of the block



- Poorly premixed parts of blocks (e.g., owing to insufficient preheating of grain composition or pitch or because of insufficient premixing of green scrap) might give other, almost undetectable, defects in carbon cathode blocks. Parts with a different density in the green state may form parts with mechanical strains in the fired state, which are precracks. During preheating of the cell, the carbon bottom blocks will withstand bending tensions, and these precracks might start growing. Of course, the edges of these precracks are inside the blocks and are not very wide, but because of the bending tensions, the width of the cracks that reach the surface might be sufficient for infiltration of electrolyte and even aluminum. Thin cracks that reach the surface of the block are almost undetectable.
- Insufficient firing of carbon cathode blocks may lead to the exfoliation (chipping, spalling) of the upper part of blocks owing to excessive sodium swelling (compared to other parts of the blocks). Usually, it is almost unrealistic for the producer of carbon cathode blocks to deliver product that is not fired according to the temperature regime. However, it is necessary to keep in mind that the depth of the chambers in baking furnaces may reach 7 m, and

temperature gradients are inevitable. Currently, in the best constructions, the temperature drop along the height is 50°, but the temperature drop might be significantly larger. The variation depends on how the green carbon cathode blocks are placed in the chambers and how the chambers are filled. For the open type of carbon baking furnace, the amount of carbon filler above the green carbon blocks during firing might also be critical. This is essential even for graphitic carbon blocks (which usually demonstrate low sodium swelling); however, the grains of coke between the graphite grains might also be subjected to excessive sodium swelling (Fig. 2.40).

Another reason for exfoliation might be insufficient calcination of anthracite.

- Inclusions may have considerable dimensions. The source of metallic inclusions is mechanical parts of equipment (including calcinators, crushers, and disintegrators). Mineral inclusions are quite rare in graphitic and graphitized blocks. The source of mineral inclusions is usually calcite layers in anthracite deposits. During purification, some parts of calcite may remain in the anthracite. Calcite inclusions in carbon cathode blocks are rapidly dissolved by cryolite and the cavities filled by bath; they appear in the block (Fig. 2.30b).
- Traces of oil (which might appear on the surface of blocks during mechanical grinding and finishing) are also not desired. Spots of oil are seen on the surface, but oil might also penetrate inside the block, and during preheating this oil will evaporate and may start burning.

Cracks and chips on the edges and corners of cathode blocks and other geometrical deviations are less dangerous, but are still not desirable. They arise for the following reasons:

- Cracks and chips may appear owing to an excessive speed of the grinding instrument during the surface finishing of blocks. Large grains of graphite and anthracite (imperfect sewing) and big pieces of baked shapes and green shapes, considered to be defects, are implemented in the process as raw materials (Fig. 2.41).
- Geometrical deviations in normality (orthogonality) and parallel alignment 1065 appeared during the mechanical finishing.

Attempts to implement nondestructive quality control for carbon cathode blocks and to reveal internal defects has a 40+-year history, and we cannot say that these attempts have stopped. Typically, the next attempt to implement another nondestructive method of quality control is made following a series of unexpected shutdowns.

These attempts are initiated by customers, but producers also carry out research in this direction. Another question to discuss is where the nondestructive control device should be placed: near the producer's storage house or at the customer's quality control?

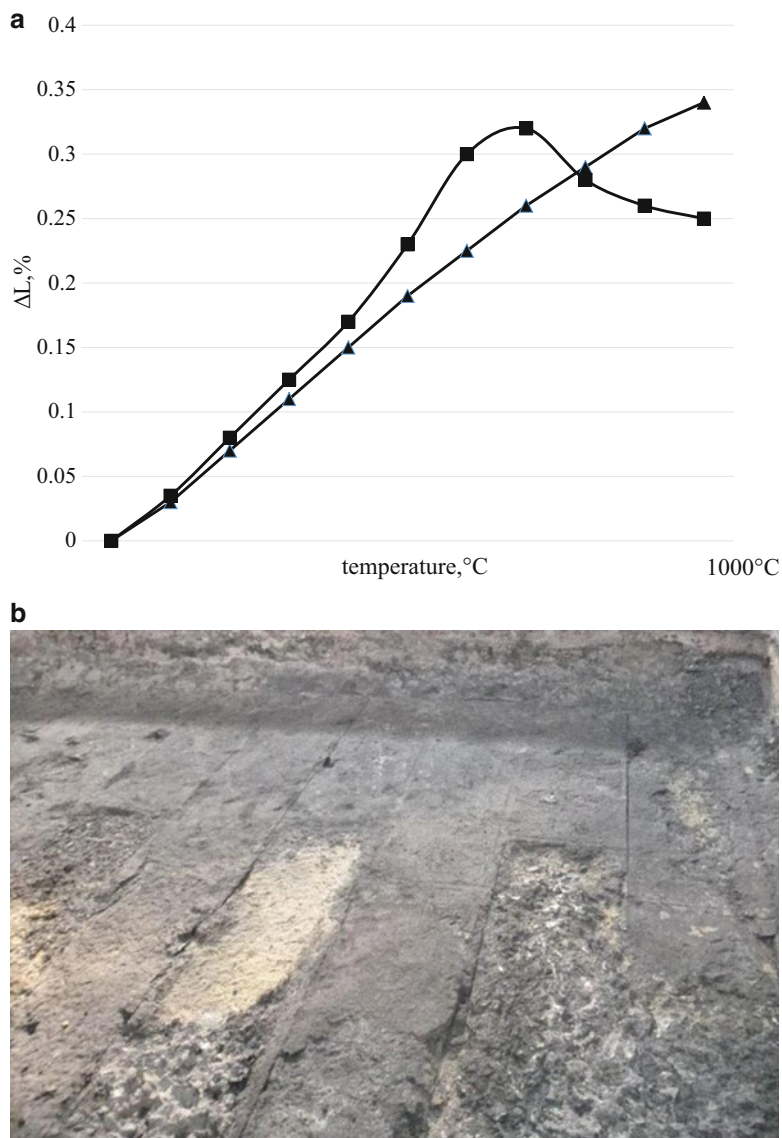


Fig. 2.40 (a) Expansion of normally fired (*black triangle*) block and of insufficiently fired carbon block (*black square*) (redrawn from [10]). (b) Exfoliation of cathode block after startup of reduction cell

The simplest method is sound propagation in the block, where the sound appears from the knock of a hammer in the hands of a worker. Sometimes an experienced worker can recognize internal cavities or cracks based on the hammer's sound. Some producers and customers apply sonic and ultrasonic devices, sometimes with

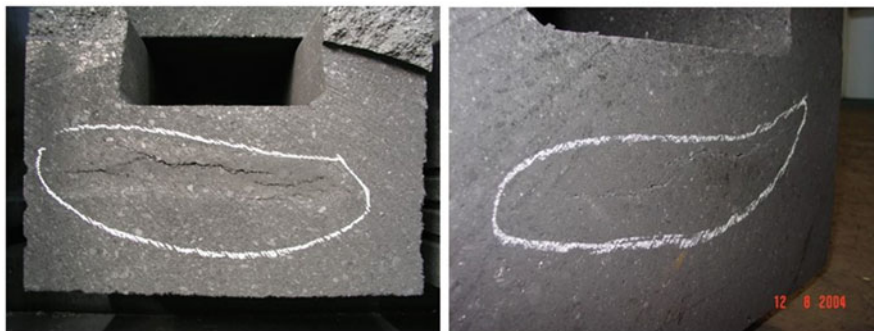


Fig. 2.41 Examples of internal cracks inside carbon cathode blocks that are not seen on surface but are seen on cross section after cutting

good results. However, there are indications that these ultrasonic detectors do not guarantee with complete certainty that they will reveal internal defects. Probably, one of the main problems of sonic and ultrasonic testing is that all these devices require tight contact between the sensor and the tested blocks.

It is possible to test some parts of selected blocks, but it is almost impossible to implement automatization and constant control on a production line. Constant control on a production line (scanning) might be possible if it were possible to conduct inspections without contact between the sensor and the block. However, sound or ultrasound waves dampen in the air.

Some R&D has been done on the application of the electro-impulse resonance method for the detection of internal defects. Probably the most advanced nondestructive method of defect visualization in cathode blocks might be the X-ray scanning and visualization technique. The apparatus is complex and expensive; it is sensitive to dust and should be situated in a special room. Yet it does not guarantee 100% detection of internal defects. TV X-ray complexes are less expensive and usually reveal cracks (Fig. 2.42), giving 2D images. X-ray tomography may produce 3D images and easily reveal all kinds of cracks, but it is more expensive and requires much more time to construct 3D images.

However, the philosophy of continuous constant processing and technology, giving homogeneous mixing, homogeneous structure, and constant control of the process and properties, probably predominates in industry today.

Constant visual inspection of surface defects, performed by both the producer and the customer, also gives positive results. Brightly illuminating the inspection area and vacuum cleaning all surfaces of cathode blocks prior to inspection are also useful.

2.3.4 Testing and Characterization

The properties of refractory materials are described in Chap. 1 as an overview of these properties and variations in their values. Because carbon cathode blocks are

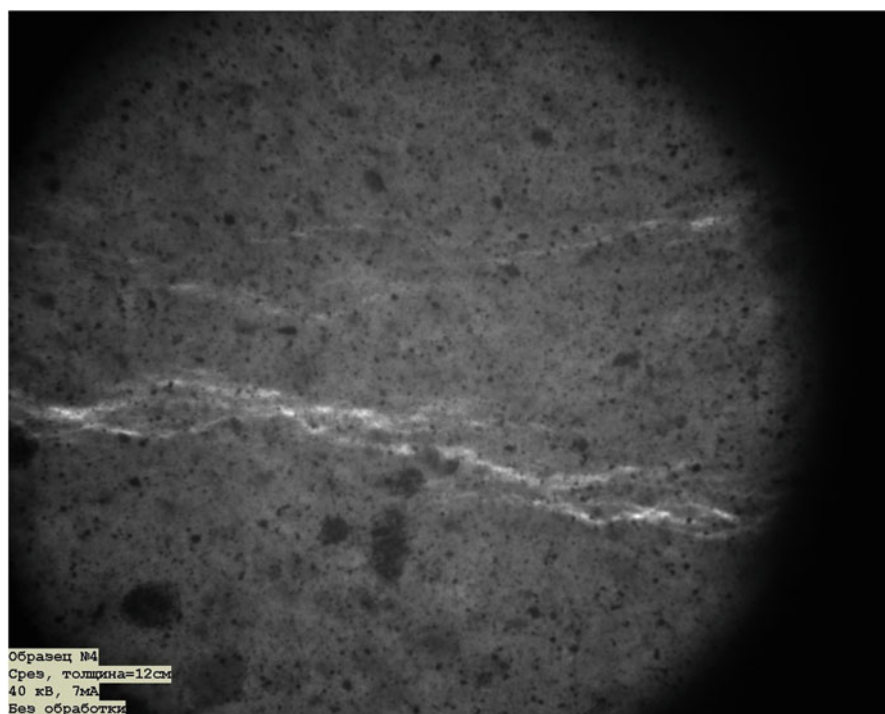


Fig. 2.42 X-ray detection of cracks in carbon cathode blocks

not common refractories, we will devote more space to their properties. Carbon cathode blocks are manufactured according to the specification of properties (Table 2.3). Professor Øye, along with coworkers, made a profound generalization on the standardization of the properties of carbon cathode blocks [10, 15]. Probably the most important properties are electrical conductivity and sodium swelling. These properties make carbon cathode blocks different from all other refractories.

The electrical conductivity of carbon cathode blocks is a function of temperature (Table 2.3), and it changes during service life (Tables 2.4, 2.5, and 2.6) [3, 10, 16].

The voltage drop in cathode carbon blocks depends on the electrical resistance and the current density [3]:

$$\Delta U = RI(2.5 + 0.92H - 1.1h + 132/b), \quad (2.15)$$

where R is the electrical resistivity (Ω cm), I is the current density (A/cm^2), H is the height of block (cm), and b and h are respectively the width and height of the slot (cm).

In general, it is possible to say that an electrical resistance of 30–40 $m\Omega$ cm (typical for anthracitic graphitic blocks with 30% graphite) corresponds to a power consumption of 230–262 kWh/t, an electrical resistance of 20 $m\Omega$ cm (typical for

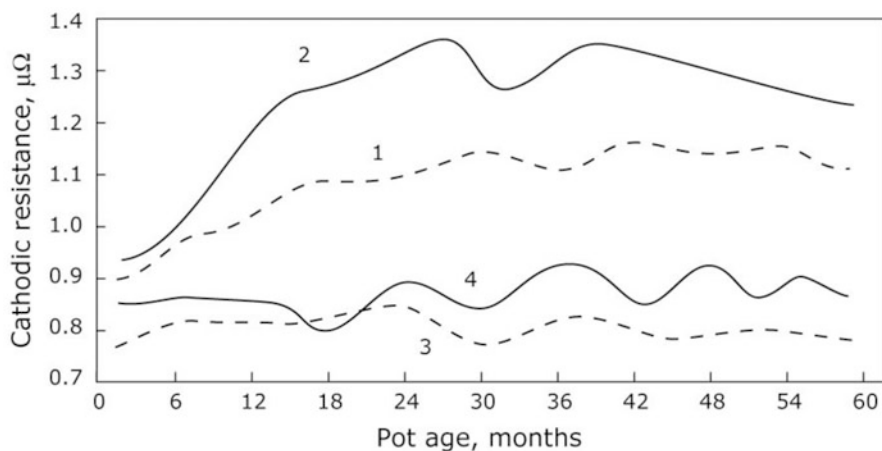


Fig. 2.43 Time dependencies of electrical resistivity of different grades of carbon cathode blocks during service in reduction cells according to [17]

graphitic blocks) corresponds to a power consumption of 130 kWh/t, and an electrical resistance of 10 m Ω cm (typical for graphitized blocks) corresponds to a power consumption of 65 kWh/t (Figs. 2.34 and 2.43).

According to ISO 11713-2000 [18] and ASTM C611 [19], electrical resistivity is measured on samples cut off from a carbon block in a parallel direction and in a normal direction. Also, the electrical resistance is measured on blocks by the contact method on every block at checkout control before storage.

The thermal conductivity of graphite decreases with temperature increases, and the temperature dependence of an anthracite block is low (Table 2.4). Graphitization leads to an increase of the thermal conductivity. Yet all these dependencies are more of academic interest, because when infiltrated with bath, anthracitic graphitic and graphitized materials have a thermal conductivity that is increased several times.

A sodium expansion test is a method of determining the linear expansion of carbon from the intercalation of sodium atoms in the crystal lattice of carbon at reduction. The radius of a sodium atom is significantly larger than the distance between the interlayers of carbon atoms, and this causes an expansion on both the micro and macro scales. Sodium swelling is a phenomenological characteristic. It is comparative, but it is a starting point for engineering calculations. A sodium swelling test lasts 1.5 h. During the test, fluorine salts totally impregnate a carbon sample; the intercalation of sodium is probably also finished in the entire volume of material. In reduction cells, fluorine salts may reach the lower edge of the bottom block within 1–2 weeks, but they also may reach it within several months. We do not have sustainable, verified data on the kinetics of intercalation at service.

In anthracitic graphitic carbon blocks with 30% graphite, linear expansion due to sodium swelling may be up to 0.7%, which corresponds to 3 cm for a block 3.5 m in

length. The strains and microcracking may take place owing to this expansion, and the block may also bend. This may lead to the appearance of cracks, through which cryolite (and then aluminum) penetrates to the bottom of the cathode.

There are two modifications of the sodium swelling test ISO/WD 15379-1.2 [21, 22]: with and without pressure. In both variants, negative potential is applied to the test sample of the cathode carbon block that is dipped in cryolite and aluminum in the vessel while the vessel is in the furnace.

The test sample is a cathode in an electrolytic cell. In the variant of testing without pressure, the change in the dimensions of the test sample is recorded (Fig. 2.35), beginning from the start of the electrolysis process in this cell. In the variant 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%.

Additional research on the kinetics of sodium intercalation in a carbon lattice together with information on the rate of capillary movement of the melt in permeable pores in carbon will likely give information about the interaction of carbon with cryolite, and these tests will be improved. Sodium swelling depends on the CR as well as on the direction of pressing of blocks, but the most important thing for the producer of carbon blocks (that does not depend on producer) is that sodium swelling strongly depends on the material of the block—it is low for graphitized blocks and considerably higher for anthracitic graphitic blocks (Fig. 2.35).

The mechanical properties of carbon cathode blocks are the cold crushing strength (CCS) [23, 24], bending or flexural strength according to ISO 12986-1, ISO 12986-2, ASTM C651, DIN 51944-1999, and DIN 51902-1997 [25–29], and elastic modulus according to ASTM C747, ASTM C1025, and DIN 51915-97 [30–32]. The strength properties are determined at ambient temperature, but samples are taken in directions normal and parallel to the directions of pressing at fabrication.

The strength characteristics of carbon materials largely do not depend on temperature, at least at temperatures of aluminum reduction, so the temperature dependence of strength for carbon cathode materials more likely is of academic interest. It is well known that the static elastic modulus (determined at mechanical testing) is significantly lower than values obtained via ultrasonic methods.

Producers of carbon cathode blocks try to lower the compression strength, bending strength, and elastic modulus in order not to overtemper the material, since overtempering may lead to cracking. From the viewpoint of thermal shock resistance, the elastic modulus (as well as linear expansion) should be low, while the thermal conductivity should be high. Currently, customers require many mechanical properties of carbon cathode blocks, and most of them are found empirically.

Carbon cathode blocks are brittle (although from an academic point of view, carbon cathode blocks demonstrate an elastoplastic behavior) [33]. According to Panov [33], the fracture toughness of carbon cathode blocks is only $0.15 \text{ MPa} \cdot \text{m}^{0.5}$.

Allard [34] gives values of $0.3\text{--}1 \text{ MPa} \cdot \text{m}^{0.5}$ for anthracitic graphitic blocks, with a tendency to decrease in the case of graphitic materials. The critical crack initiation

stress and critical crack propagation stress are not determined, causing customers and producers to base specifications on empirical knowledge. It is likely that in the future it will be useful to include the fracture toughness K_{IC} , Eq. (1.4), in specifications. For research purposes, the energy of crack initiation and the energy of crack propagation might be useful, while forecasting the service life of a cell and slow crack growth might be essential.

In contrast, there is almost no degradation in strength characteristics at high temperatures [10], and the strength itself is not a limiting property at service; usually, cathode blocks disintegrate owing to the appearance of cracks. However, we are doubtful that an optimal complex of thermomechanical properties for carbon cathode blocks—leading to estimation and direct calculation of service life—can be known.

Although there is no direct proportionality, the thermal conductivity for carbon cathode blocks follows electrical conductivity, which has a priority. For design purposes, the high thermal conductivity of a carbon cathode block may be compensated by the low thermal conductivity of heat insulation materials. Because the thermal conductivity of carbon is high, it is difficult or impossible to measure it using static methods, so the comparative ISO 12987-2003 [35] dynamic method is used (measurement in normal and in parallel directions). The knowledge of thermal conductivity temperature dependence is of limited value because the change in thermal conductivity due to infiltration by electrolyte is significantly bigger. Linear expansion is measured according to DIN 51909-97 [36] (measurement in normal and parallel directions) and ISO 14420 [37].

The porosity of carbon cathode blocks should be low, the pore size distribution should be uniform, and the percentage of permeable porosity (which is derived from the permeability) should be low. These requirements are based on the necessity to diminish bath penetration through the cathode block to the refractory level. Figure 2.36 gives an example of different pore size distributions in the carbon cathode blocks of different producers. The open porosity in all these blocks was in the range of 20%.

Research has been published [38] suggesting that the considerable number of shutdowns of cells may be connected with the large number of large pores and cavities in the rammed peripheral seam through which a considerable amount of liquid bath penetrates during the startup period.

It is considered that pores of 1–10 μm naturally exist in carbon materials, while pores of 15–100 μm are due to the peculiarities of technology. Large pores greatly increase the value of gas permeability, and a large gas permeability is typical of materials with an irregular pore size distribution. The total porosity and open porosity for carbon blocks of two different producers may be similar, but the values of gas permeability may differ by a factor as large as 10. In the best samples of blocks, the porosity is monomodal, though a bimodal pore size distribution is more typical (Fig. 1.5). Sometimes it is possible to see an irregular pore size distribution with pore sizes ranging from 5 μm up to 100–130 μm . In the future, the average pore size in carbon cathode blocks should probably be limited to 10–15 μm , while the permeability should be limited to 0.3–0.4 μm^2 (3–4 nPm or 3–4 μdarcy).

The apparent density conveys information on the ratio of the space occupied by pores and not directly points on the graphite content (for a certain porosity), while the true density conveys information on the level of calcination of anthracite and the graphitization in graphitic materials. Some producers of carbon cathode blocks use the apparent density as an industrial parameter; it is determined by weighing blocks after baking (not waiting for mechanical grinding and sampling from lab tests before storage). The apparent density is determined according to ISO 12985-1,2 [39, 40], DIN 51918-1999 [41], and ASTM C559 [42], the porosity is determined according to ISO 12985-2 [40], ASTM C1039 [43], and DIN 51913- 2001 [44], while the true density is determined according to ISO 9088-1997 [45], ISO 21687 [46], and DIN 51913-2001 [44]. The standards for determining the gas (air) permeability (ISO 15906 [47]) and pore size distribution are valid for carbon and refractory materials and are described in Sect. 1.2.

The ash content shows the amount of admixtures in carbon materials. For carbon materials, ash consists of oxides of sodium, potassium, calcium, and iron. For specialists in refractory materials, it is strange to unite these oxides in one group and use one word, ash, to describe it. Still, if the ash content is within certain limits, it influences only the thermal and electrical conductivities. The ash content is determined according to DIN 51903 [48] and ISO 8005 [49].

2.3.5 Grades of Carbon Cathode Blocks

There is not just one decision to make in the question of the grade of carbon cathode blocks for the design of reduction cells. There are many pro and cons, and many properties that change during service life must be taken into account. The general tendency is to install graphitic or graphitized carbon cathode blocks.

Professor Øye [10] gives data from Wilkening [50], Table 2.7, with two main characteristics that strongly depend on the grade of the carbon block: sodium swelling and electrical resistivity. Another characteristic that it is probably necessary to include is wear resistance (Table 2.10).

Table 2.7 Temperature dependencies of electrical resistivity and thermal conductivity in different grades of carbon cathode blocks according to [10, 17]

Grade of carbon cathode block	Temperature, °C	0	200	400	600	800	1000
Anthracitic graphitic (30% graphite)	Electrical resistivity, $\mu\Omega$ m	43	41	39	37	36	36
	Thermal conductivity, Wt/m K	6	7	8	8	8	8
Graphitic (100% graphite)	Electrical resistivity, $\mu\Omega$ m	20	18	18	18	18	18
	Thermal conductivity, Wt/m K	30	29	27	24	23	22
Graphitized	Electrical resistivity, $\mu\Omega$ m	10	10	10	10	10	10
	Thermal conductivity, Wt/m K	125	90	75	60	55	50

Recall that sodium swelling is an irreversible process that takes place at the beginning of startup and service life without any continuation (not to mention mechanical tensions), and the electrical resistivity changes during service life, but it is not only the electrical resistivity's influence on cathode drop that ultimately influences the energy consumption of reduction cells during service.

On the contrary, sodium swelling locks all gaps, cavities, and poor joints in the lining, preventing leakage of electrolyte in the lining. Sometimes on smelters following a retrofit and after cathode carbon blocks are changed for a higher grade, problems with leakage arise.

An uninvestigated problem of the graphitization of anthracite in blocks at service in the presence of sodium (which we will discuss later) has two practical consequences:

- Graphitization promotes stable electrical characteristics of semigraphitic blocks at service (due to the possible increase in electrical conductivity);
- The transformation of anthracite to graphite is accompanied by a negative volume effect, increasing the porosity and, possibly, the dimensions of permeable pores and the capillary flow of electrolyte to the refractory lining.

There is evidence that the service life of cells with graphitized cathode bottom blocks decreases by 15–20%, and there are no proven data on the increase or decrease of service life of cells with impregnated graphitized blocks.

Recall that cathode voltage drops depend not only on the electrical resistivity of a carbon block but also on the cathode–collector steel bar connection. The question of how to choose the grade of carbon cathode block depends on the forecasted power losses due to voltage drops, local economic circumstances, and the price of electricity. In [51], the cathode voltage drop at 350-kA cells at graphitized blocks is 220 mV, while blocks with 75% graphite provide 284 mV.

As mentioned previously, there is no single technical decision on the best variant of grades of carbon cathode blocks; when working out the design of a cell, it is necessary to find an optimal compromise of properties, taking into account not only the constantly changing technical parameters but also economic circumstances and the prices for electricity in the region. However, it is necessary to consider that the energy consumption of a cell will increase owing not only to a voltage cathode drop but also to a voltage drop in the block–steel collector bar connection [52] (Fig. 2.37).

According to Panov [33], a voltage drop in the joint carbon cathode block–steel collector bar for a cast-iron connection is 10–15 times lower compared with a cathode voltage drop in a rammed or sealed connection.

Usually when there is demand to increase the production of aluminum, the standard decision is to increase the current of the cells, which requires changing anthracitic graphitic blocks for graphitic or graphitized and modernizing the cell construction, including the lining.

We will not go into details, but we can say that the grade of carbon cathode blocks does not influence the current efficiency of the reduction process, but it seriously influences the energy consumption and may have an influence on the service life.

2.3.6 *Structure of Carbon Cathode Blocks in Connection with Grain Size Composition, Sintering, and Pore Size Structure*

The grain size composition of a mix is coarse. The typical grain size composition of raw materials for the production of carbon cathode blocks (calcined anthracite, graphite, or coke) consists of three (or, rarely, four) grain fractions. The coarse fraction is 10–5 mm, the fine fraction is less than 0.075 mm, and the medium fraction is 5–0.5 mm.

For a long time, the standard problem for specialists in the technology of refractory materials was to obtain the minimum possible porosity of the green shape, which opened the possibility to obtaining the minimum possible porosity in a fired refractory material.

Well-known equations of optimal amounts of grain size fractions [53–57] help specialists obtain the desired low porosity:

$$Q_i = (d_i/d_{\max})^n \times 100, \quad (2.16)$$

$$Q_i = (d_i^n - d_{\min}^n) / (d_{\max}^n - d_{\min}^n) \times 100, \quad (2.17)$$

$$Q_i = [\alpha + (1 - \alpha)(d_i/d_{\max}^n)] \times 100, \quad (2.18)$$

where Q_i is the amount of a certain grain fraction, d_i is the volume-weighted diameter of the grain fraction, $d_{\max}$ and $d_{\min}$ are the maximum and minimum grain size dimensions, respectively, n is the coefficient of shape (0.3–0.6), and α is a coefficient that accounts for additional quantities of fine fractions.

These equations do not take into account the size of pores, and a direct attempt to reduce the open porosity to below the requirements of a customer from an aluminum smelter may lead to a large variety in pore size distributions (Fig. 2.38). The gas permeability of these blocks may also vary considerably.

Later we will discuss the influence of the pore size of permeable pores in cathode blocks on infiltration. Here we will say only that today the specialist in refractory technology usually solves problems not only related to reducing porosity but also, rather frequently, those related to reducing the pore size of permeable pores.

In conventional refractory materials, the porosity of green shapes diminishes during firing in the course of the sintering process. In coarse-grained carbon materials, during the firing process the grain structure remains almost unchanged.

The only exception is that during carburization, pitch transforms into coke. About 20% of the pitch in a pressing mix transforms into approximately 10% coke in fired material, with particles of coke being below 0.075 mm. The porosity of green shapes during firing is slightly increased. Thus, in large part, the pore size of fired carbon material is governed by the pore size distribution of green shapes.

The pore size distribution of green shapes is determined by the shape of grains; large pores form between large grains and small pores form between small grains. Hence, to obtain a pore size structure with a more or less narrow and small size distribution, it necessary for small grains to form a continuous matrix.

We now present the results of some trials.

Three grades of grain size compositions with sizes of 5–10 mm, 0.5–5 mm, and below 0.5 mm (80% were below 0.075 mm) were investigated, and the only variable was the amount of fine fraction [58]. It was considered that the coarse fractions formed the frame of the structure, while the fine fraction filled in the cavities in the frame. On filling in the cavities in the frame, it was possible to follow the change in the frame structure to a matrix structure when the coarse particles did not come into contact with each other but only fine particles made contact. The amounts of fine-grained fraction in the trials were 15, 30, 40, and 60%.

The properties of fired material correspond either to properties of the frame or to properties of the matrix. With a fine fraction of 15%, all pores were larger than 25 μm ; the same result (not shown) was seen at two grain size compositions without a fine fraction. The addition of a 30% fine fraction leads to the appearance of pores with dimensions of 3–5 μm . However, the considerable decrease in pores above 25 μm and the increase in fine pores of 3–5 μm take place only upon the addition of 40 and 60% fine fraction of carbon material (Fig. 2.39). The properties of the material also change (Table 2.8).

The matrix structure yields an increase in electrical as well as thermal conductivity. Note that upon addition of 60% fine fraction, the porosity of the fired material increased by 5%, so from the viewpoint of minimal porosity, the grain size composition was not optimal. Note also that this was a result of laboratory research. An excessive amount of fines creates considerable problems with the mixing of grain size composition with pitch and gives rise to other technological problems. The implementation of such laboratory studies also creates some problems, though those are solvable.

The pore structure of industrial grain size composition was bimodal: There were pores with average dimensions of 5 and 100 μm . After the fine fraction was increased to 40%, the total and open porosities remained approximately the same, but the 100- μm pores were eliminated (some changes in the form and shape of other pores were also seen) (Fig. 2.40) (Table 2.11).

Table 2.8 Change in electrical resistivity of carbon cathode blocks with time (lab tests during electrolysis) [10, 17]

Grade of carbon cathode block	Time, min	0	20	40	60	80	100	120
Anthracitic graphitic (30% graphite)	Electrical resistivity, $\mu\Omega\text{ m}$	35	31	27	25	25	25	25
Graphitic (100% graphite)	Electrical resistivity, $\mu\Omega\text{ m}$	22	20	19	18	18	18	18
Graphitized	Electrical resistivity, $\mu\Omega\text{ m}$	10	10	10	10	10	10	10

The amount of binder (pitch) may also influence the pore size distribution. A large amount of pitch promotes better filling of cavities in the frame by fine particles, but at the same time the volume of carburizing gases increases, giving a larger amount of relatively large pores (Fig. 2.41).

Later it will be shown that the question of whether we should obtain a low porosity or pore size distribution with a uniform grain size distribution with a small grain size for carbon cathode blocks in aluminum reduction cells should be solved as a problem related to a uniform grain size distribution with a small grain size.

For coarse-grained carbon materials, probably the most convenient method of obtaining a structure with a relatively small grain size is by the addition of fine fractions. If the amount of fine fraction exceeds 30% (preferably 40%), then the pore size will more likely be similar to the size of grains of a fine fraction. Of course, difficulties will arise in processing because relatively large amounts of fine fraction will require additional binder and additional attempts at obtaining a uniform distribution of the binder.

Another approach is the well-known rule that to obtain an optimal packing of powder (lowest porosity) of mixes with two different grain sizes, where the ratio of the dimensions of coarse fraction to fine fraction is 10:1, should be 70% coarse fraction and 30% fine fraction. This is the solution of Eq. (2.16) for the coefficient $n = 0.5$.

Thus, to some extent, the approach involving the lowest possible porosity may not be in conflict with the lowest possible uniform grain size, and solutions are possible. In carbon cathode blocks it is possible to obtain an average grain size distribution of approximately 7–10 μm , only varying the grain size and amount of fractions and the content of the binder.

In the ferrous industry so-called blast furnace carbon blocks are used for the lining of blast furnaces. Because of the dimensions, the pressure of the liquid iron and slag is significantly higher compared with those of the reduction cells, and requirements regarding pore size are more stringent.

In specifications for carbon materials in the lining of blast furnaces grades with pore sizes of less than 10 μm and even less than 5 μm exist. The structures of carbon materials with such values of pore size may be obtained by chemical interaction; varying the grain size will not be sufficient for solving such a problem.

2.3.7 Interaction of Carbon Cathode Blocks with Steel Shell and Collector Bars

The shape of slots in carbon cathode blocks may differ (Figs. 2.17 and 2.19); a two-slot block design (Fig. 2.17b) is typical for high-capacity cells. The rectangular collector bars are adjusted in the slots. These collector bars are the conductors for the negative electric potential on the blocks. The collector bars are adjusted in the

slots by cast iron, contact carbon pastes, or carbon glues. All methods of adjustment of collector bars in carbon blocks have advantages and disadvantages, and currently there is no strict preference among aluminum producers. Casting gives proof of contact between collector bars and carbon, but there is a risk of cracking in the angles of slots (Fig. 2.42) due to thermal shock.

Special furnaces for the preheating of a block and collector bars before casting diminish the possibility of cracking. There is no cracking with carbon glues and contact carbon pastes, but such contact produces a voltage drop that will increase with time.

Cracking in carbon cathode blocks may take place during preheating and startup, but more frequently, cracks in carbon blocks reach the surface during service. The main reason for cracks appearing in carbon cathode blocks is mechanical tensions due to interaction with the shell (via siding and peripheral seam) and with refractory layers, but, of course, inner defects, such as cavities and inner cracks, may dramatically facilitate the appearance of cracks on the surface. Cracks reaching the service of cathode blocks within the first 3 years of service are mostly disliked at smelters, because they cause the service life at the smelter in general to diminish considerably. However, during service life, a sort of balance exists between the tensions in the blocks and mechanical strains between the shell and the blocks, and there are many thin cracks in the blocks that are not filled by bath or aluminum (Fig. 2.52).

Computer simulations of the mechanical behavior of carbon cathode blocks and the mechanical interaction between carbon blocks and the shell and lining have not been completed. The design of a cathode for the Hall–Heroult process is still in development, and new cell designs will most likely appear within the next 10–20 years. Although not frequent, sudden shutdowns of cells still take place, and so analytical and research efforts are still required in this direction (Fig. 2.44).

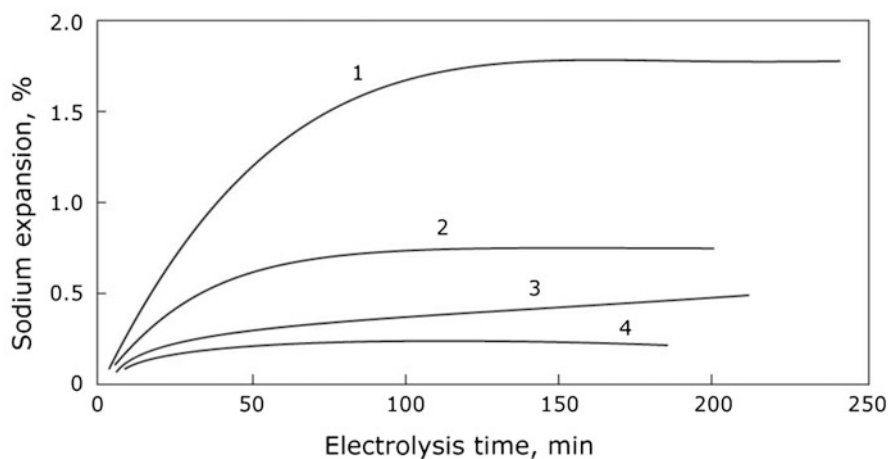


Fig. 2.44 Sodium swelling test: (1) anthracitic graphitic; (2) graphitic; (3, 4) graphitized—according to [22]

Cracks Induced by Thermal Strains and Thermal Shock

Recall that temperature gradients in carbon cathode blocks at preheating and in the moment of pouring electrolyte may reach 300–1100 °C/m at the surface of cathode blocks and up to 1500 °C/m in the direction from the surface to the refractory layer. Estimations show (Table 2.9)

$$\sigma = \alpha E \Delta T / (1 - \mu), \quad (2.19)$$

where σ is the strain, E is the elastic modulus, ΔT is the temperature gradient, and μ is Poisson's ratio.

Possible stresses in cathode blocks due to thermal gradients may be comparable to the bending strength of the blocks.

The first Hasselman criterion [61]

$$R = \sigma E / \mu \Delta T \quad (2.20)$$

has a physical meaning of maximum temperature gradient per meter, giving the possibility for a crack not to appear. The values of the calculated criterion are close to the values estimated earlier: 300–1100 °C/m at the surface of cathode blocks and up to 1500°/m in the direction from the surface to the refractory layer, which gives

Table 2.9 Information on grades of carbon cathode blocks

Grade of carbon cathode material	Resistivity, $\mu \Omega \text{ m}$	Sodium expansion, %	Wear resistance	Strength	Comments on transformations during service
Anthracitic graphitic (30% graphite)	30–40	0.7	High	CCS-30–45 MPa, moderate fracture toughness	Anthracite partially transforms to graphite, porosity increases
Anthracitic graphitic (75–80% graphite)	25	0.4–0.5	Relatively high	CCS – 25–35 Mpa	
Graphitic (100% graphite, coke binder)	18–25	0.25	Moderate	CCS 20–25 MPa	
Graphitized	11–13	0.1	Low	CCS 20–25 MPa, fracture toughness very low	Electrical resistivity slightly decreases
Graphitized impregnated	10–12	0.1	Rather low	CCS – 30–35 MPa, fracture toughness low	

additional evidence that thermal strains at preheating and startup may be responsible for the initiation of cracks in carbon cathode blocks. Durand [62] gives a value for the first criterion of thermal shock resistance of $1290^{\circ}/\text{m}$.

Hasselmann [61] presented a general trend to understand thermal shock resistance, but since that time many new criteria in thermal shock resistance were introduced. These criteria make it possible to understand what properties promote resistance to crack initiation in materials, and what properties promote resistance to the growth of existing cracks.

Generally speaking, if a material has a low elastic modulus, low thermal coefficient of thermal expansion, high thermal conductivity, and high strength, it should be resistant to thermal shocks. To be resistant to crack initiation, the material should have high strength, high thermal conductivity, and high elastic modulus, but to be resistant to the growth of existing cracks, the material should have a low elastic modulus and low thermal coefficient of thermal expansion. Here we do not take into account the peculiarities of the structure and thermal strains that may appear (and in fact do appear) on the borders of large carbon grains and carbon matrices consisting of small grains.

Usually, there are no visual cracks in cathode blocks at startup. But this does not mean that these cracks (precracks) are not formed inside the blocks. The strains are quite sufficient for the formation of precracks of subcritical dimensions. According to the slow crack growth model [63], the strains for the slow propagation of cracks are lower than strains for initiating cracks. Usually, thermal strain cracks reach the surface of cathode blocks, and the distance between them is 80–100 cm.

Normally, they are parallel to each other and normal to the surface of the cathode. However, it is necessary to remember that these cracks reach the surface after 6–36 months, although it is most likely that they will appear during preheating and startup.

During service, carbon cathode blocks are in a stress–strain state. From the viewpoint of fracture mechanics, overheating by 50°C or increasing the current density by $0.1\text{ A}/\text{cm}^2$ should not be critical for the start of a crack. Additional stress upon overheating by 50°C is significantly lower compared to strain causing fracture. However, this overheating may be critical for the following phenomena (Table 2.12):

- Stress of crack propagation;
- Slow crack growth rate, especially in a nonequilibrium stress–strain states.

This assumption may be proved by industrial experience [59] showing that the temperature changes of electrolyte at the startup period, fluctuations in the CR and in the level of metal and electrolyte, and all uncontrolled deviations of processing negatively affect service life (Fig. 2.45).

Returning to thermal shock resistance, it is possible to state [60, 64] that anthracitic graphitic carbon blocks with electrically calcined anthracite have larger values of Hasselmann criteria compared to carbon blocks from gas-calcined anthracite. This has some connection with the percentage of shutdowns of cells. The

Fig. 2.45 Pore size distributions in carbon cathode anthracitic graphitic (30% graphite) blocks of different producers, having open porosity below 20%

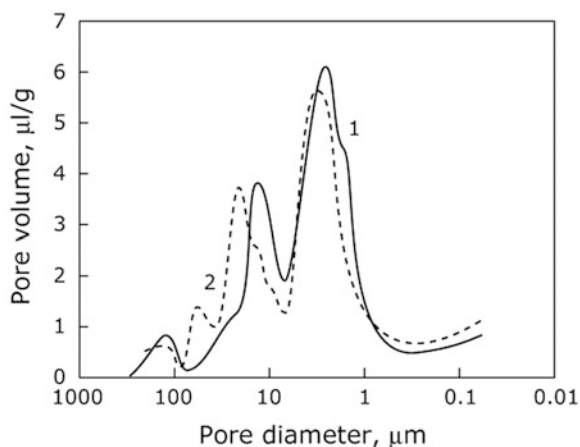
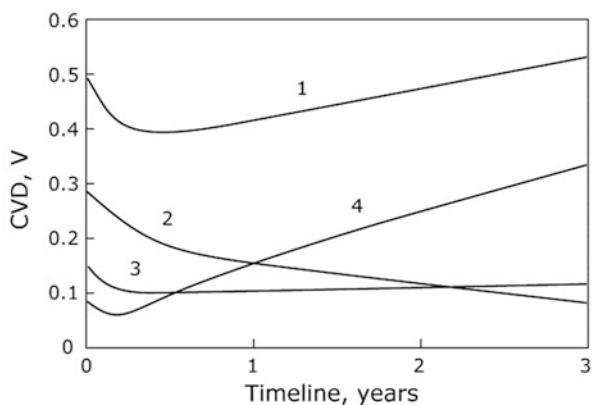


Fig. 2.46 Components of cathode voltage drop, changing with service time according to [53]



reason for this is in the looser structure of electrically calcined anthracite, resulting in a lower strength and a lower value of elastic modulus of cathode blocks.

Such materials may absorb strains and check crack development, which plays a positive role in thermal shock resistance (Fig. 2.46).

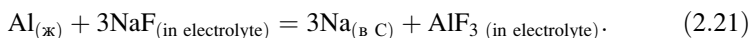
2.3.8 Interaction of Carbon Cathode Blocks with Electrolyte During Startup and in Service: Wear, Infiltration

There are two main pathways by which sodium reaches the barrier refractory layer of a reduction cell:

- Sodium diffusion in carbon lattice;
- Capillary flow of electrolyte through permeable pores of carbon cathode blocks and rammed carbon of ramming paste.

It appears that one of the consequences of both processes is the graphitization of anthracite (and coke) in anthracitic graphitic blocks (Table 2.13).

The initial reaction that leads to the appearance of sodium in carbon cathode blocks is



Sodium may exit the carbon lattice in the form of intercalation compounds, such as 1471 NaC_{64} [66, 67].

The main mechanism of the propagation of sodium in carbon is thought to be diffusion in the carbon lattice [68, 69], although it has been suggested that this mechanism involves, more precisely, the propagation of sodium in the lattice in the vapor state [70]. The reported values of diffusion coefficients [65] currently are more likely to be of academic interest, and the reported values differ more likely due to different conditions, current, CR, and other factors.

Levels of sodium saturation are reported in [65] and give a good understanding of the amount of sodium in carbon cathode blocks at service (Table 2.10).

Sodium diffusion after saturation should be constant and may stop at the leveling of sodium concentrations in the upper and lower surfaces of carbon blocks, which appears to be some sort of barrier (or probably would not in the case of activation by current). Of course, sodium penetration should depend on the CR and current density.

Reaction (2.16) may proceed not only on the upper surface of blocks but also on the surfaces of pores inside blocks. Other reactions [10] of sodium-containing substances with carbon may take place, resulting in the formation of sodium aluminates, aluminum carbide, aluminum nitride, and sodium cyanide in the volume of carbon cathode blocks.

The “dry” penetration of sodium to the refractory layers due to the diffusion of sodium through carbon cathode blocks really should be taken into account. The consequence of such diffusion is the appearance of free silicon in the form of balls of ore drops or globules having a diameter of 1 to 4 cm, which appear owing to reactions of sodium with silica or silica-containing compounds. However, the dry penetration of sodium does not seriously deteriorate the refractory lining, which cannot be said of “wet” penetration or the capillary flow of electrolyte through permeable pores of carbon cathode blocks and rammed carbon of ramming paste.

Table 2.10 Grades of carbon cathode blocks and sodium saturation (according to [10])

Grade of carbon cathode material	Na saturation, kg/m ³
Gas-calcined anthracite	60–70
Electrically calcined anthracite	60–70
Graphitic	30–35
Graphitized (at 2300 °C)	15–20

Transformations in Carbon Cathode Blocks During Service Life

Liquid electrolyte penetrates carbon cathode blocks through permeable pores, sodium intercalates in the lattice of carbon, and amorphous carbon undergoes graphitization. All these processes increase the electrical and thermal conductivities.

The details of the graphitization process are unknown. One belief is that sodium itself cannot be a catalyst of graphitization at temperatures below 1000 °C, and the graphitization proceeds via the formation of carbides with their subsequent decomposition [10, 71]. According to [72], an anthracitic carbon block after 1 year of service contained 25% graphite. After 2 years of service, the rate of graphitization becomes stabilized [73] or diminishes [74]. The density of graphite is 2.15–2.25 g/cm³, while the density of anthracite is at the level of 1.7–1.86 g/cm³. The volume effect of graphitization is negative and equals

$$\Delta V/V = 77 - 83\%. \quad (2.22)$$

Thus the graphitization of anthracitic or semigraphitic blocks is followed by an increase in pore volume, and the pores are filled in with bath. The process of graphitization may also be followed by the fracture of coke bridges between the grains of graphite and anthracite, which in a pessimistic variant may cause cracking.

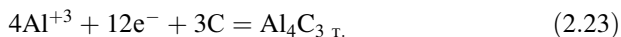
After several years of service, an anthracitic block has an electrical conductivity similar to the electrical conductivity of a semigraphitic block with 30–50% graphite, yet it will never have the electrical conductivity of a graphitic block [75–77]. According to lab tests, there is no degradation of the electrical conductivity of graphitized blocks, while the degradation of semigraphitic blocks is lower compared to graphitic blocks (Table 2.5).

Formation of Aluminum Carbide, Chemical Erosion Mechanism of Wear of Cathode Blocks, and Wear and Erosion Tests

The hardness of graphitized and graphitic materials is sufficiently lower compared to anthracitic graphitic materials; consequently, the wear resistance of graphitic materials is also sufficiently lower. The wear resistance of anthracitic graphitic blocks under the influence of abrasive and erosion wear by alumina particles in the electrolyte is not critical or almost not critical for the service life of cells, while the wear resistance of graphitic and graphitized blocks is critical. Wear resistance testing of carbon cathode blocks is essential. There have been several approaches to testing erosion on carbon cathode blocks, beginning with early investigations of the wear resistance of carbon cathode material in a water slurry of alumina [78].

According to Prof. Øye [10], the current understanding is that the wear of carbon cathode blocks is mainly the process of the formation of aluminum carbide. The

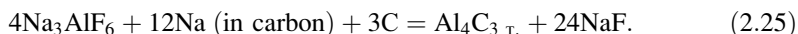
reaction between aluminum and carbon is possible from the viewpoint of thermodynamics within all ranges of temperatures in the cell [10],



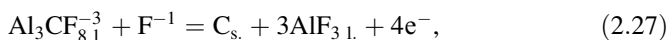
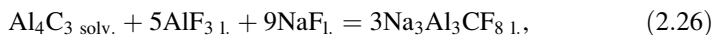
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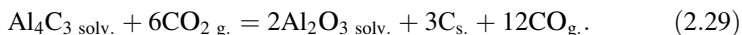
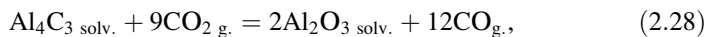
Also, the formation of aluminum carbide due to reaction (2.17) may be shown as



The formation of aluminum carbide does not lead to the degradation of carbon materials. A light yellow film of aluminum carbide is formed on the surface of the cathode, reaches a certain thickness, and starts acting as a barrier. However, the solubility of aluminum carbide in aluminum is several orders of magnitude lower compared with the solubility of aluminum carbide in electrolyte [10]. Cryolite film and alumina act together and dissolve the protective film of aluminum carbide. Aluminum carbide dissolves in electrolyte,



and is oxidized at the anode:



A kind of chain reaction takes place, while the reaction products are moved away from the reaction zone due to the circulation of the bath and aluminum in the cell. According to [10], this chemical process, for one thing, is almost independent of the quality of carbon material, but, for another, the value of aluminum carbide formation in wear is much stronger than physical wear.

The reactions of the formation of aluminum carbide may take place on the surface and at the internal surface of pores inside a cathode block. The reaction takes place with positive volume effect, so the formation of aluminum carbide in pores may follow the mechanical tensions and even cracking owing to these tensions. The probability of the reaction increases as the level of graphitization decreases.

Lab investigations have shown [10] the following:

- The wear rate by electrolysis increases as the current density increases but levels off at current densities above 0.8 A/cm^2 ;

- Electrochemical wear is much higher than physical wear and is the same for graphitic and anthracitic materials;
- The presence of alumina slurry suppresses electrochemical wear;
- The physical wear rate increases strongly with velocity and increased concentration of an alumina slurry;
- The physical wear rate of graphite is about five times the physical wear rate of anthracitic carbon;
- The physical wear ratio graphite/anthracite is about the same in room-temperature abrasion tests and in cryolitic melts;
- The mechanisms of wear in industrial cells are a combination of physical and chemical wear in spite of the fact that physical wear is much smaller.

Industrial investigations, prompted by industrial experience on implementation on graphitic and graphitized carbon blocks, have revealed several dependencies.

Industrial practice gives wear values of around 2.3–3.3 cm/year for graphitized blocks, 1.2–1.7 cm/year for graphitic blocks, and 0.8–2.2 cm/year for anthracitic graphitic blocks (70–85% graphite) [78, 79]. Probably the best proof of the fact that anthracite-based materials are less subject to wear is well known to industrial specialists: the profiles of the cathode bottom of graphitized or graphitic blocks with anthracite-based ramming paste (Fig. 2.47). Other publications contain other values of wear [80], which is quite obvious because the wear rate depends on several factors (e.g., current, current density, type of a cell, CR), which are impossible to maintain on one level in industrial cells of different constructions.

There is a direct proportionality between the wear rate in industrial conditions and the cathode current density, which may reach 70–80 mm/year [81]. A larger open porosity of graphitized carbon cathode blocks promotes increased wear rates owing to the increased formation of aluminum carbide, shown in the lab and at an industrial scale [82, 83].

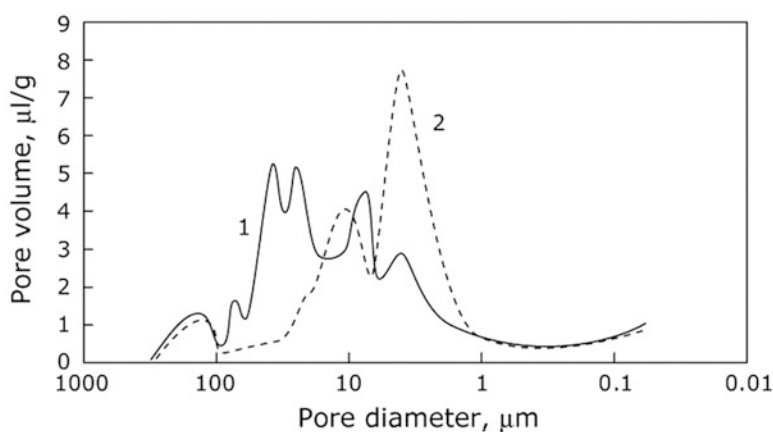


Fig. 2.47 Pore size distributions in carbon cathode blocks, produced on the same carbon plant with a 1-year time interval

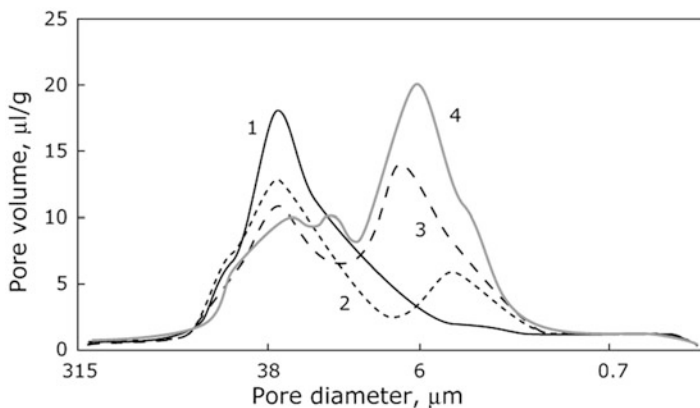


Fig. 2.48 Pore size distribution in carbon materials with changing amount of fine (<0.075 mm) fraction: (1) 15%; (2) 30%; (3) 40%; (4) 60% [59]

Erosion increases wear, and the combined mechanism of chemical wear takes place. At the smelter, a decision must be made to modernize and install graphitic or graphitized blocks instead of semigraphitic ones, and increased wear takes place. Anthracite is significantly harder than graphite, yet there is no direct proportionality between wear rates and the graphite content in blocks [84].

The problem of wear is serious. The profile of cathode wear having a W-shape is well known to industrial specialists (Fig. 2.48). Of course, this leads to a shortening of service life.

Special studies aimed at increasing the wear resistance of graphitized and graphitic cathode blocks have been undertaken. Special research was designed to form a gradient structure with different electrical resistivity along the length of a block. Another approach is to increase resistance to wear. Impregnated graphitized blocks demonstrate higher wear resistance. There have been attempts to increase the wear resistance of graphitized blocks, impregnating the blocks with phenolic resin with additions of zirconium and titanium oxides. In contrast, a significant increase in wear resistance may be achieved on anthracitic graphitic blocks with 80–85% graphite (Fig. 2.49).

In the literature [84, 85], lab tests give reasonable values of the wear of different grades of carbon blocks, which give a more or less similar rating of wear during industrial electrolysis. Lab wear tests are a good instrument for R&D practice on carbon cathode blocks with respect to the reduction process. In lab tests, wear depends on CR and cathode density [86, 87]. Lab testing [10] has revealed that graphitized cathode blocks demonstrate a wear resistance that is 7–10 times lower compared to anthracitic grades.

A variation of the cathode test with vibration (which imitates the movement of the metal) is combined with lab electrolysis. In Thornstad's variation [88], both electrochemical and abrasion resistance are taken into account. This form of testing is very complex. A test sample under negative potential is in an alumina crucible

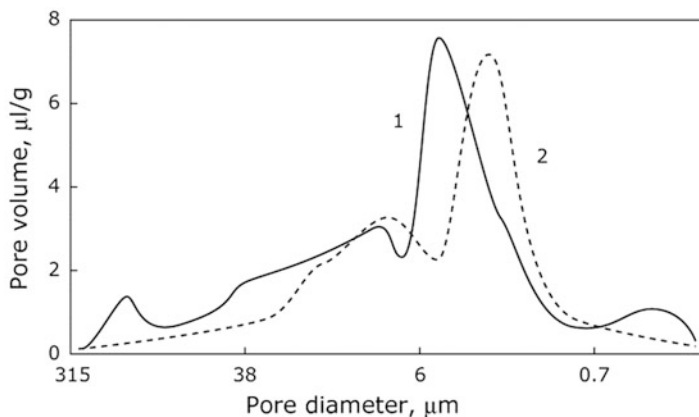


Fig. 2.49 Pore size distribution in industrial carbon materials (1) before and (2) after fines were increased to 40% [59]

with aluminum and bath with 8% alumina. The crucible is in the lab furnace, the temperature is increased up to 960 °C, the anode is made of tin oxide, and the rotor is made of boron nitride. The time of testing is 6 h. The registered parameters are voltage and CO/CO₂ concentration. After testing, a visual inspection is carried out, but the wear forecast is made based on the volume of CO/CO₂ output.

According to [88], there was good agreement between forecasted wear and actual wear in cells.

Research on increasing the wear resistance required special lab testing, which was invented at SINTEF [86, 89]. The test, based on a concept of wear by the electrochemical formation of aluminum carbide, is performed in a lab reduction cell at 980 °C, CR of 2.2, current density of 0.75 A/cm², and rotating speed of 0.6 m/s.

Coatings of carbon cathode blocks may significantly diminish the wear of carbon cathode blocks. The most promising material for coatings is titanium boride, although there are alternatives.

Infiltration of Electrolyte in Permeable Pores of Carbon Cathode Blocks

The open porosity of carbon cathode blocks is 14–22% (in graphitized blocks, up to 28%), and the permeability of carbon cathode blocks is 0.15–0.65 μm². Almost all pores are permeable; some small amount of closed pores may be in anthracite grains (if anthracite is used for production), and so open porosity is very close to true porosity—this is the peculiarity of carbon materials.

According to an estimation of Prof. Øye [10], a permeability of 0.4 μm corresponds to an infiltration rate of 3.2 cm/h for a liquid with a viscosity of 0.1 Pa/s.

According to the experiments of Brilloit et al. [90], bath penetrated around 18 mm for 1.5 h at 1010 °C, CR = 2.25, CD = 0.75 A/cm². Other estimations can be found in refs. [14, 91, 92]. According to Feng [92], electrolyte penetrated

from 0.4 to 15 mm for different carbon materials over 1.5 h at 1000 °C, at the same CR and current density.

Industrial experience provides evidence that sometimes the melt of electrolyte reaches the lower surface of carbon cathode blocks within half a year, but sometimes it reaches the refractory layer within 1–2 weeks. The value of irreversibly spent cryolite at startup for cells around 30 m² is up to 15 t. It looks like there may be constant electrolyte flow through the pores of cathode blocks if some barrier is not formed.

There are several reasons for the contradictory data regarding the time needed for electrolyte to reach the refractory level [10, 58–60, 64]:

1. Depending on the method of shaping (extrusion or vibropressing), the raw materials, and the peculiarities of the processing, the porosity of carbon cathode blocks and the pore size distribution may vary;
2. There is always a temperature gradient of 150–400 °C at the surface of the cathode block at the moment the electrolyte is poured (e.g., 900 °C in the middle and 600 °C at the periphery);
3. The designs of cells differ, the methods of preheating and startup differ, and consequently the temperature gradients between the upper and lower surfaces of cathode blocks differ;
4. At different smelters, the CR during startup may be from 2.3 to 4; consequently, the viscosity of electrolyte also differs.

In pores having a small diameter, the interactions between pore walls and liquid are considerable, and the fluid spreads [58]. The main constituents are capillary forces:

$$P_k = \frac{-2\sigma_{\text{El}} \cdot \cos \theta}{r_k}, \quad (2.30)$$

where P_k is the capillary pressure, σ_{El} is the surface tension of the electrolyte, and θ is contact angle of wetting of carbon by the electrolyte.

The capillary pressure is inversely proportional to the pore radius, and the flow of electrolyte in porous media may be considered to be the flow of viscous liquid in channels with a small radius. Laminar flow takes place [59], and the rate of flow is directly proportional to the square root of time.

Another type of flow occurs in pores when the pore surfaces are wetted by liquid. According to [59, 60], the viscous friction of liquid influences the type of flow. The flow rate is proportional to time to a power of 0.2–0.3.

The existence of the first or second type of flow depends on the balance between capillary forces and external pressure. In porous materials with a bimodal structure, two types of flow may coexist. According to [60], the critical radius of permeable pores, at which one type of flow changes to another, is

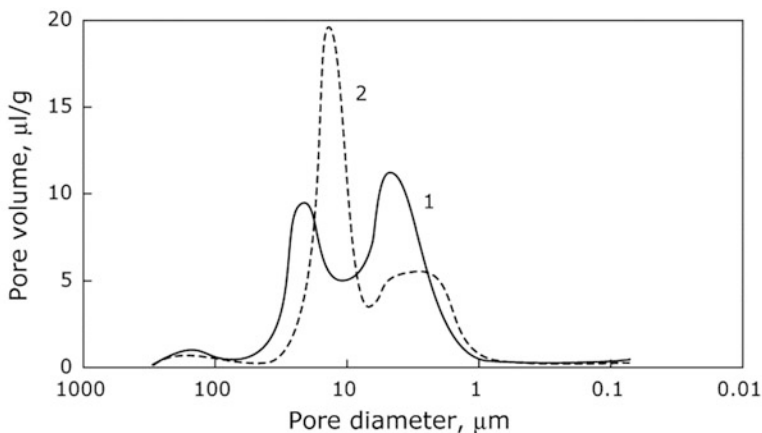


Fig. 2.50 Pore size distributions in carbon compositions: 5–10 mm: 40%, 0.5–5 mm: 20%, <0.075 mm: 40%, with a pitch amount of (1) 18% and (2) 24% [59, 60, 64]

$$r_k = \frac{-2\sigma_{\text{EI}} \cdot \cos \theta}{g(\rho_{\text{Al}} \cdot h_{\text{Al}} + \rho_{\text{EI}} \cdot h_{\text{EI}})} \quad (2.31)$$

A laminar electrolyte flow will occur in carbon cathode materials with pores greater than 25–30 μm . Computer simulations [58, 59] have shown two types of flow in the porous structure of carbon blocks in isothermal conditions. Electrolyte will flow in a laminar regime in large pores and cracks with above-critical dimensions down the lower surface of cathode blocks at a speed of 5–7 mm/h. The infiltration of carbon cathode blocks with porosity below the critical diameter proceeds at a speed of 2–2.4 mm/h (Fig. 2.50).

However, at startup, the temperature field in carbon cathode blocks is far from isothermal [59, 60] (Fig. 2.50). The movement of the crystallization point of electrolyte at startup takes place at a speed of 4.3–4.6 mm/h (of course, this speed may depend on the type of preheating, startup, CR, and so forth).

A comparison of movements of the crystallization point of electrolyte and the speed of penetration of electrolyte shows that the latter may be significantly faster for pores above the critical diameter (Fig. 2.49). This means that in such a case in nonisothermal conditions (startup), the movement of penetration of electrolyte in large pores will be determined by the movement of the crystallization point. In carbon cathode blocks with pores below the critical dimension, the movement of electrolyte through pores will be sufficiently slower compared to the movement of the crystallization point. This means that electrolyte may reach the refractory barrier layer through the pores of carbon cathode blocks within several days.

That is probably the answer for various industrial situations in which sometimes the melt of electrolyte reaches the lower surface of carbon cathode blocks within half a year, but sometimes it reaches the refractory layer within 1–2 weeks.



Fig. 2.51 (a, b) Cracking of carbon cathode block in angles of slot

C showed two types of behavior of electrolyte flow through porous carbon cathode blocks [58–60, 64] at startup:

- In carbon cathode blocks with pores below the critical dimension ($25 \pm 5 \mu\text{m}$), the velocity of filtration of electrolyte in a flow-spreading regime will be 2–2.4 mm/h, which is lower than the velocity of the crystallization point movement (4.3–4.8 mm/h). Owing to an increase in the thermal conductivity of carbon blocks and increased heat flow, the crystallization point after a certain period (7–8 days) will go up to the upper surface of the cathode and block the penetration of liquid electrolyte (Fig. 2.51). The interaction of electrolyte and the refractory layer will start after many months because electrolyte will crystallize in the pores of a carbon cathode block, not reaching the refractory layer.
- In carbon cathode blocks with pores above the critical dimension, the velocity of filtration of electrolyte in a laminar regime will be 5–7 mm/h; it will be greater than the velocity of the crystallization point movement (4.3–4.8 mm/h). The penetration of electrolyte will be governed by the movement of the crystallization point; after 96–110 h, the interaction of electrolyte and refractories will start up, resulting in the formation of so-called lenses (to be described later).

Selected industrial trials show [38, 58, 64] that electrolyte may reach the refractory barrier layer within 4–6 days. This was shown from a set of experimental cells with thermocouples under the carbon blocks and in refractory layers. It was considered that electrolyte had reached the thermocouple (in an alumina cover) when the thermocouple stopped indicating the temperature.

2.3.9 Carbon Ramming Paste

From a materials science point of view, carbon ramming paste between carbon cathode blocks and in seam lining is the same carbon cathode material. The finished properties of baked ramming paste are the same, and the testing is almost the same. Yet it is an unfinished product that will acquire its properties only after preheating and startup.

The decision to use carbon ramming paste between carbon cathode blocks and in peripheral seams sometimes is met with some puzzlement among refractory producers, who know that in ferrous metallurgy, this technical decision ended many years ago. Yet the decision has served aluminum producers for many years, and they do not seem inclined to introduce something new.

Raw materials for carbon ramming paste are the same: gas-calcined or electrically calcined anthracite (Sect. 2.3), sometimes a small amount of grained graphite, and SiC grain. The raw materials for binders should make it possible to install ramming paste between blocks when the temperature of the ramming paste is approximately 30–40 °C. To provide good rammability at ambient temperature, usually producers add some organic substances to coal tar pitch or use synthetic organic binders.

Initially, hot ramming pastes were used in repair shops of the smelter, but cold ramming pastes give fewer problems because of ecological issues. Certain effects are made to reduce the polyaromatic hydrocarbons in binders to avoid fumes at preheating. The processing of ramming paste is very similar to the preparation of anthracite graphite carbon cathode blocks—only without shaping and baking parts (Fig. 2.19). The raw materials are preheated and mixed in mixers with pitch-based preheated binders and then packed into packs or barrels. Regarding the final properties the ramming material acquires during preheating of cells and startup, it is necessary to remember that the temperature of carburization goes from the surface of the rammed material to the lower end of the shaft or seam, and the process takes a rather long time.

Testing

Based on a generalization of testing of cathode materials [93], ramming pastes before installation are tested for rammability [94], apparent density [95], dilatation (expansion–shrinkage curve during baking) [96], and baking loss and loss of volatiles [97]. Also, the determination of organic binder content might be useful [98]. The green apparent density is measured on rammed samples, while rammability is measured using a Fisher sand ramming machine (Fig. 2.52). Density is measured as a function of the number of strokes.

Ramming paste has numerous key properties, one of which is the expansion–shrinkage dilatation curve and its mismatch, the expansion curve of the cathode block. During preheating, the organic binder of ramming paste carbonizes, and the volatiles fly away. At the moment of carbonization of the binder, some shrinkage is

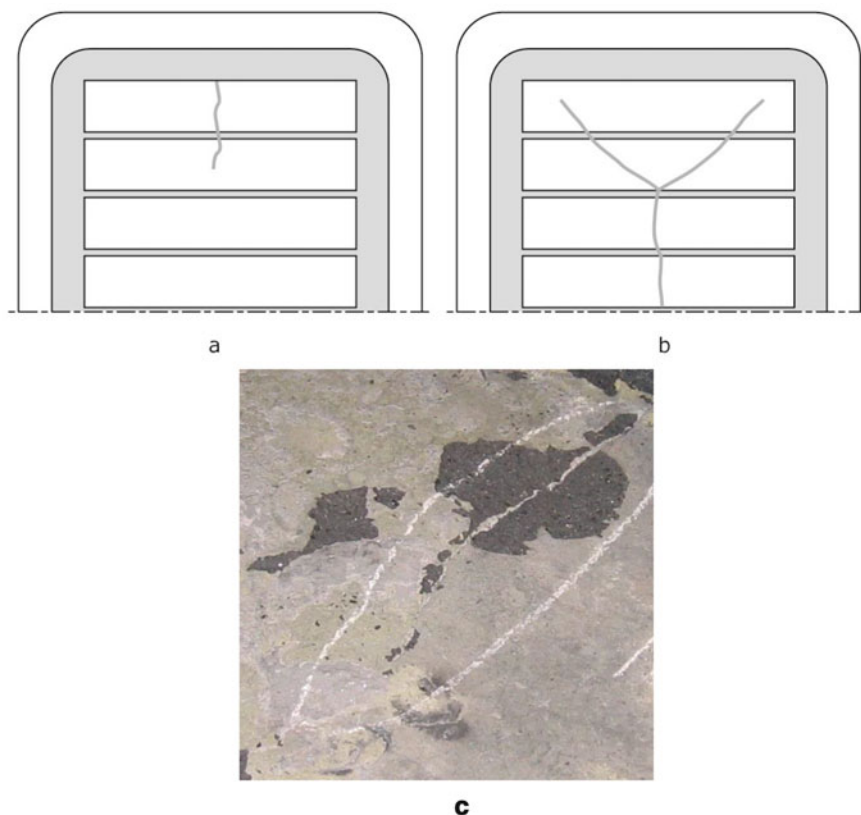
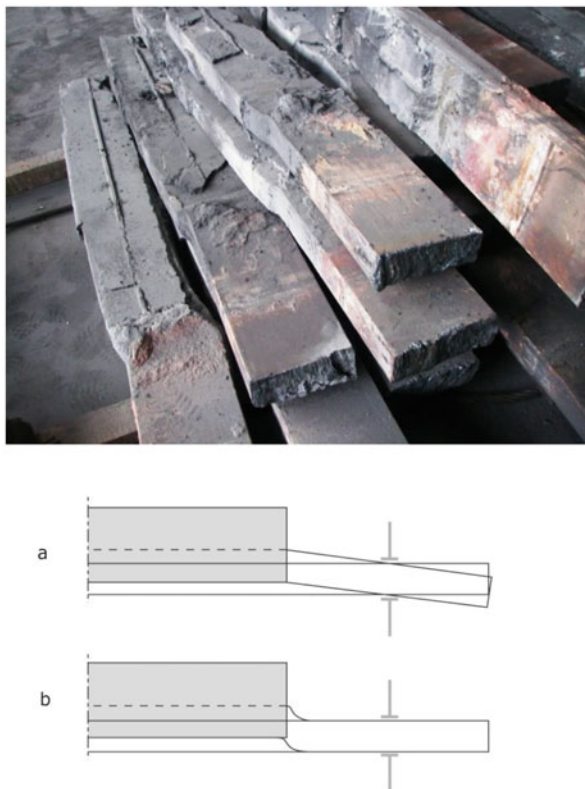


Fig. 2.52 (a–c) Cracks in carbon blocks at end of cell

inevitable; however, the carbon block expands, and the question is whether, in the course of preheating, any gaps will appear between the paste and the blocks (Fig. 2.53). After baking, the ramming paste is tested for apparent density [39–41], open porosity [43, 44], CCS [23, 24], thermal conductivity [35], and electrical resistivity [18, 19]. Ash content can also be measured [48, 49] (Table 2.11).

Currently, the most popular preheating methods are gas-fired preheating and resistance preheating of reduction cells. During preheating, the cathode bottom becomes a unit, and the organic binder of ramming paste in the shafts and seams loses volatile matter and becomes hard. Of course, the surface and subsurface layers of the ramming paste acquire the service temperature significantly more quickly than the bottom layers. The pore structure of the ramming paste is formed during baking. Even if the grain size composition of the ramming paste is chosen properly, the pore size distribution in baked ramming paste may vary, depending on the preheating regime. Generally speaking, the pore size distribution of a ramming paste installed in a peripheral seam as well as in the shafts between blocks may have

Fig. 2.53 (a, b) Busbar with slope



different values because the temperature increase in these different places will differ. Figures 2.65 and 2.66 demonstrates the difference in pore size distribution of ramming paste in a peripheral seam and in the shafts between blocks (Fig. 2.67).

The ratio of the surface of shafts between blocks filled with ramming paste to the surface of the cathode is usually 0.6–0.9%. However, we recall that local infiltrations of electrolyte may cause local overheatings, so pore size control of the ramming paste is also desirable.

The ratio of the surface of a peripheral seam filled with ramming paste to the surface of the cathode (if combiblocks are not the part of the construction) is 1.5–2.5%. At startup, usually the temperature of the peripheral seam is low and significantly lower than the freezing point of electrolyte. Even in normal operation, the temperature of the peripheral seam is not high, and usually it is covered to protect against the penetration of electrolyte with a side ledge. However, sometimes [38] during dry autopsies, peripheral seams are fully infiltrated with electrolyte, so it is worth controlling the pore size distribution (Table 2.14).

Table 2.11 Influence of fine fraction (<0.075 mm) on properties of carbon materials [58]

Amount of fraction <0.075 mm, %	Specific surface area, cm ² /g	CCS, MPa	Apparent density, of green shapes, g/cm ³	Apparent density of fired materials/g/cm ³	Electrical resistivity, mΩ m	Thermal conductivity, W/m K	Shrinkage at firing, %	Total porosity, %
15	473	5.7	1.38	1.27	266.4	0.44	0.14	27.4
30	844	24.2	1.46	1.38	100.2	0.97	0.13	21.1
40	1092	33.3	1.51	1.39	78.3	2.09	0.20	20.6
60	1590	31.3	1.55	1.31	74.8	1.25	0.27	25.1

Table 2.12 Properties, thermomechanical strains at preheating and startup, and calculated values of first Hasselman criterion of thermal shock resistance in carbon cathode blocks of different producers [60, 64]

Plant	Bending strength, MPa	Cold crushing strength, MPa	Elastic modulus (static), GPa	Elastic modulus (dynamic), GPa	Thermal coefficient of linear expansion $\times 10^{-6}$, degree $^{-1}$	Thermo mechanical strains, MPa	R' , °
1	13.5	45	3.8	12	3.1	11.0	922
2	13.5	39	3	10	3.9	10.9	750
3	12.2	34	2.6	8.5	2.6	6.3	1150
4	11	35	3.3	10	2.9	8.9	905
5	10	33.5	2	7.6	3.1	5.8	1086
6	11	39.8	2.7	8.2	3.2	8.1	1128
7	10	33.2	2.4	8	3.4	7.6	864
8	13.4	39.5	2.7	8	3.6	9.1	1032

Table 2.13 Sodium saturation level in carbon cathode materials according to [65]

Grade of carbon cathode material	Na saturation, wt. %	Na saturation, kg/m^3
Gas-calcined anthracite	4	60–70
Electrically calcined anthracite	4	60–70
Graphitic	2	30–35
Graphitized (at 2300 °C)	1	15–20

Fig. 2.54 Cracks in cathode blocks

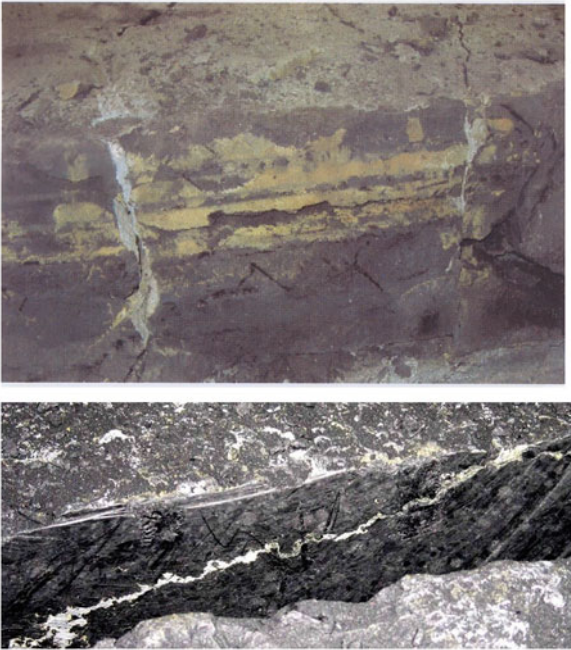


Fig. 2.55 Cavities in blocks, probably originating from small cracks

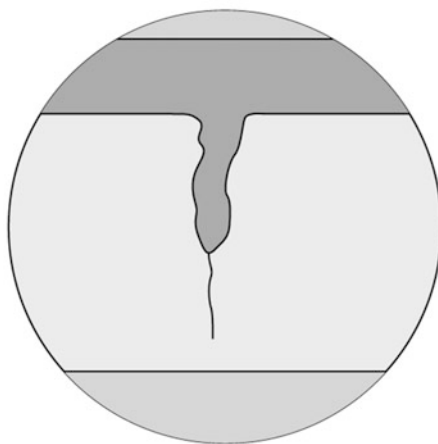


Table 2.14 Properties of ramming paste

Property	Value
Apparent density, g/cm ³	
Green	1.5–1.62
Baked	1.34–1.48
Cold crushing strength, MPa	16–26
Open porosity, %	18–27
Electrical resistivity, mKΩ m	65–110
Volume expansion, %	0–2.5
Relative shrinkage, %	<0.15–0.3
Thermal conductivity < Wt/m K	5–7
Baking loss, %	9–10
Thermal coefficient of expansion, Kelvin ⁻¹ 10 ⁻⁶	4
Ash, %	<5–7

Installation of Ramming Paste

Ramming paste installation is done by machine or hand rammers. Ramming paste preheated to 30–50 °C (in the repair shop) is poured into shafts at a certain height and rammed. Usually, the brick layers cause five to seven ramming cycles, which means that each portion of ramming paste is rammed in the shaft, and then the next portion is poured. It is necessary to obtain good and constant densification during ramming. Before the installation, it is necessary to check the green apparent density in the rammed state [99–206]. At installation, the simplest way to check on whether the proper density has been achieved is by the use of an impact penetrometer. The depth of penetration gives an idea of the rammed density. Overcompaction is also

undesirable because it may lead to stratification at preheating and startup. Poor compaction leads to high porosity and the appearance of large pores—channels that allow for the penetration of electrolyte.

The preparation of ramming paste remains state of the art; the same may be said about the installation, even with the help of ramming machines (Fig. 2.56). During preheating and startup, the ramming paste is considered to absorb thermal tensions and sodium swelling. Usually, baked ramming paste is more porous than carbon cathode blocks and less strong; however, the hardness of ramming paste is superior to the hardness of graphitic and graphitized cathode blocks because of the hardness of anthracite, which is the main constituent (Fig. 2.57).

It is not easy to separate the deviations of properties from the defects of installation of ramming paste, which finishes with cell shutdowns. Usually, the stratification (Figs. 2.58 and 2.59) of rammed paste is caused by either overcompaction or problems with the binder (which may be caused by too low a ramming paste temperature). Also, it might be caused by preheating of the cell (Figs. 2.60, 2.61, 2.62, 2.63, 2.64, 2.65, 2.66, 2.67, 2.68, and 2.69).

Gaps between the rammed paste and the cathode blocks appear owing to problems with the binder (which may be caused by too low a temperature of the



Fig. 2.56 Aluminum carbide in crack in carbon cathode block

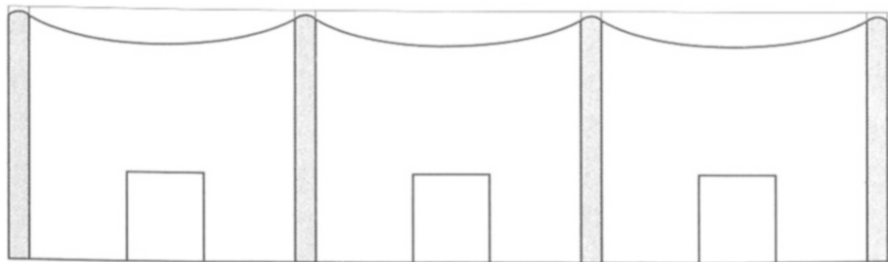


Fig. 2.57 Profile of cathode bottom: graphitic blocks with anthracite-based ramming paste

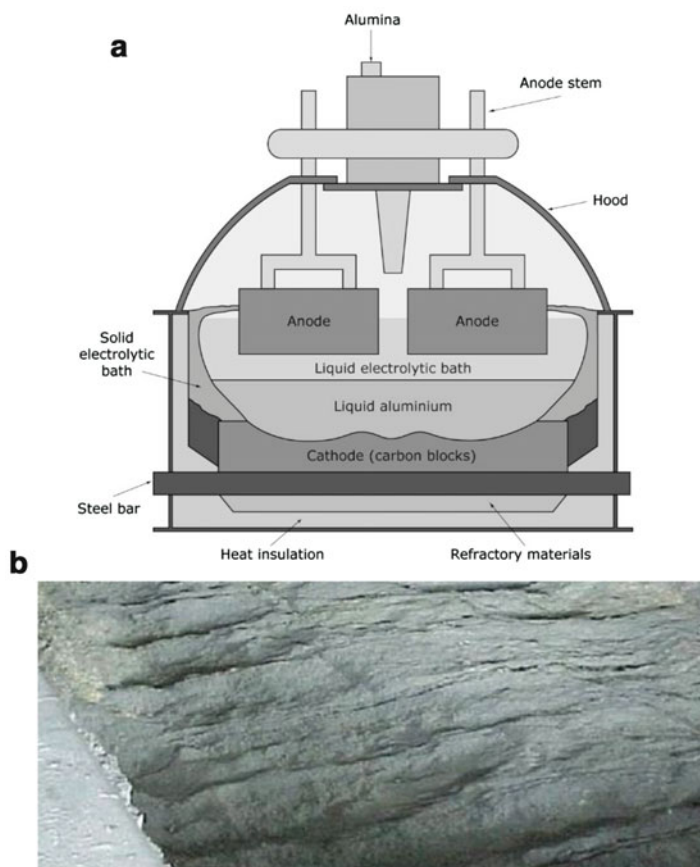


Fig. 2.58 (a, b) W-shaped profile of cathode bottom from graphitic or graphitized blocks after 3–4 years of service

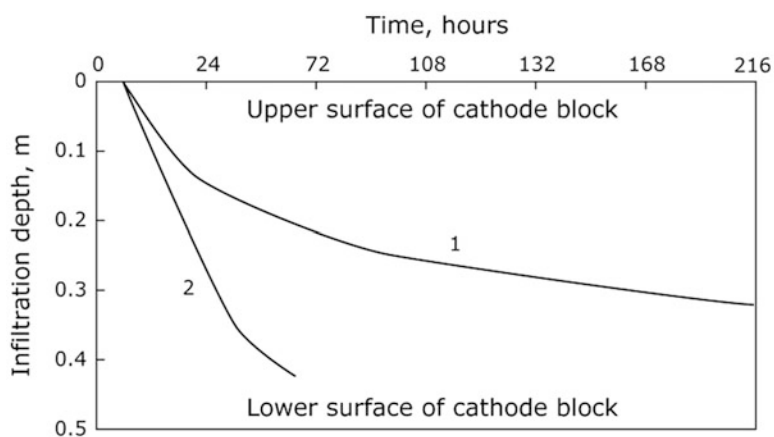


Fig. 2.59 Isothermal regime of electrolyte flow in porous carbon cathode blocks: 1—flow in permeable pores, with dimension below the critical radius (25 μm); 2—flow in permeable pores with dimensions above critical pore diameter

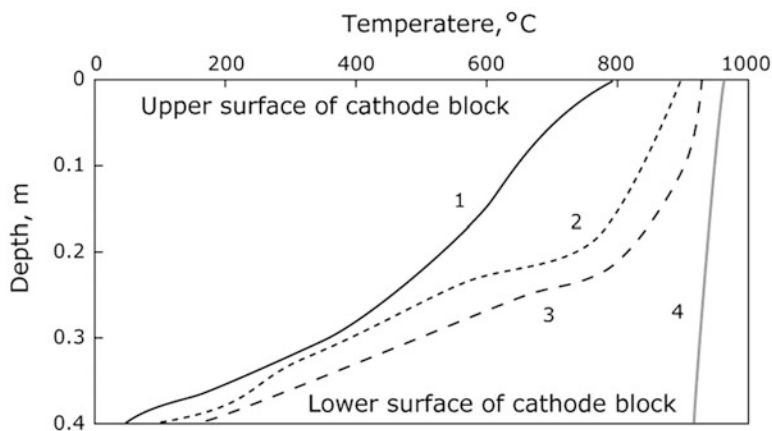


Fig. 2.60 Temperature gradients between upper and lower surfaces of carbon cathode blocks at startup of reduction cells according to Panov [33]: 1—before pouring electrolyte; 2—after 23 h; 3—after 7 h; 4—after 3 months of operation

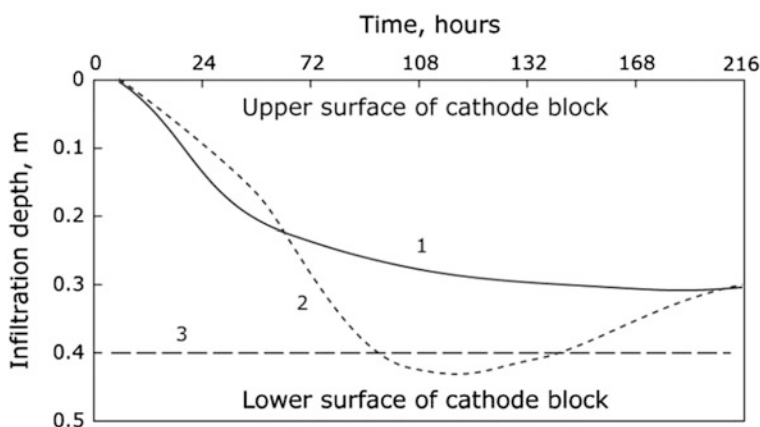


Fig. 2.61 Nonisothermal flow (at startup) of electrolyte through porous medium of carbon cathode blocks: 1—through permeable pores below critical radius ($25\ \mu\text{m}$); 2—through permeable pores above critical radius; 3—movement of crystallization point of electrolyte [60, 64]

ramming paste or cathode blocks). More rarely, it is caused by problems with the grain size composition. Also, it might be caused by preheating and problems with a mismatch between the thermal expansion of the ramming paste and the cathode blocks. This is likely the most serious defect, which causes immediate leakage of the electrolyte in the refractory layer.

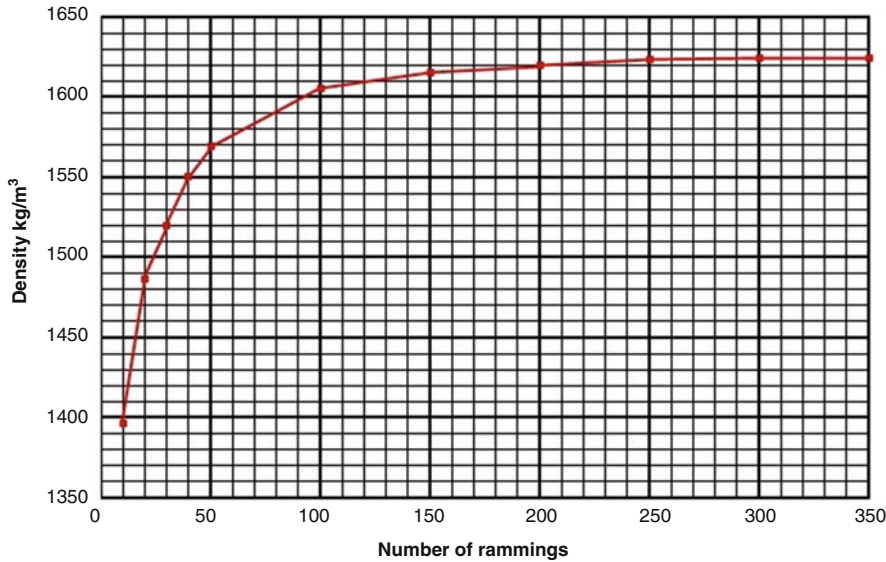


Fig. 2.62 Rammability test

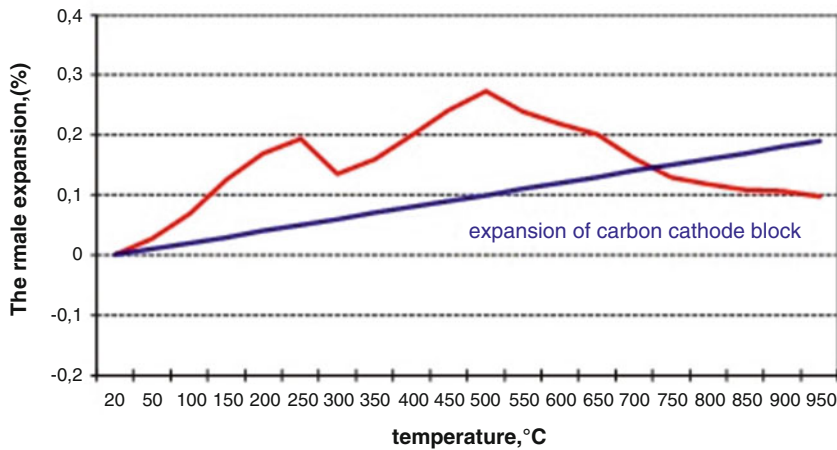


Fig. 2.63 Expansion/shrinkage/dilatation curves of ramming paste in comparison with expansion of carbon cathode block

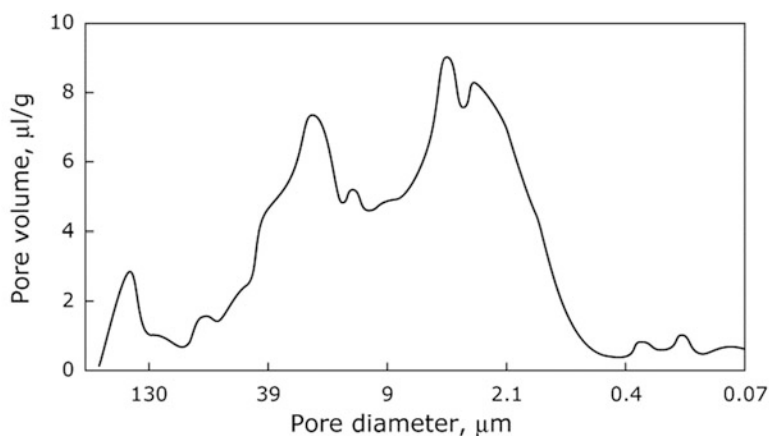


Fig. 2.64 Pore size distribution in baked (without infiltration of electrolyte) ramming material from shaft between carbon blocks; porosity is 18%

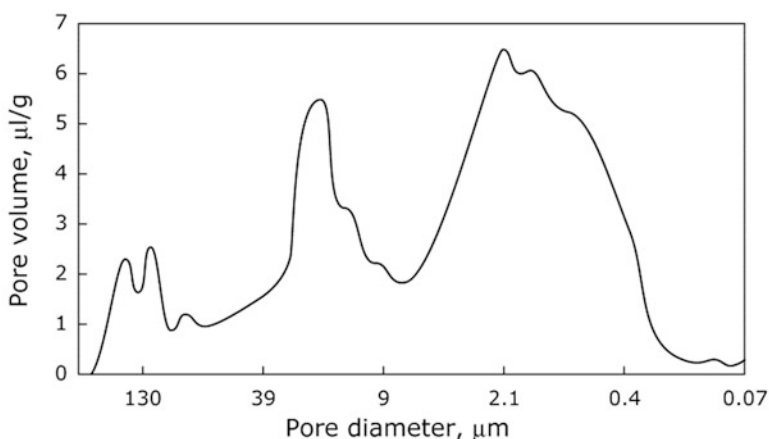


Fig. 2.65 Pore size distribution of baked (without infiltration of electrolyte) rammed material from peripheral seam; porosity is 21.2%

2.4 Coatings of Carbon Cathode Blocks and New Cathode Materials

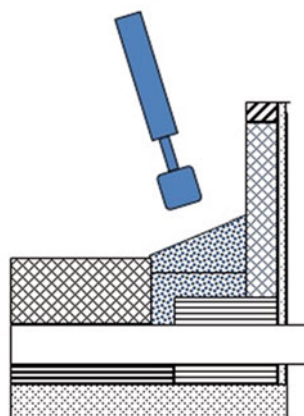
Carbon cannot be considered optimal cathode material for Hall–Heroult reduction cells. The optimal cathode material should have [99]

- High electrical conductivity,
- High thermal shock resistance,

Fig. 2.66 Machined
ramming of peripheral seam



Fig. 2.67 Hand
ramming of peripheral seam



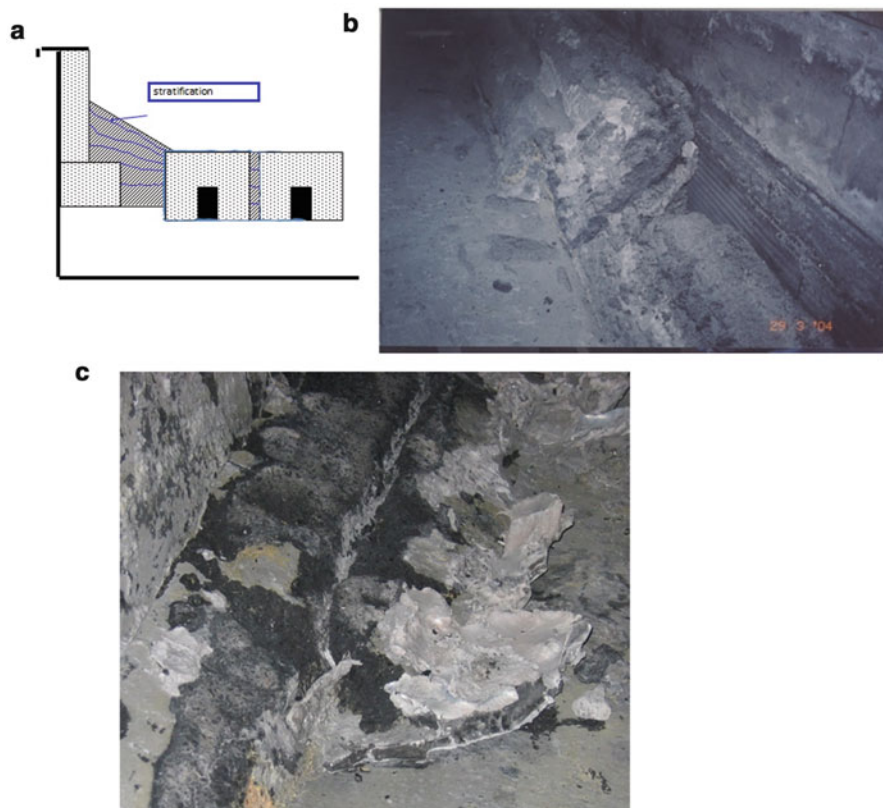


Fig. 2.68 (a–c) Possible stratification of ramming paste at preheating of cell in shafts between blocks and in peripheral seam (strongly undesirable)

Fig. 2.69 Gap between ramming paste and cathode block after preheating and startup (strongly undesirable)



- Low porosity,
- Good wettability by molten aluminum,
- High wear resistance,
- Small rate of electrolyte flow in capillary permeable pores,
- Good contact with current conductors,
- High chemical inertness,
- High resistance to sodium intercalation and to the movement of sodium to refractory.

No known carbon material satisfies all these requirements. Large-scale research on noncarbon cathode materials for the Hall–Heroult process was carried out beginning in the 1980s [10]. At that time, it was believed that the implementation of noncarbon cathode materials would give a longer service life and considerable energy savings as a result of decreasing the anode–cathode distance (ACD) and the cathode voltage [100–103]; some improvements were expected from increasing the current efficiency.

Yet it is necessary to remember that expectations on energy savings could be fully met with the implementation of a drained cathode construction. In a drained cathode, aluminum will flow to some vessel owing to the slopes of the cathode; the aluminum film will be very thin. This design really confers the ability to decrease energy consumption as a result of the decrease of the voltage drop. It has been reported that the wetted surface of a traditional reduction cell permitted a 1–2% increase in the current efficiency and an improved cathode current distribution [104] (Fig. 2.70).

Closer to meeting the previously stated requirements are some carbides, borides, and nitrides of refractory metals and their compositions. The chemical requirements for such materials are

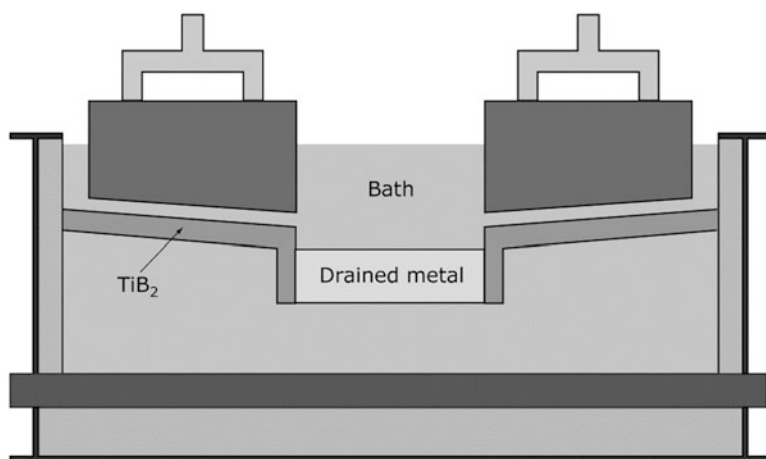
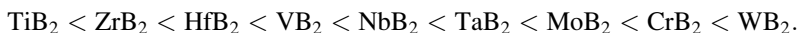


Fig. 2.70 Schematic view of drained cathode

- No interactions with aluminum,
- No interactions with electrolyte,
- No solubility of these materials in molten aluminum.

Thermodynamically, many compounds do not interact with molten aluminum. However, it is necessary to take into account that in a Hall–Heroult process on the surface of a cathode, there is always a thin film of electrolyte, so it is necessary to consider the possible interaction of the material with electrolyte (in the absence of oxygen). The third requirement is low solubility in molten aluminum.

We will not pursue a full theoretical analysis on the fulfillment by the aforementioned nonoxygen high-temperature materials of these three (no interaction with aluminum and electrolyte, no solubility in aluminum) requirements. Thermodynamically [3, 10, 105], the Gibbs energy of interaction of a compound with the components of alumina-electrolyte melts at 1100 °C (which is partly the theoretical analysis) is increasing in the scheme

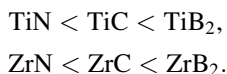


The possibility of carbides interacting with aluminum is increasing in the scheme



Nitrides of refractory metals interact with aluminum, yielding aluminum nitride [106]. The absence of interaction of borides and carbides, which are on the left side of the schemes, was proved experimentally [107].

A thermodynamic analysis of interactions at 1230 K or at 957 °C of borides, carbides, and nitrides with electrolyte containing 10% alumina gives the following rows of resistivity:



Hence, the materials that most closely satisfy the previously stated conditions (no interactions with aluminum, no interactions with electrolyte, no solubility of these materials in molten aluminum) are titanium boride and titanium carbide.

There is information on industrial trials of wetted cathodes made from TiB_2 -TiC and TiB_2 -C; good results might be obtained with the compositions TiB_2 - ZrB_2 , TiB_2 -TiN, TiB_2 - MoSi_2 [108, 109], and TiB_2 - WSi_2 [110].

Recall that titanium boride is soluble in aluminum [10]. The reported solubility of titanium boride [111] is $(\text{ppm Ti}) \times (\text{ppm B})^2 = 1.21 \times 10^4$ at 960 °C, and typical wear due to solubility is 0.98 kg/m² [112]. The consequence is that even if one does not take into account abrasion wear and the solubility of titanium boride grains, the coatings should be thick, and the thickness should be several millimeters.

From a materials science point of view, the requirements are the minimum possible porosity and the absence of additives that promote corrosion. Such materials—dense titanium boride-based compositions—were made in the 1980s and 1990s. They were compositions with a titanium boride matrix (usually 70–80% TiB_2 , with admixtures of carbon, carbides, borides, and ferrous and nickel alloys), with good electrical conductivity and relatively high corrosion resistance, produced by hot pressing, self-propagating high-temperature synthesis (SHS), or sintering, in the form of plates with a thickness of 10–20 mm. The main barriers to the use of such plates in reduction cells of existing constructions were their high cost and the absence of glues for gluing or adjusting these plates to current conductors. The problem of implementing titanium boride plates may arise as a part of the project on drained cathodes and inert anodes.

The main advantage of titanium boride-based coatings is that the application of coatings does not require changing the design of the cell and is not costly. Another advantage is that the depth of the coating is millimeters, and again it is not costly. There are many papers on titanium boride coatings of carbon materials using a plasma spray method, electrochemical deposition, and slurry methods. Usually, researchers start their investigations by trying to make a dense coating. Making a dense titanium boride coating on carbon by a more or less industrial technique is not an easy job, and the continuation of these research projects tended to use technologies of porous titanium boride coatings. The follow-up papers considered whether porous titanium boride coatings might enhance the wetting of cathodes by aluminum, enhance erosion resistance, and to some extent be a barrier to the penetration of sodium and electrolyte in cathodes.

Investigations on applications of wetting coatings on the bottom cathode of reduction cells may be divided into investigations on the application of coatings on carbon blocks at the plant of the block producer and investigations on the application of coatings on carbon cathodes in a prefabricated constructed cell. In the first variant, there are no limitations on the temperature of the process, while in the second variant, the temperature of the process should be limited to 900–1000 °C.

Plasma sprays of titanium boride require special equipment, preheating of carbon blocks, probably a protective atmosphere, and likely intermediate coatings to achieve good adhesion and a long service life [113, 114]. In plasma, particles have a temperature of several thousand degrees, and it is possible to make dense titanium diboride coatings. However, such temperatures require protection of the surface of coated material from oxidation and from cracking due to a mismatch in thermal expansion coefficients. The thermal spray-coating process usually takes place at 1200–1300 °C, and attempts to make titanium boride coatings by thermal spray did not yield dense coatings.

For starters, there are plasma spray devices that make it possible to apply coatings on large objects, so it is theoretically possible to perform the plasma spray process in a cell. Additionally, it looks more attractive to make such coatings at the plant, producing cathode blocks, to make the bottom cathode lining from such blocks, and to cover the surface of the shafts between the blocks, interblock shafts and peripheral seams by titanium boride slurry.

It is possible to make electrolytically deposited coatings in special cells and in cells in operation [115, 116]. Thermodynamically, it is possible to obtain deposited coatings, combining the addition of titanium compounds in electrolyte and boron oxides to carbon anode material. Metal oxides dissolve in electrolyte; the ions of metals discharge at the cathode and deposit on the cathode as titanium boride and titanium carbide. The problem involves the poor controllability of the process and the need to fulfill the required purity of aluminum (in titanium and boron content). Once small amounts of boron oxide and titanium (in the form of oxide of salt) are added, it is possible to obtain metal of the required purity and quality, but the coating process lasts for a long time and is poorly controlled.

Many papers describe the process of coating of carbon cathode blocks by pitch composite or resite composite [117] and their good adhesion to carbon blocks. The filler is titanium boride. Sometimes fillers are not only titanium boride but also carbon fibers [118–120]. At preheating of the cell, the pitch carbonizes, giving a coke (carbon) matrix. Although thermodynamic calculations were presented and the appearance of titanium carbide was mentioned as a possibility, it seemed unlikely that the reaction of carbon with titanium would proceed at a high rate at 900–1000 °C.

A series of publications was devoted to the implementation of titanium boride coatings having an oxide binder [121–123]. A slurry of alumina sol with titanium boride filler is applied on the surface of a carbon cathode bottom by spraying it with a brush. The coating is dried, so the water evaporates, and then during preheating, alumina sol transforms into alumina, which becomes the binder for titanium boride filler. In the formed coatings, the content of titanium boride particles is 70–80%, so they form a continuous matrix, which makes the coating electroconductive. It has been said that the alumina that appears is in alpha modification, which is less soluble in cryolite. The advantages of this method are that the shafts and seams are coated in the same way as the carbon blocks. Another advantage is that the material becomes hard at relatively low temperatures.

The application of alumina sol is a typical nano method. In this particular case, it allows us to make a relatively dense coating at a relatively low temperature (conventional sintering of alumina particles requires temperatures of 1200–1500 °C). The thickness of these coatings is up to 2–3 mm.

The alumina binder of the coatings slowly dissolves in cryolite, and within 2–3 years, the surface of the cathode becomes free of this coating. The advantages of such a coating may be the decrease in cryolite penetration in the cathode during startup and the possible prolongation of service life owing to the existence of the coating on the surface for a certain period. There is information on another mechanism of exfoliation of such coatings [124]. One mechanism is the dissolution of alumina binder in cryolite; another is the formation of aluminum carbide under the coating, which results in mechanical tensions between the surface of the cathode and the coating and subsequent cleavage.

It is probably necessary to keep in mind that the general feature for all research devoted to the technology of titanium boride coatings in constructed cells is that at temperatures below 1000 °C (it is very difficult to achieve higher temperatures at an aluminum smelter), the coatings will be porous, and the porosity will be relatively

high. The binder in pitch titanium boride compositions is about 30%; the pitch transforms coke with a negative volume effect (the coking value of pitch is about 50%). Pores should appear in such coatings. The same situation occurs with alumina sol binder. The alumina particles that appear occupy about 30–40% of the pores compared to the volume of alumina sol binder of the initial mixture.

Another approach is to use the technology of “gradient” coating on carbon cathode blocks. It is applied in the shop of a carbon-producing plant. After preshaping of the green mixture of graphite and anthracite in the mold of a vibro press, a thin layer of titanium boride particles is placed on the upper surface, and the entire pressing is performed, so that the layer of titanium boride particles with a binder is pressed in the green shape.

The following procedures are conventional. A green shape is placed in the baking furnace, and a coating of titanium boride (composition of coke with titanium boride) appears on the surface. This layer is about 10 mm thick, is porous, cannot protect the carbon part of the block from cryolite penetration, and, of course, should improve wear resistance. There has been no research information devoted to decreasing the cathode–anode distance in cells with such a cathode bottom [125].

The cost of dense titanium boride plates (porosity below 5%) is 10–20 times higher than the cost of cathode carbon materials, even the most costly graphitized impregnated blocks. Dense titanium boride materials have excellent strength, wear, corrosion resistance, and wettability, yet their application may be economically efficient in connection with implementing the construction of a reduction cell with an inert anode and wettable cathode.

The idea of porous titanium boride coatings, which to some extent increase wear resistance and improve the wettability of cathodes by molten aluminum, might be efficient for graphitized blocks [28, 126]. This research will require not only a good coating with good permanent adhesion but an investigation of construction and reduction technology as well.

2.5 Side Lining Materials

The side-wall lining of reduction cells should withstand the following events:

- Chemical interaction with electrolyte (Sect. 2.3);
- Erosion interaction of circulating metal (due to Lorentz forces) and bath with particles of alumina;
- Oxidation of upper part of side wall (above bath) in complex oxidative-reduction atmosphere of CO/CO₂ and vapors of fluorine and sodium compounds;
- Oxidation of back side (contacting the steel shell) if there are gaps between the shell and the side lining or air leakage in the collector bar windows.

The side lining materials of reduction cells are carbon blocks and SiC blocks. Anthracite-based carbon side blocks have been used for many years. As a

continuation of R&D in the application of carbon side blocks, many approaches were offered (Table 2.15):

- Anthracitic graphitic side blocks (with synthetic graphite);
- With the addition of SiC;
- With impregnation of the surface with molten and gaseous silicon;
- With impregnation by salts of boric acid;
- Graphite-based blocks with increased oxidation resistance.

Trials using SiC side-wall blocks started in the 1980s, and now it is a proven lining element for cells with a high current. Anthracitic graphitic side-wall blocks are still used in cells with low current, and they will probably be changed for SiC blocks if the design of these cells is not changed. For Soderberg technology reduction cells, the application of SiC is not effective (or should be accompanied by a complex work on design and thermal balance).

The technology of carbon side-wall blocks is very similar to that of anthracitic graphitic cathode bottom blocks (Figs. 2.20 and 2.21). The requirements for carbon side-wall blocks are similar to the requirements for bottom blocks, only easier: moderate strength, moderate sodium swelling, and relatively high resistance to oxidation and to corrosion by bath and by aluminum.

The main advantages of SiC side lining compared to carbon side lining are higher corrosion resistance to electrolyte and aluminum, higher oxidation resistance, and higher thermal conductivity. Higher electrical resistivity is also an advantage.

The thickness of carbon blocks is 150–200 mm. The higher corrosion resistance of SiC permits one to use side-wall blocks with a thickness of 50–100 mm (more frequently, 65–70 mm) (Fig. 2.71).

It is necessary to emphasize that according to the principles of reduction cell design, the side lining should be covered by a 30- to 50-mm side ledge, which is the side lining's main protection from corrosion. Thus, for proper thermal balance, the guaranteed frozen side ledge has a priority in design.

2.5.1 Carbon Side Linings and the Causes of Their Decay

The side lining of cells withstands

- The chemical action of electrolyte [10],
- Erosion by bath with alumina particles and aluminum circulating owing to Lorentz forces and to the movement of gas bubbles that appear during reduction,
- Oxidation by oxygen from air in the redox atmosphere and the vapors of fluorine and sodium compounds in the upper part of the lining (above the melt),
- Oxidation near the shell (in the case of oxygen flow because of poor airtight seal of the busbar windows).

Table 2.15 Properties of carbon side lining materials

Material	Anthracitic	Anthracite + graphite	Anthracitic, with increased oxidation resistance	Anthracitic, with increased oxidation and erosion resistance	Graphitic, with increased oxidation resistance	Graphitic, with increased oxidation resistance
Properties						
Density, g/cm ³	1.83	1.94	1.82	1.88	2.07	2.13
Apparent density, g/cm ³	1.52	1.54	1.49	1.54	1.56	1.63
Porosity, %	17	20.5	18	18	25	23.5
Thermal conductivity < Wt/mK at 20 °C	9	13	8	9	28	32
Cold crushing strength, MPa	26	25	30	33	23	34
Bending strength, MPa	9	9	13	13	12	15
Sodium swelling (rapoport test), %	0.7–0.8	0.7	0.7–0.8	0.7–0.8	–	–
Oxidation resistance, %	2.9	2.8	0.9	0.9	0.5	0.7
Ash, %	2.9	2.8	0.9	0.9	3.5	9

Fig. 2.71 Side ledge in reduction cell

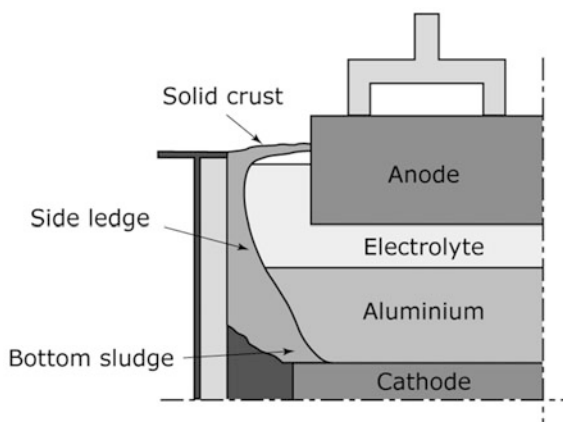
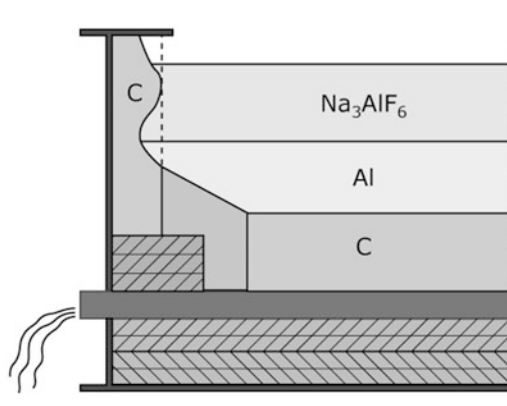


Fig. 2.72 Schematic degradation of carbon side-wall block



According to the Hall–Heroult reduction cell heat balance [2, 127], approximately 35% of heat is transferred away through the sides (Fig. 2.6).

Consequently, the requirements for the side lining materials of a reduction cell are

- High thermal conductivity,
- High corrosion and erosion resistance to bath and aluminum melts,
- High oxidation resistance.

Carbon anthracite side-wall blocks (Figs. 2.72 and 2.73) have been used for a long time. The reaction between air oxygen and carbon starts at 400–500 °C; at 900 °C, the reaction rate is considerable. Additives to the material of carbon side-wall blocks slow down oxidation. The carbon side lining deteriorates owing to oxygen in the upper part (Figs. 2.72 and 2.73) or in the lower part from the side of the shell (in the case of air leakage through busbar windows).



Fig. 2.73 Ruined carbon side lining in cell

Bath and aluminum circulation enhance the wear of carbon side-wall blocks due to erosion, so a combination of chemical attack and erosion takes place. The biggest wear occurs at the border of bath and aluminum, as the formation of aluminum carbide is enhanced in the presence of cryolite, which acts as a solvent for oxide layers and aluminum. Chain reactions (2.27–2.30) are discussed in Sect. 2.3.

Producers of carbon materials offer several ways to increase the properties of carbon side lining (Table 2.15). There were variants of anthracite-based carbon side lining materials with increased thermal conductivity and corrosion resistance:

- With graphite,
- With boric acid salt impregnation,
- With addition of SiC,
- With Si-impregnated working surfaces.

There have been no significant results in the application of carbon side-wall materials with enhanced characteristics in the reduction cells, and the current technical practice is to use SiC side linings. Yet it is necessary to mention that a carbon side lining is in use in low-current cells, especially in Soderberg technology.

2.5.2 SiC Side Lining

Attempts to use SiC as a side lining material started in the 1980s when problems with carbon side linings began at reduction cells with increased current. The technical solution was the application of nitride-bonded SiC. Within the next 20 years, several variants of SiC side lining designs were tested (Figs. 2.74a–f and 2.75):

- SiC block 20–30 mm thick, preventing the carbon block from making contact with the bath and aluminum (Fig. 2.74a);
- SiC block 20–30 mm thick in contact with the steel shell, preventing leakage of melt in the case of carbon lining damage (Fig. 2.74b);

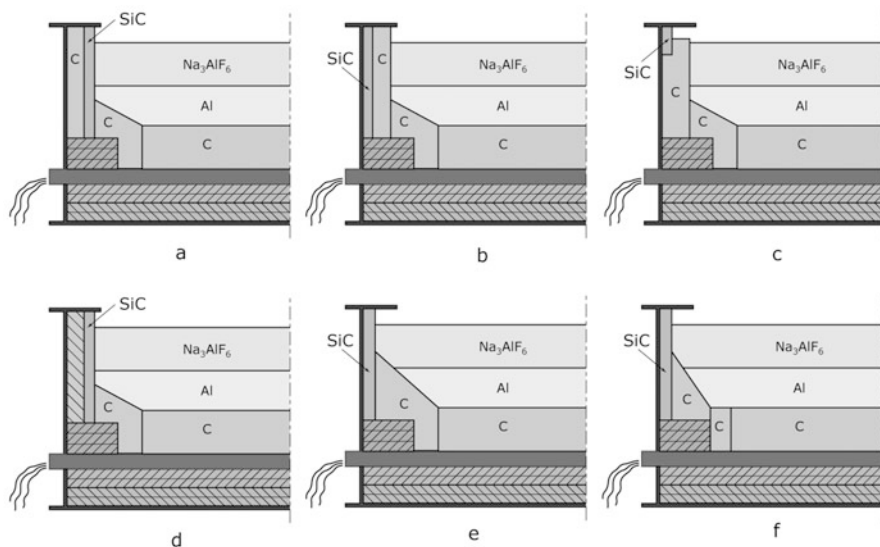
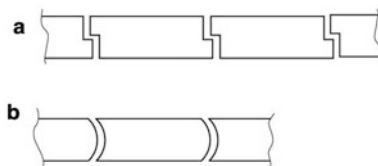


Fig. 2.74 Tested SiC side lining variants

Fig. 2.75 Tested variants of joining side-wall SiC blocks: (a) step; (b) rounded and curved side surface

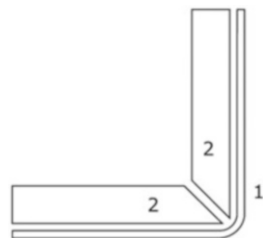


- SiC “ring,” promoting increased heat transfer in the upper part of the side lining (Fig. 2.74c);
- SiC block 20–30 mm thick, with a 10- to 20-mm heat insulation layer for decreasing heat transfer (Fig. 2.74d);
- SiC block 60–100 mm thick, in contact with the steel shell, with carbon artificial side ledge, preventing the SiC block from making contact with the bath and aluminum (Fig. 2.74e);
- SiC block 60–100 mm thick, in contact with the steel shell, with carbon side-wall block, preventing the SiC block from making contact with the bath and aluminum (Fig. 2.74f).

This design was called combiblock.

In the course of the trials, designers arrived at a solution involving SiC blocks 60–100 mm thick without heat insulation with a carbon artificial side ledge, preventing the middle and lower parts of the SiC blocks from making contact with the bath and aluminum. The upper part of the carbon artificial side ledge

Fig. 2.76 Shape of SiC side lining of corners: 1—steel shell; 2—SiC corner blocks



was slightly above the border cryolite–aluminum. This is the typical construction (Fig. 2.74e). The continuation of this design with an artificial side ledge was the combiblock (Fig. 2.74f).

As we know, carbon side-wall blocks are installed side to side. The thickness of carbon side-wall blocks is 150–200 mm, while the thickness of SiC blocks is significantly smaller. There were trials that involved installing SiC side-wall blocks having a step (Fig. 2.74a) or a rounded and curved side surface (Fig. 2.74b) to prevent electrolyte leakage through shafts. The trials showed that the flat-side-to-flat-side variant with mortar between the blocks, covered by a side ledge, allowed for normal cell operation.

Combiblocks have strong and weak features. For instance, the application of combiblocks helps to diminish the so-called human factor in the construction (homogeneities of ramming paste at production and ramming, problems related to pore size distribution, lamination of ramming paste, problems of heating at cell startup). Combiblocks are more reliable in achieving the desired properties, which is important for heat balance.

Additionally, the weight of a combiblock is significantly higher, comparing with carbon side wall block or SiC sidewall block which presents some problems during construction. Another problem is the minimization of shafts. Usually, the thickness of SiC side-wall blocks is 65–70 mm. There was a tendency to increase the thickness of side walls to 100 mm for installation in the 350–400-kA reduction cells; however, trials showed that a proper thermal balance in cells protects side walls better than increasing the thickness of the SiC.

Initially, the corner side-wall lining in the corners of reduction cells was accomplished using straight blocks with inclinations (Fig. 2.76), but a more accepted variant now is a rounded corner block (Fig. 2.77a, b). There still exist variants involving the installation of carbon corner blocks (where the sides are lined with SiC) or simply filling the corners with carbon ramming paste.

2.5.3 Variants of SiC Materials (and Others) as a Side Lining

Nitride-bonded SiC (silicon nitride–SiC material) is not the only variant for application as a side lining material. Here is a list of variants:

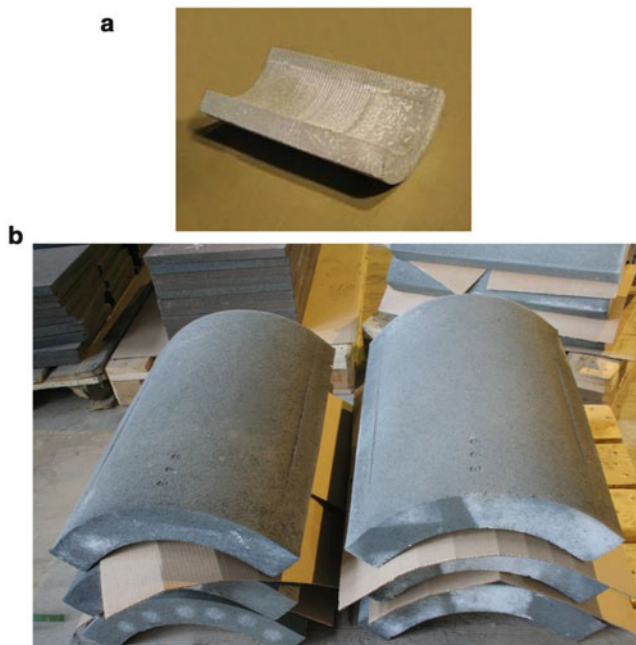


Fig. 2.77 Shape of SiC side lining of corners: (a, b) rounded corner block

1. Oxide-bonded (aluminosilicate), sintered, porosity about 15%
2. Oxide-bonded, sintered, porosity 5–6%
3. Nitride-bonded SiC (bonded with silicon nitride)
4. SiAlON-bonded SiC (comments in what follows)
5. Self-bonded SiC: Si-SiC
6. Self-bonded SiC: SiC-SiC
7. Recrystallized SiC
8. Aluminum nitride
9. SiC-TiB₂
10. Oxide materials

As shown in laboratory experiments, nitride-bonded SiC is as corrosive-resistant as aluminosilicate-bonded SiC (sintered in air). Currently, nitride-bonded silicon carbide is the only material used as SiC side lining.

Nitride-Bonded SiC: Elements of Technology

Conventional refractories shrink during thermal treatment and sintering. Shrinkage is about 10–20%; owing to the sintering process, refractories become stronger and less porous. The process for the formation of nitride-bonded SiC is known as

reaction sintering. During reaction sintering, the porosity decreases and strength increases, but the shrinkage is less than 1%. The melting point of SiC [128] and the energy barrier for the dislocation's movement (Nabarro–Peierls barrier) are very high, so the sintering of SiC takes place at 2100–2300 °C.

Reaction sintering makes it possible to diminish the temperature. During a reaction, sintering in green shape silicon reacts with nitrogen (in nitrogen atmosphere), and silicon nitride appears according to the reaction



Silicon nitride occupies some part of the space between the grains of SiC. To determine the volume of silicon atoms, we divide the atomic weight of silicon by its real density:

$$\text{Atomic volume of silicon} : \frac{28}{2.3} = 12.17, \quad (2.33)$$

$$\text{Atomic volume of Si}_3\text{N}_4 : \frac{140}{3.19} = 43.89. \quad (2.34)$$

One of the reagents (N) enters the reaction zone outside; hence, the mol volume of reactant (Si₃N₄) is greater than the initial atomic volume of reagent (Si), and the volume change is 120%:

$$\Delta V/V = V\text{Si}_3\text{N}_4/3V\text{Si} = 43.89/(3 \times 12.17) = 43.89/36.51 = 1.2. \quad (2.35)$$

Thus, in the process of reaction sintering, the porosity diminishes because the volume of the reagent (Si₃N₄) appearing in the pores is greater than the volume of the initial silicon grains. The theoretical decrease in porosity in nitride-bonded SiC is easily calculated, taking into account the porosity of the green shape and the amount of silicon in the green mixture.

The weight of Si₃N₄ is greater than the weight of Si in the green shape:

$$\Delta m/m = m\text{Si}_3\text{N}_4/3m\text{Si} = 140/84 = 1.67. \quad (2.36)$$

The theoretical weight increase of the green shape in the process of sintering of nitride-bonded SiC is easily calculated, taking into account the amount of silicon in the green mixture. Yet it is necessary to take into account that in industrial furnaces, the real weight increase is 60–80% of the theoretical. The ratio of real weight increase to theoretical weight increase may be a good estimate of the completion of the nitridation process. Nitride-bonded silicon nitride is a material with a porosity of 14–19%; the structure of the material is represented by large grains of SiC surrounded by fine grains of silicon nitride (Figs. 2.78 and 2.79).

Fig. 2.78 (a) Structure and (b) principal scheme of formation of N-SiC

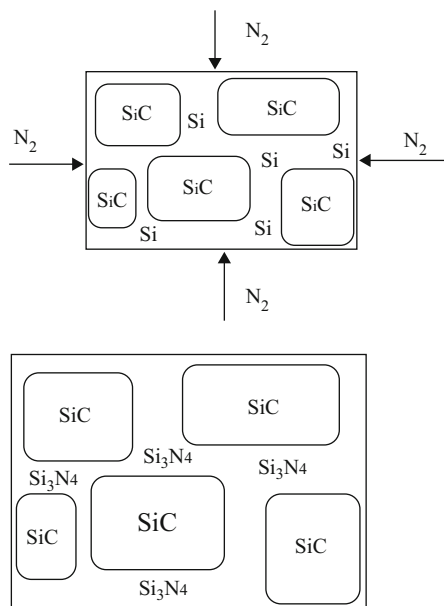
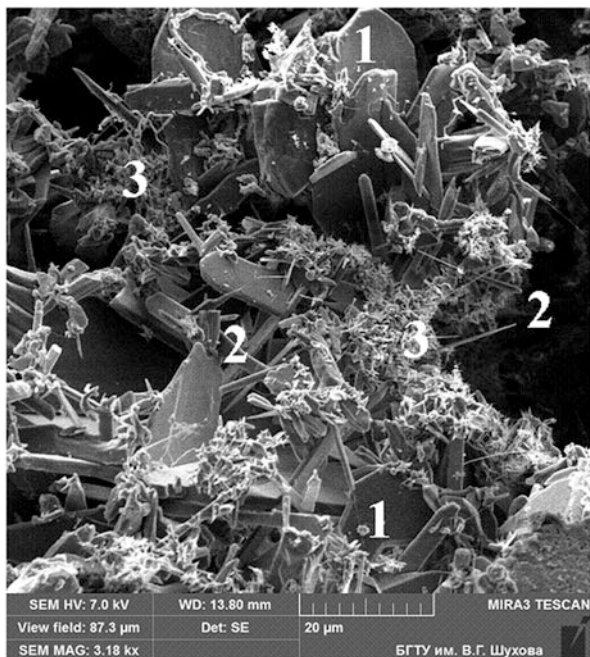


Fig. 2.79 Structure of nitride-bonded SiC.

1—coarse SiC grain;
2—needlelike α - Si_3N_4 ;
3— β - Si_3N_4



Usually, N-SiC producers finish the process of thermal treatment above the melting point of silicon, which is 1410 °C. In the green shape, the silicon is in the form of fine grains, and the surface of the reaction is rather high. If the green shape is fired at an increased velocity, silicon might melt, and the surface of the reaction will diminish several times; as a consequence, full nitridation will not take place.

According to [129], the reaction between silicon and gaseous nitrogen starts at 1100–1200 °C. The reaction may take place with solid silicon and in the gaseous phase owing to the evaporation of silicon. At a certain temperature, the pressure of silicon becomes high enough, and the vapors of silicon will react with nitrogen. The silicon nitride that appears will condense on the surface. The limiting phase for the reaction between the gaseous nitrogen and solid silicon will be the diffusion of nitrogen atoms to silicon through the layer of silicon nitride. According to [130], on the surface of silicon there will appear areas of silicon nitride and areas of nonreactive silicon, and through those, the evaporation of silicon takes place (Fig. 2.81).

The reaction of silicon and nitrogen is strongly exothermic, ΔQ (1400 °C) = 720 kJ/mol [134]; the material is heated additionally owing to heat escape, and the final stages of N-SiC formation are poorly controlled. In the final stages of nitridation, the temperature of the process is higher than silicon's melting point, and presumably at least some part of free silicon is in the gaseous phase. The difference between the temperature in the middle of the shapes and near the edge might be critical from the viewpoint of final properties.

In refractories, there are usually no gradients of porosity and density, while in N-SiC, gradients of porosity and density always exist [135, 136]. Sometimes the gradients of porosity are 1–2%, but sometimes they may reach 5–7% (Fig. 2.80, Table 2.16). The reason for this is the overheating of the middle of the shapes due to the exothermic reaction of silicon nitration (Fig. 2.81). Volatile silicon tends to move in places with a lower temperature; presumably the reaction of silicon and nitrogen predominantly takes place near the edges of shapes. This is the cause of the different colors of the finished product at its cross section.

In the industrial technology of Si_3N_4 -SiC material, such factors as the rate of heating, the width of blocks, grain size composition, and the porosity of the green

Fig. 2.80 Porosity gradients in different 70-mm-thick N-SiC blocks according to [136]

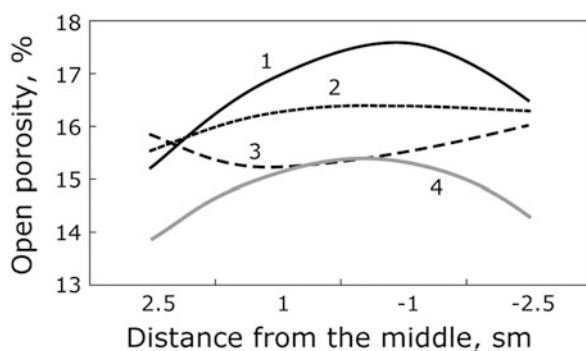


Table 2.16 Porosity and composition of N-SiC near the surface and in the middle (the porosity of the green shape is 17–19%, and the width of the green shape is 70 mm) [136]

	Near surface	Middle
SiC, %	76.80	78.80
Si ₃ N ₄ , %	24.40	22.70
$\alpha/(\alpha + \beta)$	0.49	0.46
α , %	12.00	10.40
β , %	12.40	12.30
Si free, %	0.20	0.10
SiO ₂	—	—
(Al ₂ O ₃ + Fe ₂ O ₃ + CaO), %	1.30	1.28
Fe ₂ O ₃ , %	0.94	1.00
Porosity, %	16.6	16.20

shape should be taken into account at all times [131, 132]. A temperature difference of 40–60 °C might be critical. When the temperature reaches the melting point of silicon, the vapor pressure of silicon increases approximately 10 times, because volatile silicon is much more reactant to gaseous nitrogen, a sort of self-propagating chain process: as the temperature increases, the silicon vapor pressure increases, giving rise to an increase in the reaction rate and heat release, which increases the temperature, and so on (Fig. 2.81).

The gradients of porosity in Si₃N₄-SiC materials appear because of the evaporation of silicon in the zone with the maximum temperature and the diffusion of silicon vapor to the zone with a lower concentration of silicon vapor, that is, to the periphery of the shapes—with the following reaction in the gaseous phase and the appearing silicon nitride. Silicon nitride condenses in pores on the surfaces of existing particles, but predominantly at the peripheral parts of shapes (Fig. 2.82).

One more peculiarity of the process is that in the presence of minor oxygen concentration (which always exists in industrial furnaces with a flowing atmosphere of nitrogen) silicon may react with oxygen, giving volatile silicon monoxide SiO:



Silicon may react with this minor oxygen not only in the solid state. Gaseous silicon reacts with oxygen at higher rates. Another aspect of processing silicon nitride-bonded SiC materials is the formation of silicon oxynitride, Si₂ON₂, which almost always takes place in industrial N-SiC processing. The source of oxygen might be minor leakages in the muffle of the shuttle furnaces and temporary organic binders, which evaporate during firing.

The possible reactions are as follows:

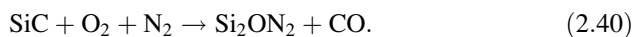


Fig. 2.81 Schematic illustration of self-propagating chain process during $\text{Si}_3\text{N}_4\text{-SiC}$ fabrication [131–133]

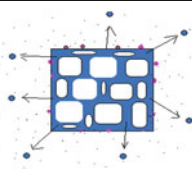
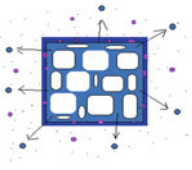
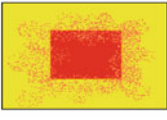
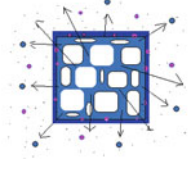
	$T = 1200\text{-}1300^\circ\text{C}$ reaction (1) takes place between solid and vapor Si. The Si vapor pressure is 10^{-5} - 10^{-4} torr, the main reaction is between solid Si and nitrogen. Heat output due to reaction (1) is not big. The temperature gradient between the edge and the middle is small. The predominant reaction product is $\beta\text{-Si}_3\text{N}_4$
	
	$T = 1350\text{-}1420^\circ\text{C}$ reaction (1) takes place between liquid and vapor Si. The Si vapor pressure is about 10^{-4} - $5 \cdot 10^{-4}$ torr. The temperature gradient between the edge and the middle is small. Heat output due to reaction (1) is big, as vapor pressure increases.
	
	$T = 1440\text{-}1460^\circ\text{C}$ reaction (1) takes place between liquid and vapor Si. The Si vapor pressure is about 10^{-3} torr. Heat output due to reaction (1) is big, as vapor pressure increases. The temperature gradient between the edge and the middle is about 40-60 degrees. Silicon vapor moves to the edges. The predominant reaction product is $\alpha\text{-Si}_3\text{N}_4$
	

Fig. 2.82 Gradients of silicon nitride concentrations in $\text{Si}_3\text{N}_4\text{-SiC}$ blocks [133, 137]

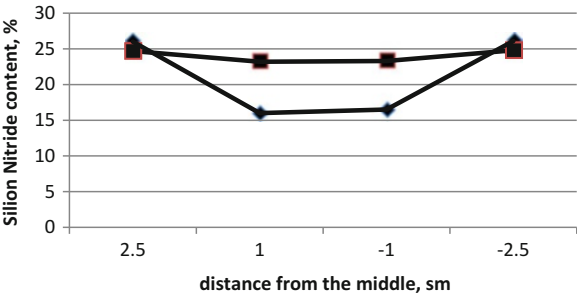


Table 2.17 Composition of silicon nitride-based constituent in Si_3N_4 -SiC materials according to refs. [133, 138]

		SiC	Si_3N_4	Si_2ON_2	SiO_2
According to [138]	Peripheral part	62–89.3	6.7–38	0–4	–
	Middle	74–79.1	15–26	0–5.9	–
According to [133]	Peripheral part	69.6–78.5	19–22	2.5–8.4	0.3–0.5
	Middle	76.2–80.6	13.4–15.9	6–7.9	0.1–0.3

Table 2.18 Lattice parameters of α - and β -modifications of silicon nitride according to ref. [128]

Modification	Lattice parameters, pm			Volume of elementary lattice, nm^3	Length of Si–N bond, pm	ρ , g/cm^3	Number of formula units in lattice	Tetrahedron edge distance, pm
	a	c	c/a					
α	781.8	559.1	0.7151	0.29596	171.5–175.9	3148	4	271.2–291.3
β	759.5	290.23	0.3821	0.14498	170.4–170.7	3211	2	277.4–290.2

The region of existence of silicon oxinitride is narrow [134], and in industrial processing of Si_3N_4 -SiC materials the formation of 2–5% silicon oxinitride (and sometimes up to 7–8%) is a conventional secondary process (Table 2.17) [7, 8].

It is believed that the reaction of nitrogen and solid silicon gives predominantly β -silicon nitride (Fig. 2.83a), while the reaction of nitrogen with volatile silicon gives α -silicon nitride (Fig. 2.83b). Cubic γ -modification of silicon nitride may be synthesized only at high pressures. The parameters of α - and β -modifications of silicon nitride are quite similar (Table 2.18).

In N-SiC refractory products, the silicon nitride phase is normally a mixture of α - and β -modifications, but the α/β ratio may differ considerably. In some N-SiC refractories, α - Si_3N_4 predominates, while in others, β - Si_3N_4 does.

According to Skybakmoen [138], the α/β ratio may range from 0.2 to 1.5–2 (statistics from 25 samples). In his investigation, the β -modification of silicon nitride crystallizes mainly in the center of shapes.

Returning to the problem of what modifications of silicon nitride appear from solid, liquid, and gaseous silicon according to reaction (2.32), we can state that it looks like the predominant modification due to reaction with gaseous silicon would be the alpha-modification, and the predominant modification appearing at temperatures below the melting point of silicon owing to reactions with solid silicon would likely be a beta modification. However, both modifications may also appear.

Usually, there is no commercial N-SiC with 100% α - or β - Si_3N_4 (Table 2.16).

Combiblocks

As stated previously, there are currently two variants of side linings of reduction cells: an N-SiC side lining with rammed carbon paste and a combiblock (Fig. 2.84a, b)—N-SiC block with glued carbon block (or artificial side ledge).

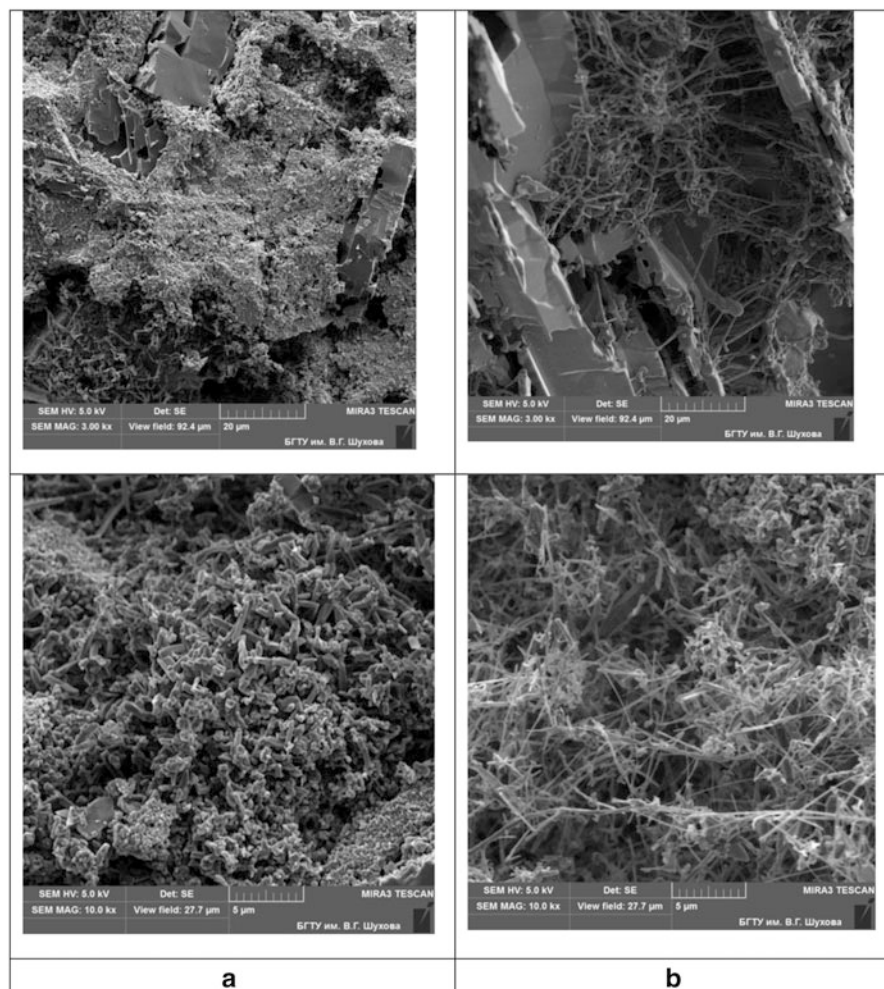


Fig. 2.83 Structures of Si_3N_4 -SiC materials with different magnifications: (a) predominantly β - Si_3N_4 ; (b) predominantly α - Si_3N_4

An N-SiC lining is the same as described previously. As for the carbon part of combiblocks, depending on the design of the cell, it may be anthracitic graphitic (usually with 0% graphite) or graphitic (specifications for the carbon part of combiblocks appear in Table 2.19). Usually, the glues that are used are carbon-containing phenolic or nonphenolic thermal-setting or air-setting resins.

There are advantages and disadvantages in the application of combiblocks. SiC blocks weigh on average 30–45 kg and are relatively easy to install manually.

Fig. 2.84 (a, b)
Combiblocks

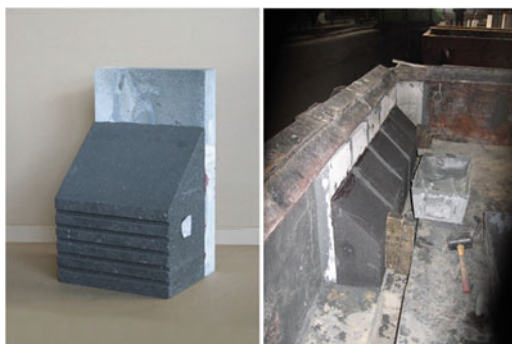


Table 2.19 Properties of carbon part of combiblocks

	Unit		Value	
Graphite content	%		~30	100
Real density	g/cm ³	ISO 9088	≥1.89	2.0–2.2
Apparent density	g/cm ³	ISO 5017	≥1.55	1.58–1.65
		ISO 12895-1		
Porosity	%	ISO 12895-1	≤22.0	≤19
Thermal conductivity	Wt/mK	DIN 51908	≥10	≥30
		ASTM C767		
		ISO 12987		
Cold crushing strength	MPa	ISO 10059-1	≥30	26–30
Flexural strength	MPa	ISO 12986-1	≥10	≥10
Elastic modulus	GPa	ASTM C747	>10	>10
Thermal expansion coefficient (25–525 °C)	10 ⁻⁶ K ⁻¹	DIN 51909	≤3.0	2.4–3.0
Ash	%	ISO 8007	<3	≤1
Electric resistivity (20 °C)	mKΩm/ m	ISO 11713-2000	30–40	15–20

Combiblocks weigh from 60 to 80–85 kg and require some mechanization in installation. Problems with gaps appear in the installation of combiblocks (especially in the case of steel shells of two or three runs). Gaps between combiblocks are highly undesirable, but it is not easy to solve this problem when the width of a combiblock is 300–400 mm. Thus, some smelters buy SiC blocks from one producer and the carbon part of combiblocks from another producer, first install the SiC lining, then install the carbon part of the combiblock, and then make the ramming of the peripheral seam (but with combiblocks, the peripheral seam is not wide).

Defects in Nitride-Bonded SiC Side Lining

Usually, though a SiC side lining has constant properties and characteristics, sometimes nonconditioned materials appear.

Chippings (Fig. 2.85) in N-SiC side lining blocks are very rare and easily seen. More often there may be deviations in the geometry of normal conventional N-SiC blocks, where the geometrical tolerances are not within the requirements. For example, the width may be 348 instead of 350 mm according to drawings. Yet these 2 mm, multiplied by 40, will give a gap of about 80 mm for one side, and it will be necessary to cut off the special fitting blocks, but silicon carbide is very tough to cut.

Other possible defects are of a chemical nature and derive from peculiarities of processing, as discussed earlier. As stated previously, nitride-bonded silicon carbide refractories are never (or almost never) homogeneous. The exothermal reaction of nitration gives excessive heat that promotes the excessive volatility of silicon. Everything results in gradients of porosity (Fig. 2.80, Table 2.16) and in gradients of silicon nitride and SiC concentrations (Fig. 2.82, Table 2.17) along the width of blocks.

At refractory plants and in repair shops, this phenomenon is called the *green middle*. Here it is necessary to define the green middle, which originates from unreacted silicon and a slightly different color in the middle of blocks (Fig. 2.86).

The best way to determine whether a block (as a representative of a batch) may be installed in a reduction cell is probably to measure the porosity, concentration of silicon, and concentration of silicon nitride in the middle and near the edge of the block.

At any rate, the silicon content should be below 0.5%, otherwise it is an indication that the reaction between silicon and nitrogen stopped before it completed.

It is not easy to give strict instructions on the differences in porosity and concentrations, but we consider that a difference within 3 to 4% might be acceptable.

Fig. 2.85 “Chipping” in SiC block



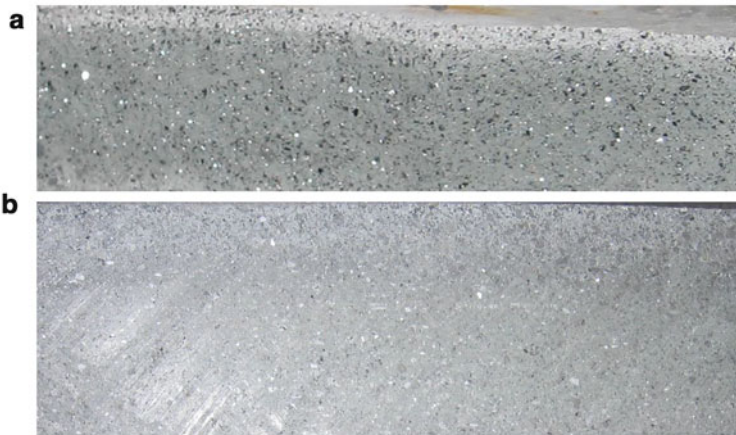


Fig. 2.86 (a, b) Different color at cross section of N-SiC block

The different color on the surface of nitride-bonded SiC blocks (Fig. 2.87) has the same origin as gradients of porosity and concentrations inside the blocks and is less dangerous.

In the process of a sintering vapor reaction, silicon may fly in different directions, but not to contacts with other blocks. Recall that this evaporation of silicon may promote inhomogeneities, but it is only an indication of possible deviations.

Changes in SiC Lining in Service and the Mechanisms of Decay

Changes in N-SiC side linings occur from the first hour of baking and startup and do not stop until the final hours of service [139–141]. Yet in a properly designed cell (from the point of baking, startup, reduction technology), the cell will no shut down because of the side lining.

More likely, the entire degradation mechanism of SiC-Si₃Ni₄ side lining is oxidation [142–145] according to reactions (2.37)–(2.40), with the following reactions of silicon oxide with salts [Eqs. (2.41)–(2.44)]. It is necessary to mention that temperatures of 800–900 °C are not critical for the oxidation of SiC and Si₃N₄. Yet in the presence of sodium and fluorine compounds, the reactions proceed more rapidly. The volume effects of SiC and Si₃Ni₄ oxidation are described in Sect. 1.7:

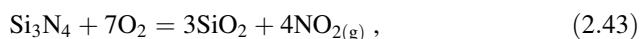
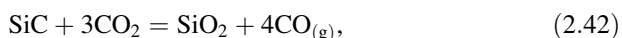
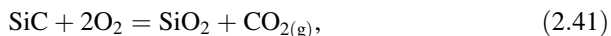
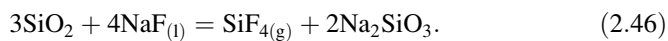
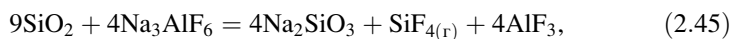
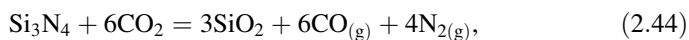
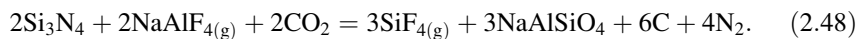
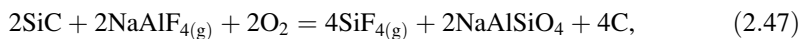




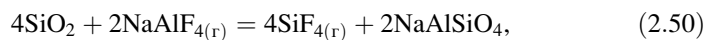
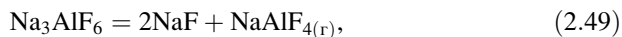
Fig. 2.87 Different colors on surface of N-SiC blocks



In the presence of CO_2 , SiC and Si_3N_4 may react directly:



The oxidation of the upper part of SiC linings probably proceeds according to these reactions:



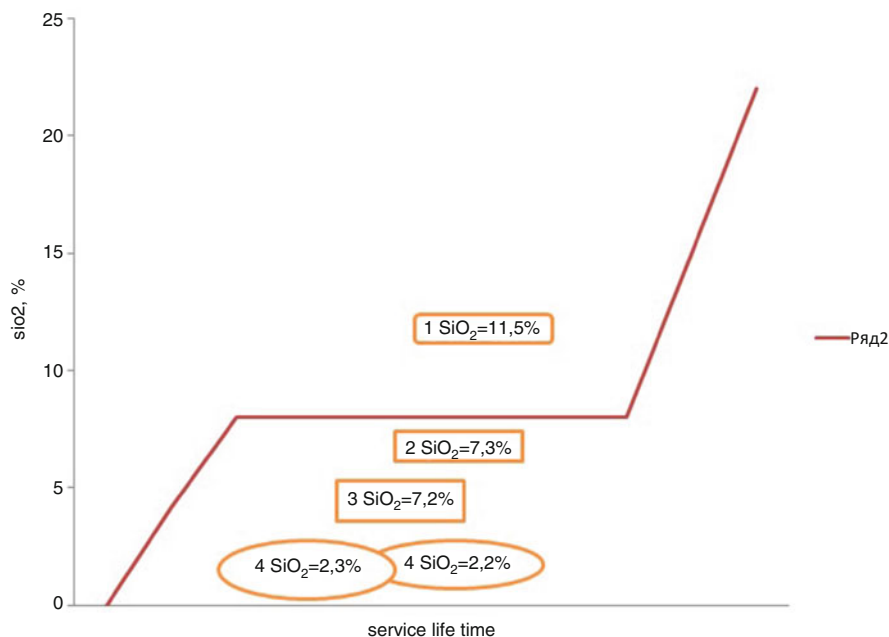
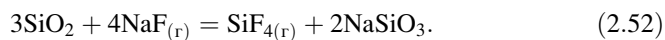
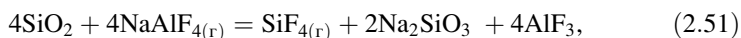


Fig. 2.88 Graph of silica content in $\text{Si}_3\text{N}_4\text{-SiC}$ side lining from refs. [133, 137, 139, 140, 142, 143, 145]; 1—after [145], side ledge is poor, side lining is overheated; 2—according to ref. [133], side lining is poor, service lifetime is 39 months, upper part; 3—according to ref. [133], side lining is poor, service lifetime 39 is months, lower part; 4—according to ref. [137], side lining is good, service lifetime is 36 months, lower part; 5—according to ref. [137], side lining is good, service lifetime is 36 months, upper part



According to [139, 140], the degradation mechanism of an SiC side lining is equal for all service conditions and has three stages of aging. In the first stage, oxidation is rather rapid and the decay of thermal conductivity is rather low, so that the second phase takes place (when the silicon oxide layer is formed). In the second phase, the rate of oxidation is constant, and the second phase lasts for a long period—a number of years. Then, when the silicon oxide content reaches 15–20%, the third phase takes place—relatively rapid growth of silicon oxide content. At the end of the third phase, the silicon oxide content reaches 28–39%, while the thermal conductivity drops to 5–7 W/m · K. The aim is to slow down the arrival of the third phase, when the thermal conductivity drops because of the increased silicon oxide content (Fig. 2.88).

Lowering the porosity during service may have a positive effect (diminishing the oxidation surface). However, it is necessary to keep in mind that oxidation reactions

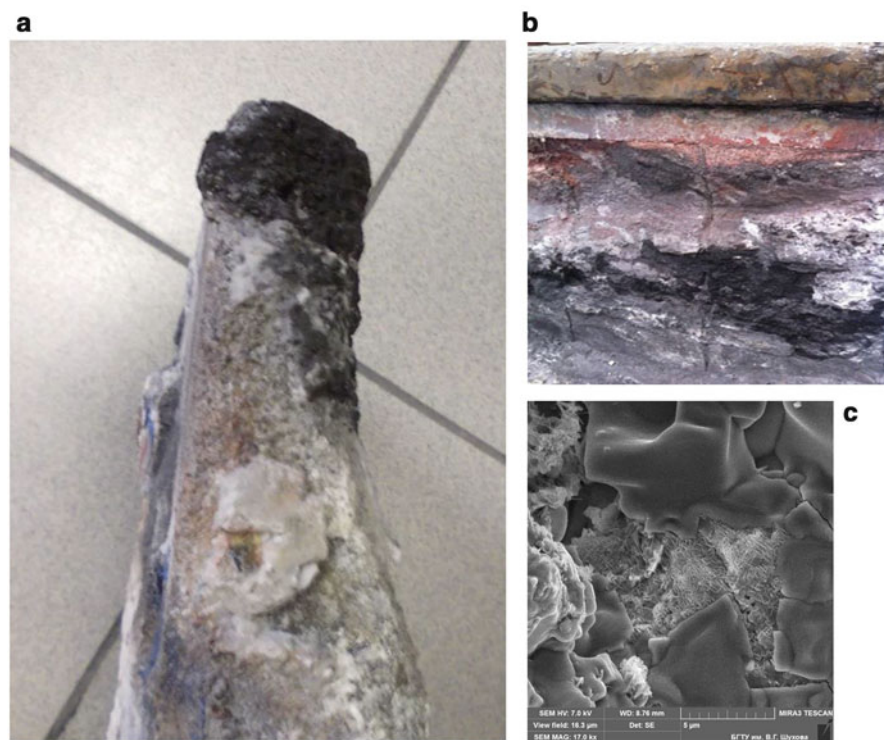


Fig. 2.89 (a) Eroded N-SiC block; (b) N-SiC blocks in lining of reduction cell with “groove” in upper part (close to deck top); (c) microstructure of corroded N-SiC material

are accompanied by a positive volume change, which may lead to cracking of the refractories (Fig. 2.90).

Sulfur from the anode may be a catalyst for the oxidation of SiC and Si_3N_4 .

Shutdowns of reduction cells due to failures of SiC side-wall blocks are not common. Once again, in normal operation, an SiC side lining is covered by a side ledge. The exceptions are startup, periods of overheating due to operation decay and possible magnetic instability, and increased velocities of electrolyte. Owing to increased velocities of electrolyte in cells, there may be no side ledge, at least on some parts of blocks or at some blocks (Fig. 2.89). The cracking of an SiC side lining (Fig. 2.90) is exotic (which may be influenced by overheating of the deck plate, for example, using a fireclay castable under the deck plate with a thermal conductivity of $1\text{--}2 \text{ W/m} \cdot \text{K}$ instead of an SiC castable with a thermal conductivity of $5\text{--}9 \text{ W/m} \cdot \text{K}$). Overheating of electrolyte for a long time with reduction technology decays will promote the dissolution of the side ledge and slow corrosion of SiC blocks. Reduction specialists know that even in properly designed reduction shops, there are local places with uncompensated magnetic fields (especially near studs in the outermost cells in a row), which are risky for an SiC lining.

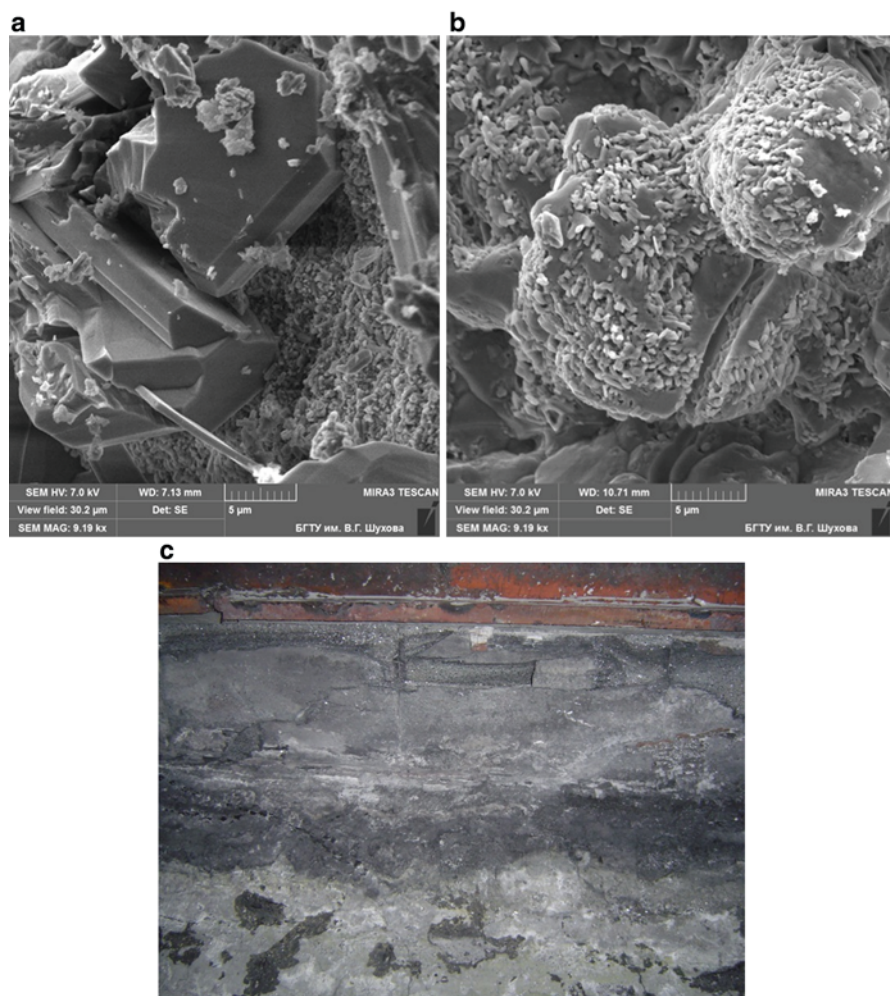


Fig. 2.90 Microstructure of N-SiC refractory before service (a), of oxidized N-SiC, (b) and SiC lining in reduction cell, broken in *upper part* (c)

Oxidation due to an overheated upper part of SiC blocks can usually be seen as white layers on SiC blocks, which may become cracked subsequently. The oxidation of a steel shell that has become overheated may yield an iron oxide layer up to 30 mm thick [140] that may become an additional thermal barrier, but it also may cause additional strain on the SiC block.

Generally speaking, temperatures in a range of 800–900 °C are not considered to be critical for the service of SiC and silicon nitride. However, everything changes in the presence of fluorine compounds and vapors of alkali compounds. The shift from passive oxidation with the appearance of a protective film of silica to active

oxidation, where gaseous reaction products are removed from the reaction zone, is also promoted in the presence of these compounds.

In refs. [139, 140], which marked the start of investigations into the aging of SiC side linings in aluminum reduction cells, the authors presented a general picture of changes without providing details or specific values. According to them, after a short period the silica content in an SiC side lining reaches 7–8% and remains more or less constant. This general view may be explained in part by a desire to simplify and in part by the fact that in reality the processes of aging in different parts of Si_3N_4 -SiC side linings proceed in different ways. Also, processes depend on conditions of service—whether the side lining is covered with a side ledge or not.

However, the data on silica content in SiC side linings are rather limited. And it is not easy to conduct an analysis. Much depends on conditions in the cell and from what place of the side lining block the specimen is taken. Although the information on silica content growth is insufficient, our limited data, collected at different aluminum smelters, show sufficient silica content, varying from 2.2 to 7–11%. The values, reported by Proshkin [145] and Yurkov [133, 137] are depicted together with a plot, taken from [3, 10, 16].

Tonessen and coworkers [146–148] performed a series of experiments testing the oxidation resistance of Si_3N_4 -SiC materials in steam according to ASTM-863 [149] and concluded that silicon nitride plays an important role in the oxidation resistance of Si_3N_4 -SiC materials. According to Tonessen, silicon nitride is not a simple “weak” phase of the composition. The complex Si-O-N phase, which may appear under certain conditions during the oxidation of silicon nitride or may be present in the material after processing, is a more oxidation-resistant phase in this composition. This observation is likely based on the fact that the space between fine silicon nitride grains is smaller compared to distances between SiC grains. According to Tonnesen, the complex Si-O-N phase is not subject to transformation to cristobalite or to other volume changes and is more oxidation resistant.

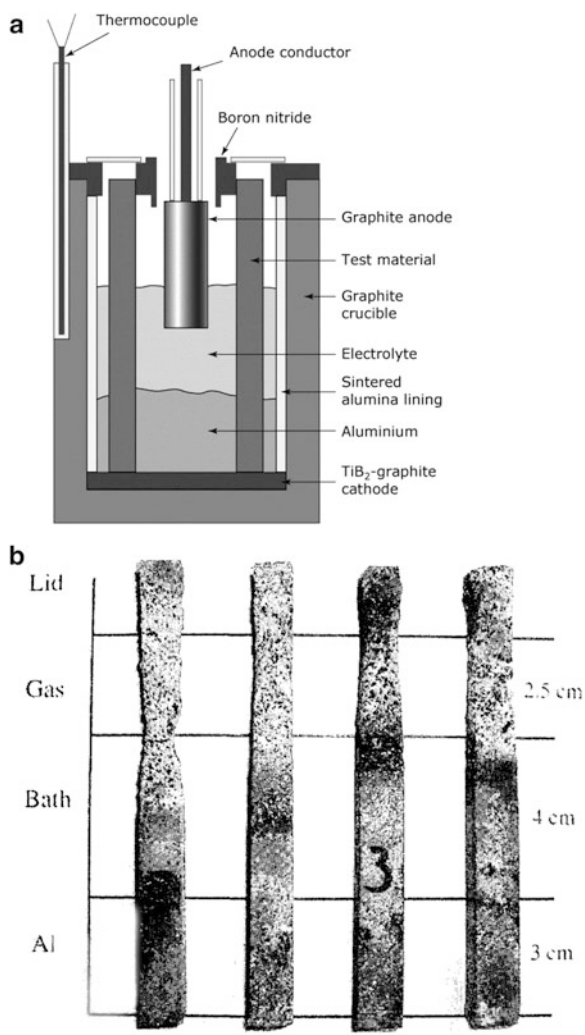
According to Tonnesen [146–148] and Laucournet [150], the permeability of Si_3N_4 -SiC materials plays an important role in oxidation resistance. It is more likely that permeability is determined by grains and crystals of grains of silicon nitride that appear. Fine crystals of silicon nitride form the pore structure of Si_3N_4 -SiC material with very low pore size distribution and permeability, which may promote good oxidation resistance.

Corrosion Resistance Tests for Bath and Molten Aluminum

The rod test is accepted for laboratory corrosion testing. All rod tests may be considered to be dynamic because in all tests the corrosive liquid moves near the tested samples either owing to the electrolysis process or because of rotation or lifting and dipping.

The rods are $10 \times 10 \times (100\text{--}130)$ mm, in the melt of the bath and aluminum. The existing variants of the rod test imitate the service of the SiC side lining in

Fig. 2.91 (a) Laboratory reduction cell for test of SINTEF corrosion resistance to bath and aluminum and samples (b) after testing [150]



slightly different ways, giving a different corrosion resistance for the materials of different producers.

There is a variant of testing with the preoxidation of samples at 900 °C in moisture for 100 h [150]. The cryolite resistance is determined by volume change after 22 h exposure to bath without voltage. This kind of testing may be considered as static, although it is a tough testing alternative.

Worldwide, the accepted test for corrosion resistance is the SINTEF test (Fig. 2.91a). A lab reduction cell [151–154] comprises a graphite crucible. On the bottom of the crucible is a TiB₂-coated cathode; the anode is in the upper part, and the tested SiC rods, dipped into the melts of aluminum and bath, are exposed to the

Table 2.20 Scale used to characterize degree of corrosion based on volume loss [151–153]

Volume loss (%)	Degree of corrosion
<0.1	0
0.11–1.00	1
1.01–2.00	2
2.01–3.00	3
3.01–4.00	4
4.01–5.00	5
5.01–6.00	6
6.01–7.00	7
7.01–8.00	8
8.01–9.00	9
>9.00	10

bath, aluminum, and oxygen in the presence of vapors. The lab reduction cell is in the furnace. The corrosion resistance is determined by the volume change (Fig. 2.91b).

The inventors [151] made a corrosion resistance scale, determined by the volume loss of the samples (Tables 2.20).

Actually, in the test [151–153], the corrosion resistance is determined at the second stage of service [139, 140], while during the test of nonoxidized samples [151–153, 164–207], the corrosion resistance is calculated in the first phase.

There are variants of the corrosion test with a supply of CO_2 to the bath with a simulation of the reduction atmosphere to the upper part of the blocks and some other modifications [154–159].

Usually, the side-wall lining does not fail; more frequently, the shutdown of a cell takes place owing to the bottom cathode block. However, sometimes there are shutdowns of cells due to the side-wall lining. Most problems with the side lining occur in connection with problems with the design of the pots or because of deviations in the reduction technology (e.g., overheating).

In the first case, the side ledge is removed owing to increased bath circulation, and in the second case, it dissolves owing to increased temperature. In both cases, the side-wall lining is exposed to the direct action of the molten electrolyte and aluminum, which might be the reason for the side lining failure.

Existing corrosion tests do not reflect all causes of side-wall lining failure, so opportunities for the enhanced development of the corrosion test do exist. There is a variant of testing [159] that involves rotating SiC rods in the melt and periodically dipping and removing the tested samples. Of course, these methods give slightly different corrosion resistance values.

Some authors claim [160–162] that Si_3N_4 is less corrosion-resistant than SiC . However, we found few experiments supporting this claim. Probably the reason for such a statement is that in an N-SiC refractory, the grains of SiC are coarse (up to 2–3 mm), while Si_3N_4 grains are fine (below 10 μm), so a kinetic factor in reactions plays a role.

According to some researchers, β - Si_3N_4 is superior to α - Si_3N_4 in terms of corrosion resistance to cryolite. We found no evidence for this. The grains of β - Si_3N_4 tend to have an isomorphous shape (sometimes a short prismatic shape) with l/d from 1 to 2–2.5. Assertions on the superior corrosion resistance of β - Si_3N_4 likely stem from the fact that the reaction surface of α - Si_3N_4 is higher because the grains of α - Si_3N_4 are elongated, tending to a needlelike and whisker shape, with $l/d > 5$, owing to the deposition of α -modification after the reaction of gaseous nitrogen and volatile silicon.

Regarding testing for corrosion resistance to cryolite and aluminum, all existing methods give an idea of corrosion resistance and are good tools for sorting and rejecting materials. Yet these methods are probably rather far from real quantitative estimations for forecasting purposes. However, it is difficult to say whether these methods might be quantitative even after significant adjustments. Also, it is worth recalling that corrosion by molten cryolite is not the only way for SiC material to change its properties. At some smelters, in specifications, a test for oxidation resistance in steam according to ASTM 863 was recently reported [149]. According to this test, samples are subjected to oxidation in steam for 500 h. The volume expansion of trial samples is a criterion of resistance to oxidation. Such testing is probably a good addition to the testing arsenal and allows the estimation of the oxidation resistance of the upper part of SiC blocks near the deck plate.

SiC-Based (and Non-SiC-Based) Side-Wall Materials and the Application Possibilities of Other Materials

Self-bonded SiC, sintered SiC, aluminum nitride (AlN), SiAlON-bonded SiC, titanium boride–SiC composition, and oxide materials were considered promising for application as side linings of reduction cells. Initial laboratory tests on the application of SiC began with oxide-bonded SiC. Those tests showed that N-SiC is as corrosive-resistant as O-SiC. There was a hope that SiAlON*-bonded SiC would be more resistant [163], but experiments proved the opposite. In experiments, AlN (sintered and reaction-sintered), SiC with TiO_2 addition, aluminum titanate, Al-Mg, and Al-Ni spinels, were also tested [163–166].

Aluminum nitride might be the ideal material for side lining because it cannot impart impurities to an aluminum melt, while the thermal conductivity of AlN is close to that of metals. In reality, AlN is not resistant to oxidation in the presence of fluorine vapors above the bath level. The vapors of fluorine compounds penetrate grain boundaries and cause intensive oxidation. According to lab corrosion tests, sintered SiC and recrystallized SiC are superior to N-SiC in terms of corrosion resistance, yet they are significantly more expensive. Attempts to diminish the sintering temperature (and the cost) by the addition of titanium diboride resulted in a deterioration of corrosion and oxidation resistance [32].

Silicon-self-bonded SiC showed good corrosion resistance in the lab; however, it is necessary to recall that Si-SiC contains up to 10% free Si, which may be an

impurity in aluminum. Even more resistant to corrosion in the lab was SiC material with oxide additives and a porosity below 5%.

The SiALONs are a class of compounds that were discovered in the 1970s [156, 157]. The name of the compounds comes from the abbreviation of the elements forming the compound—Si, Al, O, and N. A more “scientific” name for these compounds might be aluminum silicon oxynitrides.

SiAlON is a compound, or a continuous solid solution with a very large homogeneity range (the solubility of aluminum oxide in silicon nitride lattice is up to 67%); its general formula is



where z may vary from 0 to 4.2. In initial trials [137], a z -value of 3 was used, but low z -values might be of interest.

The structure may be optimized in several ways, yet the likelihood that new materials might be applied instead of N-SiC seems low. The changes might involve a drained cathode and inert anode.

Corrosion tests have shown that self-bonded SiC material has superior corrosion resistance [151]. A barrier to the application of SiC-SiC materials is their high cost (compared to N-SiC). Service records of 300-kA cells showed that a side lining is not a limiting factor of the service life of high-amperage cells. The use of new materials that differ from N-SiC seems unlikely. Yet some R&D might take place in the direction of increasing the oxidation of N-SiC and decreasing the gas permeability (N-SiC material has certain potentials for improving these characteristics).

Currently, an N-SiC refractory, for one thing, is a material that satisfies the requirements of the Hall–Heroult process on corrosion resistance and thermal conductivity; additionally, it is considered to be cost-effective, although it is not an optimal material for a side lining in the Hall–Heroult process from a materials science viewpoint.

Increased energy costs compel aluminum producers to reduce energy consumption. It is worthwhile noting that in Hall–Heroult reduction cells, 30–40% of the heat is dissipated through the upper part of the side lining (Fig. 2.6a). Recent designs (Fig. 2.6b) have accounted for the latest trends, and the lower part of the side lining has been changed into constructions with less heat flow.

Yet there is serious doubt that even if the ideal material (or combination of materials) that is resistant to electrolyte and aluminum without side ledge is found (e.g., tin oxide, ferric nickel spinel in combination with titanium boride), it would be possible to make a side lining of a reduction cell as a lining of a classical metallurgical device with proper heat insulation, which might decrease the heat flow by a factor of 10. The idea of a suitable material might be realized using a construction made from a combination of two or three different materials (e.g., tin oxide or nickel ferrite, resistant to electrolyte, and from titanium boride, resistant to molten aluminum), even despite the fact that in the existing process, the level of the boundary between electrolyte and aluminum moves along the height of the cell.

However, the heat of the reaction in the reduction of aluminum [Eqs. (2.1)–(2.8)] should dissipate; a total of up to 50% of the heat should either be utilized or dissipated. Otherwise, problems with overheating of the electrolyte will occur, and maintaining the required temperature would require increasing the surface of the cathode, where reactions (2.1)–(2.8) take place, and decreasing the cathode current density.

2.5.4 SiC Mortars, Ramming Mixes, and Castables for Installation of SiC Side Lining

According to the latest concept of reduction cell construction, SiC blocks are “glued” to a steel shell. SiC-based mortars (cements) are used as glue.

Usually, there is no problem with “gluing” an SiC block to a new steel shell (of the first runs); it is flat and smooth. However, the shells of the second and third campaigns have dents, cavities, and hollow imprints, and these should be filled in to avoid hollows filled in with air (which are very good barriers for heat transfer).

These gaps, dents, and hollow imprints are filled with SiC “leveling mixes” (Figs. 2.92 and 2.93).

An SiC lining should be installed in the steel shell of a reduction cell on a peripheral brick lining lying tight to the steel shell. Usually, an SiC ramming mix is poured and leveled on the peripheral brick lining, and an SiC block is installed on this layer, strictly normal to the surface. SiC-based mortar is uniformly placed on the back side of the SiC block to create a tight and smooth joint between the SiC and

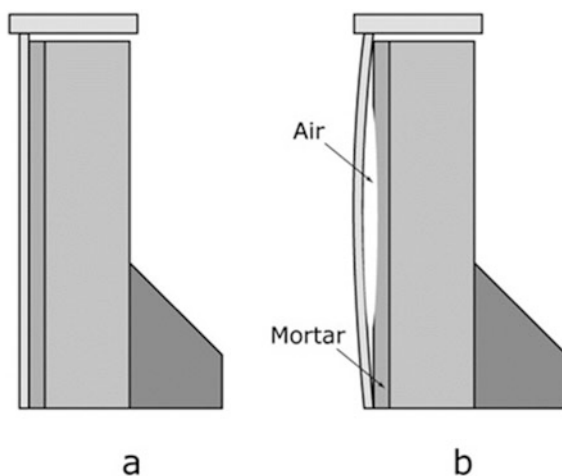
Fig. 2.92 Inner side of steel shell with leveling mix for filling in dents and cavities



Fig. 2.93 Installation of corner block in cell



Fig. 2.94 Air gap between SiC side lining and steel shell



steel. After the SiC blocks are installed and the deck plate is welded, the gap between the deck plate and the upper part of the SiC blocks is filled in with SiC-based ramming mix. The thermal conductivity of air is extremely low, and where there are air gaps, there will be local overheatings, which will cause the side ledge protecting the SiC lining to dissolve (Fig. 2.94).

If there are cavities or misprints, first it will be necessary to trowel the cavities with an SiC castable, do the leveling, and then allow it to dry. After that, the SiC mortar should be applied and the SiC lining installed (Table 2.18).

SiC mortars are high-quality cements consisting of 75–85% fine SiC. Small amounts of organics are added to the compositions for plasticity, and the addition of alumina cements, high-quality clay, fine silica, or solid/liquid sodium silicate gives

the compositions binding properties (Table 2.9). The mortars are prepared in mixers with water. They are applied on standard cement equipment—in plastic states they are placed and leveled on a torque and the main surface of the block. Then the block is installed on the side line to the shell and is knocked accurately by a rubber hammer. During installation, it is necessary to avoid air gaps (Fig. 2.94).

The difference between the mortar and the leveling mix or ramming mix is the grain size composition. Fine SiC powders are used for the mortars, while for the leveling mix and ramming paste (some producers attain the required properties of leveling mix and ramming paste in one composition, an SiC castable of concrete), producers typically use three grades of grain size composition, where the coarsest grain size may reach 2 mm. The binders for SiC castables (concretes) are either alumina cements or sodium silicate (castables on alumina cements have a limited storage time). Sodium silicate may be added to the dry mix in dry form, but a mix with liquid sodium silicate may also be prepared right before the installation of the SiC side lining. Some smelters agree to do this extra step. The difference between the leveling mix and the ramming paste is plasticity and adhesion ability; the leveling mix should be able to fill and adhere to a gap of 500×500 mm with a thickness up to 50 mm, and the bond should be rather firm (Tables 2.21 and 2.22).

The adherence ability of the mortars for gluing of SiC blocks to shells is 2503 measured according to ISO 13655-4 [167].

Table 2.21 Properties of SiC castables—leveling mix and ramming mix

Properties	Unit	Castable for leveling	SiC ramming mix
		Value	
SiC, minimum	%	84	85
Bulk density, minimum	g/cm ³	2.3	2.5
Thermal conductivity at 1000 °C, minimum	Wt/m × K	7	~6.5
Adhesive strength after heating to 110 °C within 24 h, minimum*	MPa	1.8	20
Adhesive strength after heating to 1000 °C within 3 h, min*		3.5	
Cold crushing strength, minimum	MPa	35	50
110 °C × 24 h			
1000 °C × 3 h		80	90
Modulus of rupture, minimum	MPa		20
110 °C × 24 h			25
1000 °C × 3 h			
Linear change, maximum	%	−0.1	
110 °C × 24 h		−0.3	
1000 °C × 3 h			
Storage life, maximum	Month	12	12
	мес.		

Table 2.22 Properties of SiC mortars

Properties	Unit	Value
Bulk density, minimum	g/cm ³	2.5
SiC, minimum	%	85
Adhesive strength after heating to 110 °C within 24 h, minimum*	MPa	3.5
	МПа	
Adhesive strength after heating to 1000 °C within 3 h, minimum	MPa	5
	МПа	
Thermal conductivity at 1000 °C, minimum	Wt/m × K	5

Sometimes misunderstandings occur between bricklayers and the producers of SiC-based castables. In the language of refractory producers, a castable that should be installed in the cavity of a steel shell is called a troweling mix, but bricklayers at smelters continue to call it a ramming mix. This latter term is more likely descriptive of the composition that is filled in between the deck plate and the upper part of an SiC block (Fig. 2.6).

In the fabrication of combiblocks, high-quality organic resin glues are used to glue an SiC block to the carbon part. The only requirement for this glue is likely a high adherence to install a combiblock in a cell.

The corrosion resistance of SiC mortar to cryolite in the cup test is below 1 cm², which is five to six times lower than common fireclay bricks (Table 2.20), yet modern Low Cement Castable (LCCs) demonstrate even more corrosion resistance. The adherence of such mortars is not high, which presents certain problems during the construction of cells, and there might be other variants of materials (e.g., phosphate-bonded) for the installation of SiC side lining. However, the technical specifications described earlier in this chapter provide working constructions. In well-designed reduction cells, there are no shutdowns owing to leakages of electrolyte of molten aluminum in the gaps between SiC blocks. In well-designed cells, there are no air gaps between the shell and SiC side lining that would cause overheating and oxidation or dissolution of SiC blocks.

Sometimes on smelters SiC mortars are used as brick mortar at the laying of fireclay bricks of the refractory layer below cathode blocks. In some smelters SiC castables are installed in a plastic state as a layer between carbon cathode blocks and the refractory layer. In both cases, the goal is to prevent electrolyte penetration into the refractory layer.

2.6 Refractory Barrier Materials of Cell Lining. Dry Barrier Mixes and Bricks. Properties and Chemical Resistance. Processes During Service. Interactions with Infiltrated Electrolyte. Change of Properties. Lenses

2.6.1 Bricks and Dry Barrier Mixtures

Carbon cathode blocks with collector bars are installed on a refractory layer that is made from fireclay bricks or dry barrier mixtures (DBMs). In aluminum reduction cells, this refractory layer is usually called a barrier refractory layer because the temperature under the cathode blocks is relatively small in terms of refractories. The main purpose of the refractory barrier layer is to stop the infiltration of electrolyte—in other words, to be a barrier against the infiltration of electrolyte.

The infiltration of electrolyte in refractory (and then in the heat insulation) layers has two negative consequences:

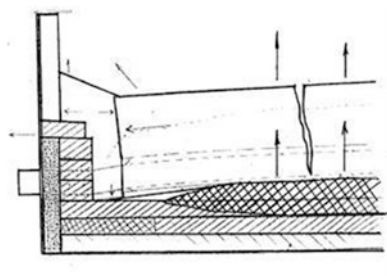
1. The thermal conductivity of refractories infiltrated by electrolyte may change by a factor of 3–5, while the thermal conductivity of heat insulation materials may change by a factor of 10–50 [168–172]. Heat flow through the bottom increases, the thermal balance of the reduction cell changes, electrolyte (with alumina) starts to crystallize on the surface of cathode blocks, forming a bottom sludge and decreasing the surface of cathode, and there might be changes with the current distributions, current efficiency, and energy consumption.
2. Depending on the circumstances, the “lens of products” of reactions of infiltrated electrolyte and the refractory barrier layer, having a thickness of up to 40–70 cm, may press the carbon cathode blocks from inside the reduction cell, causing bending strains and cracking. Such a phenomenon happens—and not rarely—if the pores in the carbon cathode blocks are above 25–30 μm (Sect. 2.3) (Fig. 2.76).

Fireclay bricks (alumina silica bricks, alumina calcium oxide silica bricks, and 2556 other silicate bricks) are not optimal barrier materials for aluminum reduction cells. As we have mentioned, cryolite-based electrolyte for aluminum reduction dissolves alumina better than anything else. Certainly, it will dissolve all alumina-based refractory compositions and almost all other oxides similar in chemical structure to alumina. From a chemical point of view, effective refractory barriers against the penetration of cryolite might be tin oxide, nickel oxide, compounds of nickel oxide, iron oxide, or zinc oxide (such as spinel NiFe_2O_4). These oxides almost do not react with NaF and aluminum fluoride [173]. Yet the cost of these materials, which is 50–100 times higher than that of firebrick, provides the impetus to find less costly variants of alumina silica materials (Table 2.23; Fig. 2.95).

Table 2.23 Chemical composition and properties of refractory barrier materials, according to refs. [10, 174–178]

	Composition, %						Apparent density, g/cm ³	Thermal conductivity, Wt/m K (300 °C)	Thermal conductivity, Wt/m K (900 °C)	Porosity, %	Permeability, μm ²	CCS, Mpa	Corrosion resistance (cup test), cm ²
	Al ₂ O ₃	SO ₂	MgO	CaO	Fe ₂ O ₃	Na ₂ O							
Bricks													
Alumina silica 1	26	68	–	–	<3	–	2.15	1.23	1.5	14	0.05–0.1	80	3.5–4.5
Alumina silica 2	35	60	–	–	<3	–	2.25	1.24	1.5	13		50	<5
Alumina silica 3	30	48	–	15	1	3	2.1	–	–	14		–	–
Alumina silica 4	22	70	–	–	–	–	2.1	–	–	14	0.1	45	3.7
Alumina silica 5	23–27	60–65	–	–	–	–	2.13–2.26	1	1.4	11–17		55–97	–
Alumina silica 6	43–46	54–57	–	–	–	–	2.26–2.31	1.24	1.34	15–17.5		28–52	–
Fireclay 1	30	50–65	–	–	–	–	2.1	1.5		22–24	0.2–0.4	25–30	6–6.5
Fireclay 2	28	50–65	–	–	–	–	2.2–2.3	1.5		20–21	0.2–0.4	20–24	5
Dry barrier mixtures													
Fireclay compositions	40–45	50–55	0.2–0.4	0.2–0.4	0.7–2.9	–	–	0.34		21.5			
Anortite compositions	26–32	60–65	0.5–1	0.5–1	5–7	–	1–2	0.43		20–25			
Olivinite compositions	3	48	–	15	1	3	–	–	0.4	–			
Low cement castable	12	44	37	–	5	–	–	–	1.2	–			
SiC mortar	4	44	42	–	7	–	–	–	0.8	–			
	8–22	70–85	–	1.5	–	–	–	2–3	–	13–15	0.05	80–90	0.5–0.8
	SiC 70–85	5–10	–	–	–	0.6–1.7	–	5–10	–	22–25		4–5	0.8–1

Fig. 2.95 “Lens” of interaction of infiltrated electrolyte and refractories



Attempts have been made to fabricate barriers between carbon blocks and refractory layers from electrolyte penetration using steel plates and plates of window glass. These barriers did not find industrial application. We will discuss other barriers later.

Alumina Silica Refractory Barriers

Long ago, refractory layers were made from powdered alumina that was poured on a layer of heat insulation. Following cell shutdown, the alumina, infiltrated by electrolyte, was used for the production of alumina. The main disadvantages of such a material are its high thermal conductivity and low resistance to electrolyte. This type of refractory lining is not used today. The properties and compositions of refractory barrier materials used in reduction cells (including corrosion resistance according to cup test) appear in Table 2.20.

Fireclay-type bricks with a porosity of 13–15% are preferred over fireclay bricks with a porosity of 22–25%, although they are more expensive. Some researchers consider a slightly lower alumina content of bricks to be an advantage. Of course, the geometrical tolerances of bricks should be rather strict and not exceed 1–2 mm, because with these tolerances, the brick lining from one side of the brick and from another side of the next brick may double. The current trend is to make brick lining from small blocks that are $250 \times 250 \times 65$ mm by $320 \times 250 \times 65$ mm (and, to avoid using bricks of standard sizes, $230 \times 114 \times 65$ mm) to decrease the number and total length of shafts between bricks.

There have been nonexclusive points of view on the optimum chemical composition of refractory barrier bricks. According to ref. [174], the upper layer (contacting the cathode bottom blocks) should be made from high-silica fireclay bricks, while the lower layer should be made from fireclay bricks containing more alumina.

According to another point of view [175], the upper layer should be made from high-silica fireclay bricks for a reduction pot with graphitic or graphitized carbon cathode blocks and from fireclay bricks containing more alumina for a reduction pot with semigraphitic blocks (30–50% carbon).

It seems obvious that fireclay bricks with a porosity of 13–15% and a permeability of $0.05\text{--}0.1\ \mu\text{m}^2$ are preferable to fireclay bricks with 22–25% porosity because the corrosion resistance (cup test) of a low-porosity brick is 1.5–2 times higher. This has also been confirmed in industrial testing. There is no doubt that strict dimensional tolerances and minimization of shafts in fireclay bricks are preferable.

There is a belief that the question of the optimal silica/alumina ratio in fireclay bricks for reduction cells will not be resolved by a strict proportion. Indirect evidence for this belief are the numerous industrial trials involving the use of silica bricks, powdered silica sand, all variants of fireclay brick, powdered fireclay, mullite bricks, alumina bricks, powdered alumina, and red construction bricks as a refractory barrier layer.

Conventional fireclay brick has been processed for centuries, and the technology of fireclay brick with a porosity of 13–15% derives from the technology of refractory materials for ferrous metallurgy. In ferrous metallurgy this type of refractory is common.

Dry Barrier Mixtures

DBMs are used instead of refractory (fireclay) barrier bricks as a powdered dumping for the installation of carbon cathode blocks, and sometimes as a dumping between barrier bricks and heat insulation. These refractory compositions are used without water and should withstand the penetration of cryolite to heat insulation layers. The active use of DBMs in the lining of reduction cells started in the 1980s. There have been no strict preferences or negative considerations on using DBMs over brick linings. Undoubtedly, DBMs are preferable to fireclay brick, having a porosity of 22–25% and dimensional tolerances of $\pm 3\text{ mm}$. There are several compositions of DBMs (Table 2.20).

DBMs are applied instead of barrier refractory bricks. There are variants of refractory linings only from DBMs (instead of a layer made entirely of refractory brick) or a partial substitution of one or two layers of bricks by DBMs.

The chief advantage of DBM application concerns time. A lining with a DBM (using a flat vibrator) takes significantly less time compared to a brick lining. The disadvantage is the dust generated during installation and vibro compaction. Another advantage is the lack of shafts through which cryolite may penetrate to the heat insulation layer. Usually DBMs are installed using a flat vibrator (Fig. 2.77), but the trend is to use more sophisticated methods, like roller trackers or roller compactors with additional vibration.

The thermal conductivity of a DBM is slightly lower than that of fireclay brick (at least at preheating startup). Usually, at retrofit of reduction cells, designers prefer not to change anything, so the heat flow through the bottom of such cells may decrease at the beginning of operation.

Publications [177, 178, 199–208] describe how cryolite reacts with grains of alumina silicates, forming a viscous layer on the surface. According to refs.

Fig. 2.96 Vibration of dry barrier mix during installation in cell



[177, 178], this viscous layer prevents the penetration of cryolite to the refractory and heat insulation lining. This layer does not crystallize or solidify and remains viscous—it does not crack (Fig. 2.96).

This mechanism may kick in, but not on the entire surface of the cell and not at just any time. In reality, even within a surface of 5 cm^2 there may be two types of interaction—that described earlier and the penetration of cryolite melt in the depth of a DBM without forming a viscous layer. In the latter case, there is no protection against cryolite penetration, and the cryolite melt will stop its penetration only when it is frozen.

Corrosion Resistance Testing

The approved method of testing fireclay brick for corrosion resistance to electrolyte is the standard ISO 20292 [179]. A hole is drilled in the brick or is preformed in a castable, then the electrolyte is poured into the hole, and the brick is placed in a furnace. Following exposure, the brick is cut, so that the change to the square of the hole may be measured. The degree of corrosion is calculated in the surface of the corrosion. The lower the square of corrosion is, the more corrosion-resistant the material will be (Fig. 2.77).

A variation in the cup corrosion test can be found in ref. [180]; it uses a graphite crucible as electrolyte. The porosity of the graphite crucible may vary. The graphite crucible is placed on a refractory layer. In this type of test, sodium vapor is taken into account. If the porosity of the graphite crucible is 12–14%, the result will reflect the interaction of refractory with sodium, which moves in graphite. If the porosity of graphite is 28%, the result will demonstrate the interaction due to the capillary movement of electrolyte through pores of carbon [181–183]. Experiments have shown that when testing a refractory in three variants, different results will be obtained with regard to corrosion resistance, which illustrates the complex character of the interactions (Fig. 2.97).



Fig. 2.97 Results of cup test for cryolite resistance of fireclay brick and low-cement castable (concrete)

Siljan [184] found a good correlation between the corrosion resistance in a cup cryolite corrosion test and the depth of cryolite infiltration. A 220-kA reduction cell was lined with eight different alumina silica refractory materials and switched off to investigate refractory conditions after 500 days. The results confirmed the good correlation. However, from a physicochemical point of view, the correlation does not appear to be a strict one between the interaction after several hours of operation and the kinetics of penetration of the melt after several months.

It has been stated [185] that there is good agreement between corrosion resistance (cup cryolite resistance test, 24 h, 950 °C) and the silica content in an alumina silica refractory. At the beginning of the process, a silica-rich layer appears that plays the role of a protective layer. Rather often the segregation of the melt on the silica-rich and fluoride-rich parts takes place (Fig. 2.78). Usually, the cup cryolite resistance of refractories increases as the porosity decreases.

Chemical Interaction of Sodium Fluoride Salts with Alumina Silica Refractories

There are many possible chemical reactions among cryolite, sodium fluoride, alumina, silica, and mullite [10, 13, 184, 186–189]. Classical considerations on the corrosion resistance of refractories have limited significance for the problem of corrosion resistance to cryolite and are good from an educational and informational point of view owing to the extra low viscosity of cryolite melt and unique corrosion ability of cryolite melt on alumina and alumina-containing compounds. The multifactorial behavior of electrolyte, multicomponent refractory lining,

multivariability of chemical reactions, and limited knowledge on the mechanisms of sodium penetration to refractory linings make physical modeling almost impossible. It is only possible to discuss approaches that could lead to partial encapsulation of refractory and heat insulation linings.

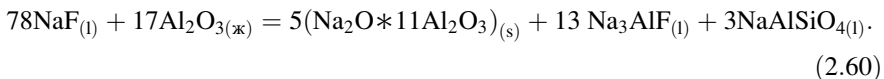
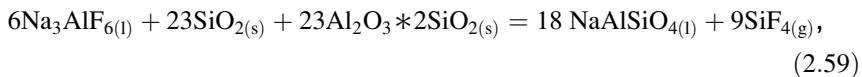
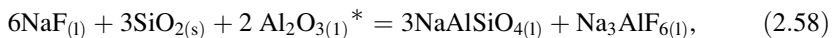
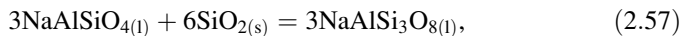
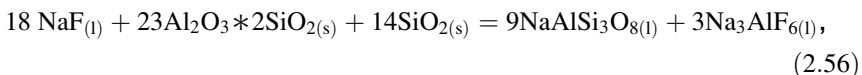
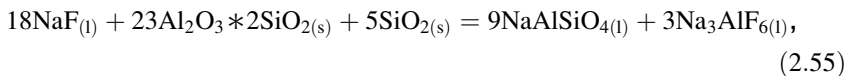
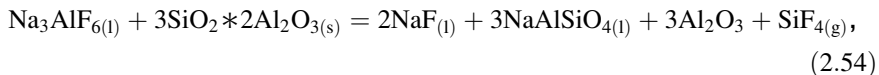
Many chemical reactions are possible thermodynamically between the components of electrolyte and the components of a refractory lining. The interaction may be described as a reaction between solid and liquid reagents on the border of a solid reagent in the case of no mixing and in the case of constant feeding with one component.

However, the dissolution limit of alumina and silica in cryolite is approximately 10% at 950–960 °C [182], and the penetrated electrolyte will relatively rapidly reach the saturation limit, become viscous, and stop dissolving the refractory. The temperature of the melt should be close to the crystallization point.

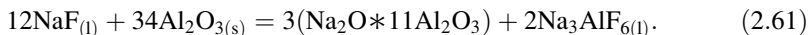
Mullite, $3\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3$, may interact with sodium fluoride (NaF), giving cryolite and nepheline, 3NaAlSiO_4 :



The possibility that cryolite will react with mullite, giving gaseous silicon fluoride, has been confirmed experimentally:



The alumina component of refractory may react with sodium fluoride, giving sodium aluminates and cryolite:



The products of the reactions of cryolite components with alumina silica refractories are albite (sodium feldspar) and nepheline, which may coexist with cryolite.

The solubility of alumina and silica in cryolite and sodium fluoride decreases as the acidity of the system decreases, and the freezing point of the system decreases as the silica content increases (from nepheline to albite).

At one time it was hoped that calcium and magnesium alumina silicate could serve as barrier layers that would prevent refractories from interacting with electrolyte [190–193]. These minerals are slightly more expensive than alumina silica refractories. The basis for such hope was the fact that the products of interactions of anortite ($\text{CaAl}_2\text{SiO}_8$), forsterite (MgSiO_4), and olivinite with sodium fluoride would have freezing points above 900 °C and the melts would crystallize [190, 191].

The volume effects for the reactions were calculated [60] taking into account that one constituent came from outer space:

For reaction (2.49): 1.21;

For reaction (2.50): 1.34;

For reaction (2.51): 1.78;

For reaction (2.52): 1.93;

For reaction (2.57): 1.31;

For reaction (2.58): 1.13.

It is almost impossible to estimate the real value of each reaction. However, calculation of the volume effect gives the real cause of the reactions, which is heaving (Fig. 2.79) of the cathode bottom owing to the interaction of infiltrated electrolyte with refractories and the formation of lenses that press on carbon cathode blocks and cause cracking (Fig. 2.80). The lenses were 250–300 mm high and 1.5–2.5 m long, and the heaving in the center was up to 100 mm.

The upper part of a lens (50–70 mm below the carbon block) is formed by albite, nepheline, cryolite, and sodium fluoride [194]. The middle part of the lens (100–150 mm below the cathode block) consists of a mix of albite, nepheline, cryolite, sodium fluoride, quartz, and mullite. The lower part of the lens (200–250 mm below the cathode block) consists of reacted material and of 30–50% of unreacted fireclay, which describes the kinetics of interaction, followed by infiltration of electrolyte.

Sodium Vapor Degradation

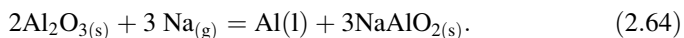
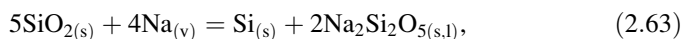
It has been considered [195, 196] that the major part of sodium formed according to the reaction



Fig. 2.98 Cell with bottom heaving before dry autopsy

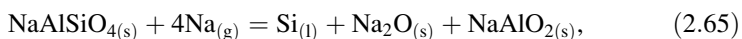


dissolves in electrolyte and oxidizes near the anode, yet some sodium is transported through the carbon cathode block downward to the lower surface of the cathode block. It has been reported that the sodium pressure might be as high as 0.02–0.03 atm (Fig. 2.98):

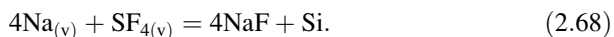
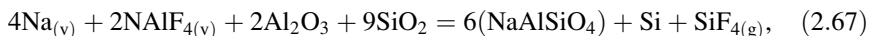


The reaction of sodium with refractory compounds yields metallic aluminum and silicon, but it has been reported that the direct transformation of fireclay shamotte compositions is possible with nepheline and albite.

Sodium also reduces albite and can react with nepheline:



Sodium may interact with SiF_4 and NaAlF_4 in the gaseous state [30]:



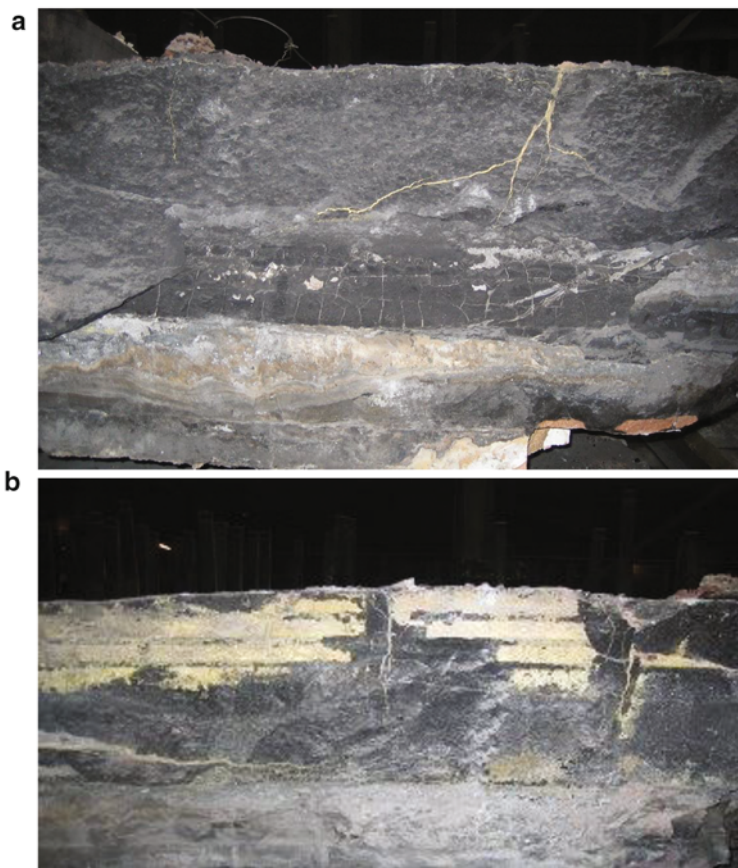


Fig. 2.99 (a, b) Cross section of cell lining showing lenses of interaction of electrolyte with refractories instead of refractory layer. One can see the flow of aluminum in the cracks of the cathode blocks

Direct evidence of silicon balls and drops to some extent proves this concept. From Prof. Øye's viewpoint, the mechanism opens the way to the transport of electrolyte through permeable pores owing to capillary forces [10] (Fig. 2.99).

Influence of Porosity and Permeability on Corrosion Resistance of Refractories

According to Poiseuille's law, the velocity of a liquid in a capillary is

$$dh/dt = (d^2 \times \Delta p) / (32 \times \eta \times h), \quad (2.69)$$

where d is the diameter of a capillary, Δp is the difference in pressure, η is the viscosity of the liquid, h is the depth of infiltration, and t is time.

The capillary pressure of the liquid is

$$\Delta p = (4\sigma \cos \Theta)/4\dot{\eta}, \quad (2.70)$$

where σ is the surface tension and Θ is the wetting angle. Combining Eqs. (2.61) and (2.62) gives

$$h = (d * \sigma \cos \Theta) / 4\dot{\eta}. \quad (2.71)$$

According to Eq. (2.69) (not taking into account the temperature gradient and possible chemical interaction of the melt with the surface of a capillary), the depth of infiltration is directly dependent on the diameter of the capillary, surface tension, and wetting angle and is inversely proportional to the viscosity.

The viscosity is strictly dependent on temperature; it is strongly recommended to maintain (at least in the design of the cell) the isotherm of the freezing point of electrolyte near the lower edge of the carbon cathode blocks. Generally speaking, the surface tension is dependent on the composition of the melt in the capillary (taking into account the interactions with the walls), but in practice the wetting angle of alumina silicate refractory by cryolite melt is close to zero.

However, Eq. (2.69) states that the diameter of permeable pores (and, consequently, the permeability) should be minimal, but the value of porosity does not affect corrosion by cryolite melt. A reasonable limitation for the pore diameter in the refractory might be 3–5 μm .

A zero contact angle of wetting gives optimal physical contact between melt and refractory at the beginning of chemical reactions. An absence of chemical interactions or a low rate of reaction gives the melt the ability to penetrate. Within some time, a viscous albite melt will appear on the surface of permeable pores, limiting the next penetration.

The viscosity of the melt in a NaF-AlF₃ system follows the Arrhenius equation

$$\eta = A \exp[B(1/T - 1/T_m)/R]. \quad (2.72)$$

The solute in the melt alumina increases the viscosity. In contrast to freezing points, the viscosity of melt strongly depends on the alumina/silica ratio in reaction products. There is evidence that the solubility of albite in cryolite is rather high. In lab tests, it has been shown that with high concentrations of silica in melt, the melt may segregate: low-viscosity melt with an increased concentration of fluorides and high-viscosity melt with a high concentration of silica. According to ref. [184], the viscosity of nepheline-rich melt may be several orders lower compared to the viscosity of albite-rich melt (Fig. 2.100).

Hence, for the formation of albite-rich, cryolite melt with low viscosity, which could be a barrier against the penetration of sodium compounds inside the refractory lining, the problem is to find conditions for the segregation of the melt into low-viscosity melt with increased alumina content and high-viscosity melt with increased silica content.

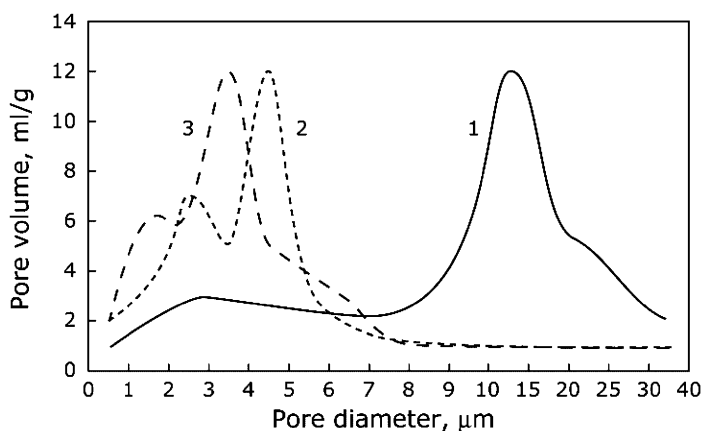


Fig. 2.100 Pore size distributions in fireclay brick (1) and in LCCs (2, 3)

Table 2.24 Properties and cup corrosion resistance to cryolite of fireclay bricks and LCC castables [197]

Property	Value				
	LCC		Fireclay		
	A	B	A	B	C
Open porosity, %	17.1	17.8	22	21.8	21.8
Permeability, μm^2	0.02	0.01	0.45	0.08	0.19
CCS, MPa	93	91	30	35.3	42.2
Al_2O_3 , %	20.7	72.4	>30	>28	>28
SiO_2 , %	65.3	22.3	~60	~65	~65
CaO, %	1.4	1.5			
Corrosion resistance, %	12	5	42	48	45

However, it is possible that this question might be resolved by changing the composition of the refractory. It is likely that the condition allowing for the formation of a viscous albite layer is a controlled input of sodium compounds. Formally, this condition is realized with excess sodium fluoride and excess reactant—a refractory with silica content above 60% [186] when there is a rapid reaction of base melt with reactant with a high specific area (small size of grains component of DBMs).

At a low rate of infiltration and low reactivity of the refractory, or, on the contrary, at a rapid penetration of cryolite through gaps, a low-viscosity melt will appear in the lining, which will become low-viscosity only in the case of real barriers. This is realized with the application of bricks with low-dimensional pores, and the chemical composition does not play a significant role.

It is more likely that structural factors (pore size distribution and consequent permeability) exert a greater influence on corrosion resistance (according to cup testing) than chemical composition [197, 198] (Fig. 2.81) (Tables 2.21 and 2.24).

More on Barriers for Electrolyte Penetration

- An alumina silica refractory is far from being the optimal material for a refractory barrier. Although some theoretical considerations on the silica/alumina ratio may exist, other variants should be found.
- There is a long history of trials with different barrier materials: silica brick, silica powder, alumina brick, alumina powder, red construction brick, mullite brick, window glass, and various combinations of mullite brick or fireclay brick in the upper and lower layers.
- Chemical considerations suggest that tin oxide, ferric nickel spinel, zinc oxide, and their variations might be good barrier materials; however, these compounds do not satisfy economic considerations. Also, these compounds are not stable to sodium vapor.
- SiC-based refractories look (in the form of preshaped or not previously shaped castables or mortars) like more likely candidates as barrier materials.
- Structural considerations suggest limiting the pore size in the refractory material and decreasing the length of the shafts between refractory barrier bricks.
- The advantage of DBMs is the absence of shafts, although limiting the pore size in a DBM is impossible.
- The resistance of LCC to cryolite is superior (according to cup tests) to medium-cement SiC castables.
- Alumina silica DBMs and refractory bricks of relatively large shapes, with low permeability and low pore size, more or less confer a service life of reduction cells of 6–7 years, with some cells reaching a service life exceeding 10 years.
- The best barrier is probably accurate temperature control of freezing point isotherms in carbon cathode blocks and limiting electrolyte flow through pores and, consequently, the pore size in carbon cathode blocks.

2.7 Heat Refractory Insulation Materials for Reduction Cell Linings

Although in refractory practice there are hundreds of heat insulation materials, the list of such materials for the lining of reduction cells is rather limited. For one thing, economic considerations add some limitations, but for another, heat insulation materials in reduction cells should withstand mechanical compression loads without deformation at temperatures up to 900 °C for a long time, and numerous inexpensive fiber heat insulation materials do not meet this requirement. In a Hall–Heroult reduction cell, heat insulation materials should withstand the pressure of the electrolyte layer, the molten aluminum layer, cathode carbon blocks (taking into account collector bars), and the refractory layer.

Currently, only four or five heat insulation materials are used in the lining of reduction cells: diatomaceous (moler) and perlite bricks, vermiculite and calcium

silicate blocks (slabs), and sometimes lightweight fireclay bricks (but their thermal conductivity is relatively high, while the cost is not negligible) and fiber fireclay bricks.

2.7.1 *Diatomaceous (Moler) Heat Insulation Materials*

Diatomaceous earth is a silica-rich porous fossil rock refuse that occurs in light gray, light yellow, and light pink colors and is formed by the shells of diatomaceous weed. The shells were deposited on the bottom of water reservoirs, and mud clay between these shells cements the deposits. Diatomaceous ore exists on all continents, with the most famous in Denmark (Fig. 2.101).

Good diatomaceous ore contains more than 70% silica. Owing to the small pore dimensions (pore diameter 5–100 μm), diatomaceous materials have low thermal conductivity.

Clay minerals, which are part of diatomaceous ores, determine the plasticity at shaping, the sintering process, and the service temperature. The three main variables in diatomaceous ores are probably the nature (and dimensions) of diatomaceous shells, the nature of clay minerals, and the ratio of diatomaceous shells to clay minerals [199, 200]. These variables vary from deposit to deposit, so the properties of diatomaceous bricks from different deposits differ.

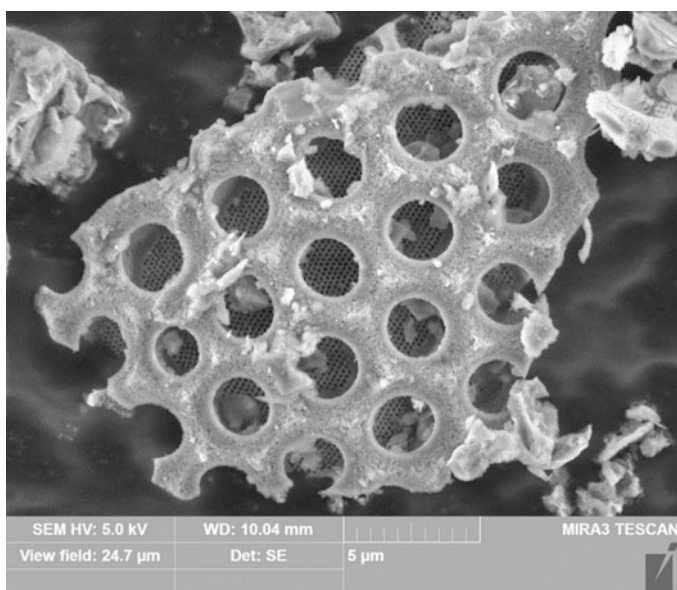


Fig. 2.101 Diatomaceous shells at multiplication

The shaping of diatomaceous bricks may be performed by pressing, by extrusion with subsequent cutting, and by slurry technology (pouring in the molds followed by drying). Sometimes, to increase porosity, wood chips and sawdust are added to the mix or to the slurry. Firing is performed at a temperature of 800–900 °C in tunnel kilns. The standard technological procedure involves cutting, which allows for strict dimensional tolerances.

The possible shortcomings are only dimensional tolerances and cavities (in case of slurry processing), but it is necessary to keep in mind the safe service temperature (Sect. 1.4). In large part, the safe service temperature is determined by the clay binder of the deposit. Figure 2.107 shows the linear change dependencies of two diatomaceous bricks made of materials from different deposits.

2.7.2 *Perlite-Based Heat Insulation Materials*

Perlite is a high-silica glassy acidic volcanic rock mineral whose chemical composition is close to that of granite and contains about 15% of chemically bonded water. At heating, owing to the evaporation of this water, perlite blows up with a considerable volume effect, forming a light porous material. The number of blowups (showing the number of times the volume increased at heating) of the best perlites is approximately 20. It is possible to obtain materials with round isolated pores at rapid heating at 800–900 °C. Perlite heat insulation materials may be made cement-bonded (without firing) and fired clay-bonded. The service temperature of good perlite-based heat insulation materials may reach up to 1200 °C and is determined by the binder. Possible defects include only the dimensional tolerances and cavities.

2.7.3 *Vermiculite-Based Heat Insulation Materials*

Vermiculite ore is a result of the erosion and disintegration of black mica and subsequent geological hydrothermal interactions. Probably the best-known deposit of vermiculite ore is in South Africa. Vermiculite is magnesium potassium hydro alumino silicate, with the approximate formula $(\text{Mg}^{+2}, \text{Fe}^{+2}, \text{Fe}^{+3})_3 [(\text{AlSi})_4\text{O}_{10}] \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O}$, a type of hydrated biotite mica. Vermiculite expands at heating to temperatures 650–1000 °C up to 18–25 times. Before expansion, its density is 2.4–2.7 g/cm³, and after expansion it is 0.15–0.3 g/cm³. The blowing up (thermal expansion) of vermiculite is usually performed in fluidized bed furnaces. Expanded vermiculite has low thermal conductivity and is a good heat insulation material.

Vermiculite-based heat insulation materials may fired or not fired. The first step in processing is refining and expansion (blowup). In the fired processing, the expanded vermiculite is mixed with clay and shaped into blocks by pressing and then fired in a tunnel kiln up to 900–1000 °C. Fired materials do not contain water



Fig. 2.102 Lining of reduction cell: installation of heat insulation vermiculite blocks

and do not absorb water from the atmosphere; the safe service temperature of fired vermiculite blocks is superior to that of unfired ones.

At processing of unfired vermiculite heat insulation materials, expanded grained vermiculite is mixed with small amounts of aqueous solution sodium or potassium (ore mixed of sodium and potassium) liquid glass. The mix is pressed and the blocks are heated at 250–300 °C. Unfired vermiculite materials are cheaper, but the final properties of the material are attained after the installation of the materials in reduction cells, preheating, and startup. At preheating, a considerable amount of water escapes from the liquid glass binder, and it is necessary to take this into account at preheating. Unfired vermiculite heat insulation materials may additionally absorb up to 3–4% water from the atmosphere at storage (in addition to 5–6% of the existing water in liquid glass binder). During the preheating of reduction cells, this water should evaporate, and this makes unfired vermiculite slightly less convenient compared to fired materials.

The safe service temperature of unfired vermiculite heat insulation materials is determined by the binder and may vary considerably depending on processing and the sodium/potassium ratio (Fig. 2.102). Materials with sodium liquid glass binder have a lower safe service temperature than materials with potassium liquid glass binder because of the different high-temperature deformations (Fig. 2.103).

Other than the safe service temperature, usually in vermiculite-based materials there are no defects, and the dimensional tolerances at pressed materials are perfect. If something does not going smoothly in the fluidized furnaces, the density of grained vermiculite might increase, which will lead directly to an increase in the thermal conductivity of the materials. However, if problems arise in connection with temperature in a fluidized bed furnace and the vermiculite does not exfoliate properly, it might start exfoliating during service, which is not desirable.

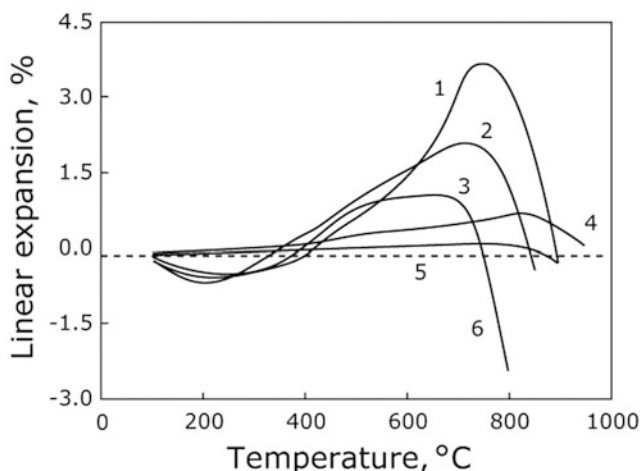


Fig. 2.103 Linear change at heating for different unfired vermiculite heat insulation materials

Beginning at 1000 °C, the slow transformation of vermiculite to clinoenstatite occurs, which may lead to cavities and decay of the thermal conductivity properties. That is why, although the melting point of vermiculite is 1350 °C, even for fired materials, the safe service temperature should be considered as 1000–1100 °C. For unfired vermiculite-based materials, the question of safe service temperature is significantly trickier.

2.7.4 Calcium Silicate Heat Insulation Materials

Calcium silicate heat insulation material is a synthetic material produced from silica (refined diatomaceous ore or milled silica sand) and calcium oxide (high-quality calcium carbonate chalk or lime) with the addition of organic fibers (to retain the shape after pressing). Pulp slurry from the mixer is squeezed out, pressed, and after exposure to air placed in an autoclave at a steam pressure of approximately 10 atm and temperature of 120–130 °C. The synthesis of xonolite [199] mineral takes place in the aforementioned conditions, and this represents the end of the technological process. The dimensions of calcium silicate boards may reach 2500 mm × 1500 mm.

At preheating and during startup of the reduction cell, calcium silicate boards lose physical water and chemically bonded water (in total, up to 10%), and the burning out and degradation of organic fibers take place.

Usually in calcium silicate slabs, there are no geometrical defects (the torque sides of blocks may be grinded); however, the technology of the material is complex and requires accurate processing: There are no problems in the service stability of calcium silicate at high temperatures if there are no problems with processing. However, the transformation of xonolite into tobermorite leads to shrinkage and the loss of insulation properties (Fig. 2.109).

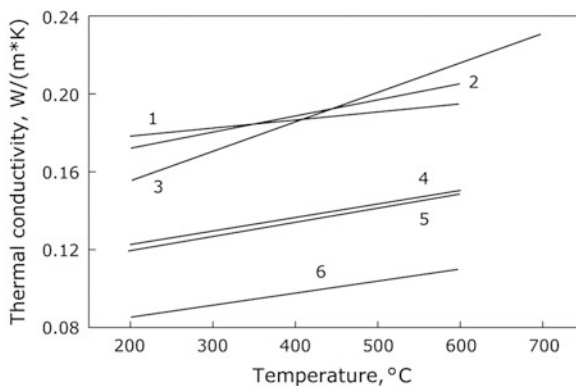
Thermal Conductivity of Heat Insulation Refractory Materials for Reduction Cells

In Chap. 1, we showed that the temperature dependence of refractory and heat insulation materials is usually a complex function. Yet for diatomaceous, vermiculite, lightweight fireclay and calcium silicate materials at temperature intervals, the temperature dependence is linear (Fig. 2.104). The linear character of the temperature dependence of thermal conductivity reveals the peculiarities of heat transfer in lightweight refractory materials [200] (Fig. 2.105).

Lightweight fireclay (density: 400–500 kg/m³) and some kinds of diatomaceous materials have the largest thermal conductivity values. The processing of lightweight fireclay materials involves relatively high-temperature firing (giving good contacts between the grains), and the pores are large (in the millimeter range). This explains the relatively high thermal conductivity of lightweight fireclay compared to materials with similar density.

The thermal conductivity of diatomaceous and vermiculite heat insulation materials is similar. Diatomaceous materials have a very fine pore structure; in such materials, the radiation effect on thermal conductivity is low. An interesting dependence of thermal conductivity vs. temperature appears in Fig. 2.105—diatomaceous bricks with densities of 400, 500, and 600 kg/m³ have different values of

Fig. 2.104 Thermal conductivity of heat insulation materials: 1, 2—diatomaceous bricks; 3—lightweight fireclay brick; 4—diatomaceous brick; 5—vermiculite slab; 6—calcium silicate slab



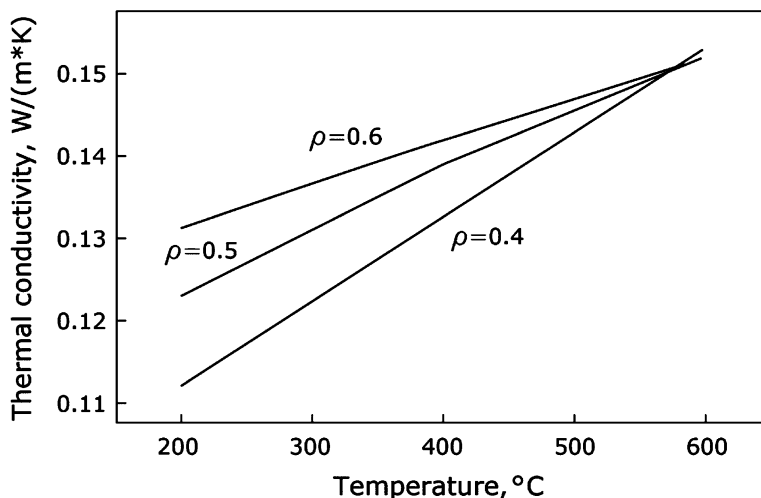


Fig. 2.105 Thermal conductivity of diatomaceous bricks with different densities

thermal conductivity at 200 °C, but rather similar values at service temperatures—400–600 °C. At such temperatures, the thermal conductivity of materials with different densities is identical (this constitutes the evidence for the effect of small pores on thermal conductivity values). From a practical point of view, this means that heat flow through the bottom of a cell will be similar for diatomaceous materials with different densities, but with infiltration by electrolyte, denser materials are preferred. In vermiculite materials, the radiation effect on thermal conductivity is low, because mica sheets are the barriers for radiation thermal conductivity (Fig. 2.104).

Calcium silicate materials have the finest structure; the thermal conductivity of calcium silicate is approximately 1.5 times lower than that of diatomaceous and vermiculite thermal insulation. The inner surface of calcium silicate materials is approximately 80 m²/g, and the particles have dimensions of 0.05–0.1 μm. Such a structure gives a very high thermal resistance of pores and intergrain contacts, which is the reason for the small conductivity of calcium silicates.

The constancy of thermal conductivity is guaranteed by the constancy in processing and raw materials. Control check tests of the thermal conductivity are strongly recommended when changing suppliers because the reference data on thermal conductivity may vary and change, depending on the raw materials used, processing, and the method of testing (Sect. 1.6).

2.7.5 Thermal Aging of Heat Insulation Materials at Service and Thermal Conductivity of Infiltrated Heat Insulation Materials

During service at elevated temperatures, there is a thermal process called thermal aging. Thermal aging of heat insulation materials takes place even in the absence of chemical reagents. At elevated temperatures and constant pressure, there is a partial sintering process at the contacts of grains, and these contacts become stronger, which increases the conductive constituent of thermal conductivity.

According to records of industrial research obtained in the course of dry autopsies [168, 170, 171, 201, 202], the increase in the thermal conductivity of diatomaceous materials in the absence of infiltration is 10–15% after 60–65 months, while the increase in the thermal conductivity of calcium silicate after the same period is 3–5%.

The increase in the thermal conductivity of heat insulation materials due to infiltration by electrolyte is significantly higher. Highly porous heat insulation materials cannot be resistant to the aggressive melts of fluoride salts. Over the course of conventional service of reduction cells, heat insulation materials are protected from infiltration by electrolyte by the barrier refractory layer. However, in reality, the electrolyte will infiltrate slowly through gaps between bricks and through large pores and holes in DBMs and possibly penetrate suddenly through cracks. According to data on dry autopsies [168, 170, 171, 201, 202], the infiltrated diatomaceous and vermiculite materials contain up to 15% cryolite, up to 29% sodium fluoride, and up to 6% calcium fluoride. The thermal conductivity of infiltrated heat insulation materials increases dramatically, giving values of 5–21 W/m · K, so the increase in thermal conductivity may be up to 25–70 times! Infiltrated heat insulation materials deform under compression much more easily, so their thickness may decrease by a factor of 2–4 (Fig. 2.106).

For producers of aluminum, this means that the heat flow through the bottom increases, and to prevent the occlusion of the bottom by sludge, producers should increase the voltage of cells, which may result in an increase in the temperature of electrolyte, the dissolution of side ledges, and power consumption losses (Fig. 2.107).

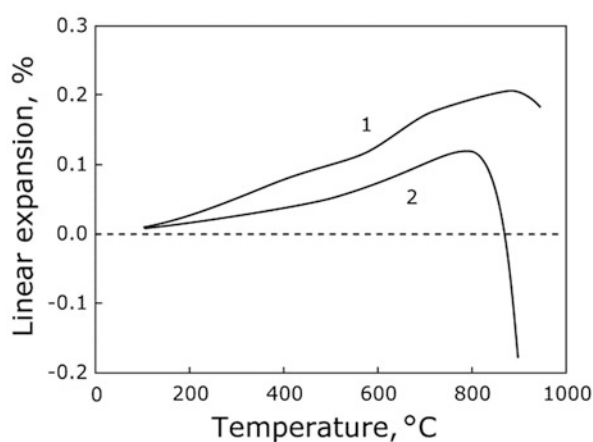
Safe Temperature of Service for Heat Insulation Materials in Reduction Cells

According to standards ASTM 155 [203] and ISO-2245 [204], heat insulation materials are divided into groups corresponding to certain classification temperatures. The classification temperature corresponds to a reheat change of 2%. The classification temperature represents a guideline for the use of heat insulation materials in the lining of reduction cells, but it does not correspond to the safe service temperature of a material.



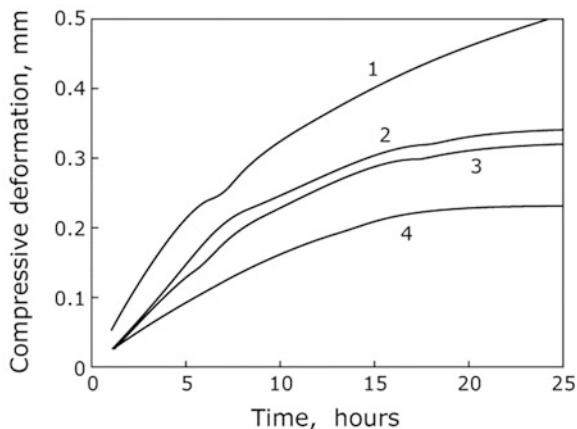
Fig. 2.106 Picture of dry autopsy: owing to pressure and the formation of a lens, the height of the heat insulation layer decreases

Fig. 2.107 Linear change at heating for diatomaceous materials from different deposits



Heat insulation materials may undergo some sintering and, as a consequence, additional shrinkage at temperatures close to the temperature limit of safe service and at constant pressure. Figure 2.87 contains the dilatation curves of two different diatomaceous heat insulation materials. The process of additional sintering starts in material 1 at 830–840 °C, so the service temperature for this material should not exceed 800 °C. This assumption is confirmed by creep testing at 900 °C (Fig. 2.108), where the time dependence for diatomaceous material never reaches the plateau within 24 h, and the reheat change (shrinkage) is more than 3%.

Fig. 2.108 Creep dependence of heat insulation materials at 900 °C: 1—diatomaceous material 1; 2—diatomaceous material 2; 3—vermiculite material 1; 4—calcium silicate material



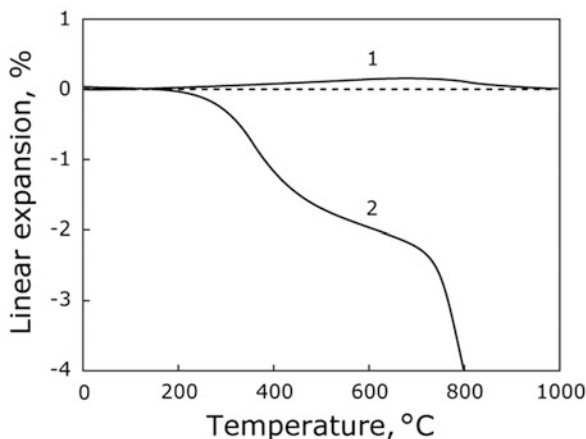
According to ISO 2245, unfired vermiculite heat insulation materials are in group 100. The dilatation curves of vermiculite materials show a large variety of behaviors at increasing temperature. It looks like materials 1, 2, and 3 were not blown up (expanded) up to certain degree, and at increasing temperatures, the materials further expand. This process cannot be considered desirable during preheating and startup in reduction cells. Also, the softening points of these materials are too low. The behavior of materials 4 and 5 fits the standards; however, the softening point of material 4 is approximately 50 °C lower than the softening point of material 5. According to the classification of ISO 2245 [204], both materials are in group 100, corresponding to a reheat change below 2%, when tested at 1000 °C.

The dilatation curves of calcium silicate materials serve only to illustrate that materials that look normal upon visual inspection may demonstrate a different behavior at heating.

In ASTM-155 [203], one recommendation is to use the material at least at a temperature 30 °C lower than the classification temperature. The best option is to have information on the softening point of the dilatation curve and the temperature load deformation behavior, because heat insulation material may demonstrate high shrinkage after the softening point (materials 1 and 3 in Fig. 2.103) and rather steep behavior (Fig. 1.19 in Sect. 1.4) (Fig. 2.108).

It should be noted that for short periods, heat insulation materials may sometimes withstand temperatures near the softening point without shrinkage [205]. Yet at preheating and startup of cells, when the carbonization process in the rammed parts has not finished and the cathode bottom might shift downward even 1 mm, that might be enough for the appearance of a thin gap between the carbon block and the rammed material through which electrolyte might start to penetrate into the refractory lining (Fig. 2.109).

Fig. 2.109 Linear change at heating for calcium silicate materials



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