— Light Metals —

SOME EXPERIMENTS IN CATHODE CARBON

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Abstract

A brief overview is given of the current status of cathode block production and the main characteristics involved. A special analysis of the problems associated with the utilization of graphite cathode blocks is made. In laboratory and industrial-scale investigations, answers were sought to questions related to the important quality features of cathode blocks, sodium resistance, the effect of non-carbonaceous additives, barrier materials and their application, as well as the appropriate operational measures to be taken.

Introduction

The term "experiment" was chosen specifically for the title of this paper to emphasize the practical aspect of lining electrolytic cells with cathode blocks. The fruitful combination of targeted experiments and operational experience has certainly improved cathode life over the last two decades. In the field of pot lining the experiment is deemed to be an essential part of progress.

Cathode blocks may be characterized by a long list of properties and other descriptive items as displayed in Table I. Only a limited number of these are normally disclosed in the data sheets drawn up by suppliers of cathode blocks. Several of the property values depend on the direction of measurement. With reference to the axis or position of the cathode blocks in the electrolytie cell, the vertical direction is believed to be of greater importance than the horizontal one, for instance, in respect to the Rapoport expansion and electrical resistivity.

On the client's side, however, potroom management looks at the performance criteria of cathode blocks

(see Table II) and is faced with the task of how to translate the relevant quality features of the various types of cathode blocks into favourable conditions of pot operation and optimal pot life. A few examples of how particular cathode block properties can be correlated with cathode durability factors in aluminium reduction cells are given in Table III.

In the following sections some experimentally established facts will be considered. These facts either have had or will have an impact on the development and utilisation of cathode blocks.

Table III. Correlation of Cathode Block Properties with Durability Factors in the Reduction Cells

Property	Practical Effect
Expansion in Rapoport test	• Change in cathode voltage drop • Early cathode bottom heaving • Early expansion pressure and pot shell deformation • Break-through of Al metal, dissolution of collector bar and premature pot failure
Thermal conductivity Thermal expansion Elastic modulus Flexural strength	• Resistance to cracking during cast-iron rodding • Resistance to cracking and spalling during preheating and start-up • Absorption of thermally and chemically induced stresses during start-up and initial pot operation
Electrical resistivity	• Initial cathode voltage drop
Thermal conductivity	• Heat transfer • Heat dissipation
Abradability Wettability, Adhesion Al-carbide formation	• Surface erosion • Ablation rate • Wear pattern

Table I: Characterization of Cathode Blocks

Group	Serial No.	Property	Measuring direction	T.D. 2)	Method of test	Determi-nation	Note
I Struct-ural	1	Real density	Indep.		Standardized	Common	Basic block characteristics
	2	Apparent density	Indep.		Standardized	Common	Basic block characteristics
	3	Total porosity	Indep.		Standardized	Common	Basic block characteristics
	4	Open porosity	Indep.		Standardized	Common	Impregnable pore volume
	5	Pore size distribution	Indep.		Available	Rare	Mainly of scientific interest
	6	Permeability	II & ⊥ 1)		Standardized	Rare	Rarely in data sheets
II Mecha-nical	7	Modulus of elasticity	II & ⊥	X 2)	Standardized	Common	Dynamic or static
	8	Tensile strength	II & ⊥	X	Standardized	Rare	Very rare in data sheets
	9	Flexural strength	II & ⊥	X	Standardized	Common	Main measurement of strength
	10	Compressive strength	II & ⊥	X	Standardized	Common	
	11	Splitting strength	II & ⊥		Special	Very rare	Related to tensile strength
	12	Abrasiveness	II & ⊥		Various	Rare	Not found in data sheets
III Purely physical	13	Electrical resistivity	II & ⊥	XX	Standardized	Common	
	14	Thermal conductivity	II & ⊥	XX	Various	common	Normally less precise
	15	Coeff. thermal expansion	II & ⊥	XX	Various	Common	
IV Chemi-cal	16	Ash content	Indep.		Standardized	Common	
	17	Ash analysis	Indep.		Available	Rare	SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, K_2O, Na_2O, P_2O_5
	18	Sulphur	Indep.		Standardized	Common	Often missing in data sheets
	19	Nitrogen	Indep.		Available	Rare	Indication of heat treatment
	20	Hydrogen	Indep.		Standardized	Rare	Indication of heat treatment
V Techno-logical	21	Electrolytic expansion test (Rapoport test)	II & ⊥	X	Various	Quite common	Very significant quality factor
	22	Wettability, impregnation rate		X	Special	Very rare	Particular investigations
	23	Al-carbide formation	Indep.	X	Special	Very rare	Particular investigations
	24	Anisotropy	II & ⊥		Available	Very rare	Dependent on forming method
	25	Intactness	Control by visual inspection, non-destructive testing				
	26	Precision of machining	Contractually specified, receiving inspection and testing				
	27	Design factors	Contractual, given by customer				

1. II = Parallel to grain or forming plane or forming axis
⊥ = Perpendicular to grain or forming plane or for forming axis

2. X = Property dependent on temperature
XX = Should be measured as function of temperature
T.D. = Temperature Dependence

Sodium resistance

Aluminium deposition at the cathode takes place in the presence of a small but definite sodium vapour pressure. The latter rises with increasing current density and higher NaF/AlF_3 ratios in the electrolyte. The expansive effect of sodium on cathode carbon is generally measured in an electrolytic test, commonly known as the Rapoport test (first published by Rapoport and Samoilenko in 1957). This test is carried out worldwide, but under quite different experimental conditions. For this reason, the various testing results are not readily comparable on an absolute scale. It has to be mentioned that the Rapoport test also includes expansive reactions of sodium, aluminium or electrolyte with the impurities in the carbon material such as sulphur, nitrogen or ash. There is little doubt that the evaluation of the sodium sensitivity of cathode carbons by means of the Rapoport test has significantly enhanced cathode block quality and its longevity.
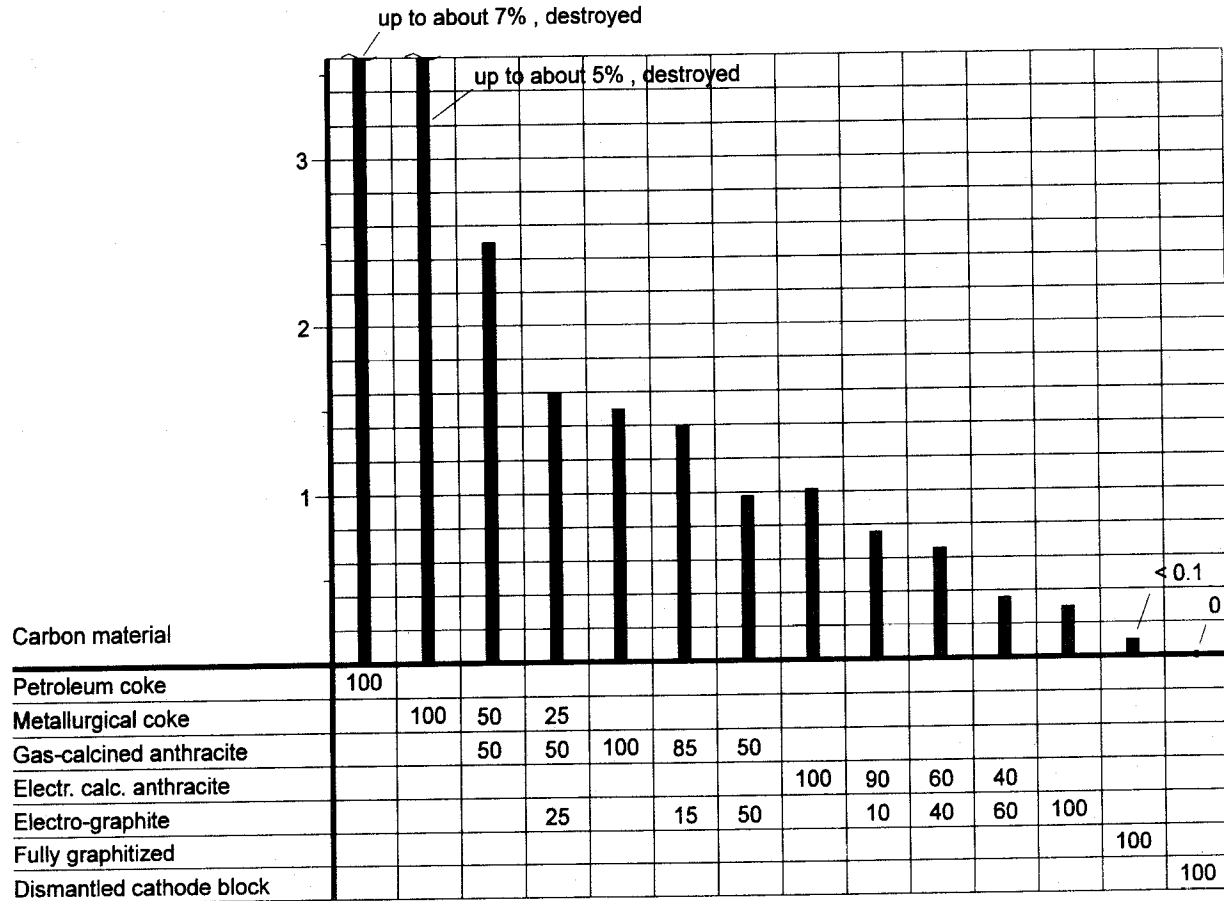
up to about 7% , destroyed

up to about 5% , destroyed

Carbon material														
Petroleum coke	100													
Metallurgical coke		100	50	25										
Gas-calcined anthracite			50	50	100	85	50							
Electr. calc. anthracite								100	90	60	40			
Electro-graphite				25		15	50		10	40	60	100		
Fully graphitized													100	
Dismantled cathode block														100

Figure 1   Developpement of cathode blocks with regard to the expansion in the Rapoport test

Table II.   Quality Assessment of Cathode Blocks by the Smelters

1	Appearance, visual defects, intactness
2	Dimensional tolerances, perfection of machining (comparison with specification)
3	Behaviour during cast-iron rodding
4	Behaviour during pre-heating and start-up
5	Initial cathodic voltage drop and change (normally increase) in voltage drop with operating time
6	Cathode bottom heaving
7	Horizontal expansion: expansion pressure, pot shell deformation
8	Surface erosion: wear rate and erosion pattern
9	Increase in heat losses, decrease in insulating capacity, change in heat balance
10	Pick-up of iron and silicon into the aluminium metal pad
11	Penetration of sodium, electrolyte constituents or aluminium into the refractory insulation
12	Pot life

The clear trend towards lower cathode block expansion is outlined in the chart depicted in Figure 1. The expansion values presented are based on our own measurements.

Sodium resistance, i.e. sodium-induced expansion, is simply a function of heat treatment. A baked carbon product which is made of calcined petroleum coke has the highest expansion and is severely cracked or even disintegrated in the Rapoport test. If this particular product is fully graphitized, its specific expansion drops below 0.1 %. The diagram in Figure 2 shows the variation of Rapoport expansion of a petroleum coke-based artefact. Its electrical resistivity takes a diverging course as a function of heat treatment temperature.

Each of the carbon materials listed in the chart in Figure 1 covers, as is well-known, a wide spectrum of grades. The quality variety of ECA depends, for instance, on the source of the green anthracite as well as on the degree and uniformity of electrical calcination.

Carbon expansion generated by sodium infiltration is not like thermal expansion. It can be greatly suppressed by counter-forces. Another important phenomenon is that sodium penetrates fairly quickly through highly dense carbon and graphite materials because it migrates through the crystal lattice. Its diffusion rate at about 980 °C is relatively high in graphite, namely in the order of 10 - 20 mm/h. Sodium also diffuses easily into sintered, completely gas-tight alumina as demonstrated by the photograph in Figure 3. The corundum tube is heavily deformed by sodium as it appears at the cathode. Pore-free silica-alumina refractories do not represent an impervious barrier to the solid-state diffusion of sodium either. Its diffusion front is sharply slowed down by temperatures below about 750 °C. Na-Al-silicates are formed and the original phase structure is altered along the path of sodium through the fire-clay bricks.
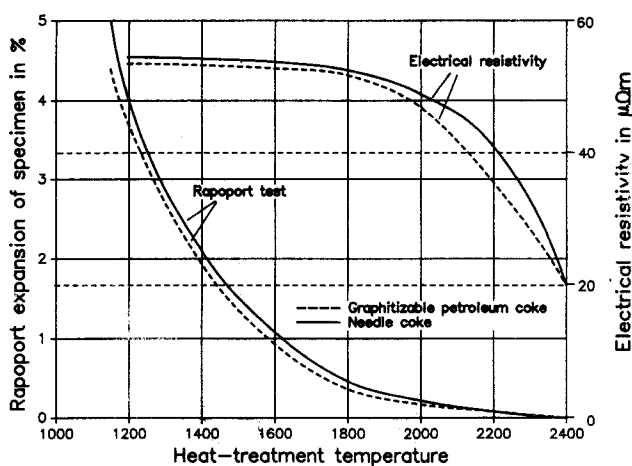
Figure 2   Rapoport expansion and electrical resistivity of a petroleum-coke-based artefact as a function of heat-treatment temperature
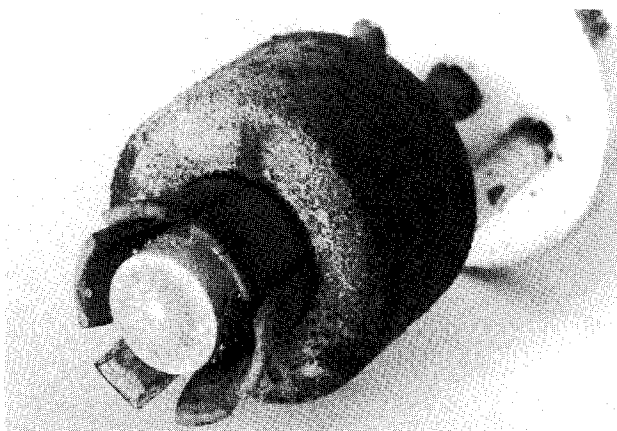
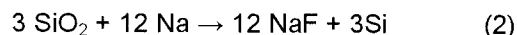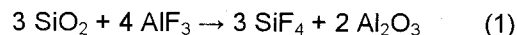Figure 3   Deformation of a sintered alumina tube by the impact of sodium

Additives

Additives to baked cathode blocks may be taken into consideration to overcome some deficiencies such as

- the sodium sensitivity of the bond structure arising from the carbonized pitch,

- aluminium carbide formation and chemical erosion,

- wear by mechanical abrasion on the top surface,

- too high a permeability for the electrolyte species.

Some ideas were derived from our work on carbon lining blocks for blast furnaces. We added silicon powder to the filler material. During the baking process to the appropriate temperature levels the admixed silicon is primarily converted to ß-SiC. It was found that sodium resistance was greatly improved and permeability substantially reduced by a factor of 10-100. The latter effect is presumably caused by partial oxidation and some nitridation of silicon to silica or silicon oxynitride.

The addition of silicon to the cathode blocks resulted in the Rapoport expansion curves as plotted in Figure 4. It can be seen that, at the beginning, the Si-doped cathode block sample exhibited a similar Na-induced expansion to the undoped sample. In the extended Rapoport test, expansion of the partially SiC-bonded artefacts exceeded those without silicon. The higher long-term expansion is probably due to reactions with liquid cryolite and aluminium which penetrated into the open pore system of the doped carbon material. It could be proven by X-ray diffraction that substantial amounts of the admixed silicon were oxidized to SiO_2. It is very likely that the following reactions were triggered by the finely dispersed silica:

$$3\ SiO_2 + 4\ AlF_3 \rightarrow 3\ SiF_4 + 2\ Al_2O_3 \qquad (1)$$
$$3\ SiO_2 + 12\ Na \rightarrow 12\ NaF + 3Si \qquad (2)$$
$$3\ Si + 3\ C \rightarrow 3\ SiC \qquad (3)$$

Tests were also made with ferrosilicon 75 (75 % Si), 45 (45 % Si) and 25 (25 % Si). It was observed that only that part of silicon which is in excess of the intermetallic compound Fe_3Si was converted to ß-SiC. A look at the thermodynamics revealed that the free energy of formation of Fe_3Si was indeed higher than that for ß-SiC. Fe_3C could be detected too. The graphs in Figures 5, 6 and 7 imply that the additions of FeSi 75, FeSi 45 and FeSi 25 could not ameliorate cathode block quality for the reasons given above. Unfortunately, our plant trial with Si-doped cathode blocks could not be completely evaluated because the potline was closed down.
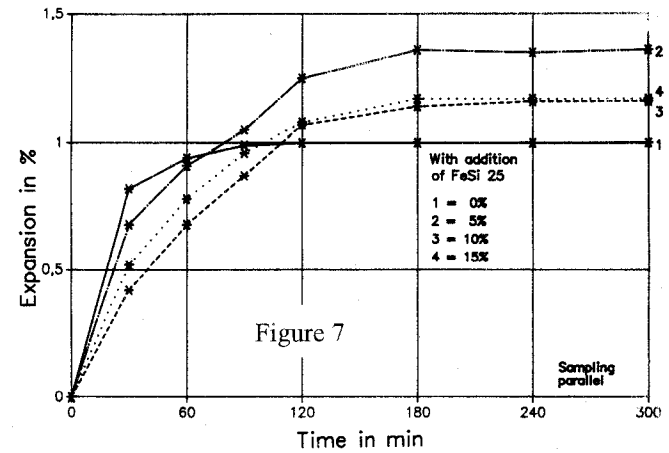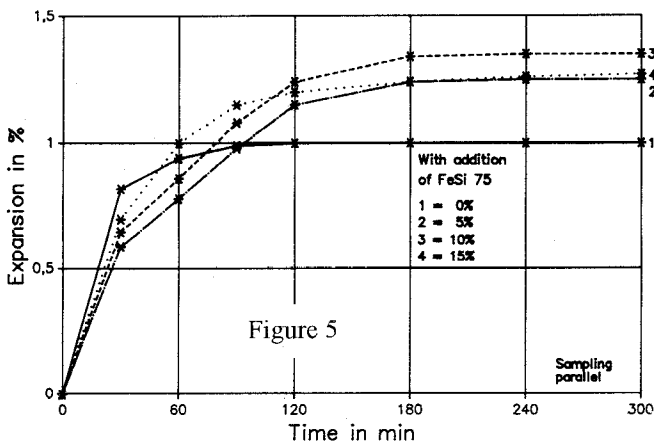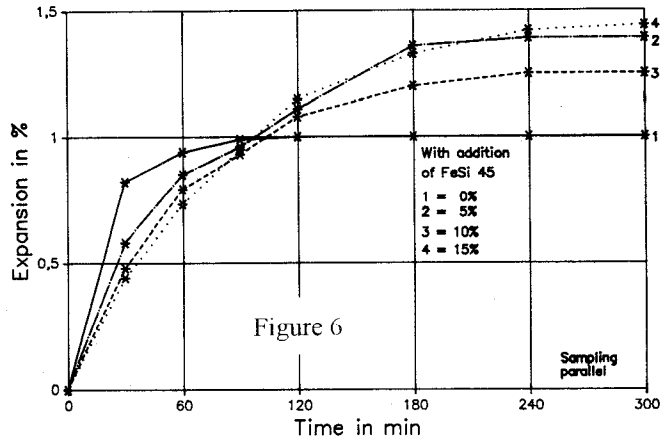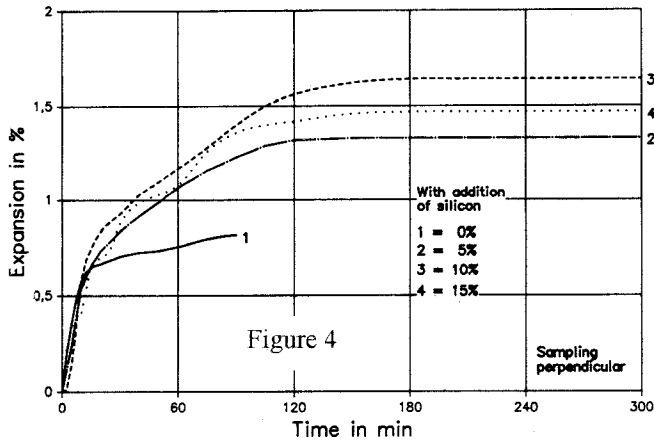
Figures 4 to 7   Rapoport expansion of bench-scale cathode blocks with addition of silicon (Fig. 4), FeSi 75 (Fig. 5), FeSi 45 (Fig. 6), and FeSi 25 (Fig. 7)

Titanium sponge was another candidate powder to be added and subsequently converted to its carbide during the baking process. Since TiC is a good electrical conductor, its presence in the cathode block matrix diminished the electrical resistivity, but it is attacked and decomposed by aluminium. Cathode blocks which are subjected to graphitization can be doped with titanium oxide (TiO_2) since this is easily reduced to TiC at graphitization temperatures. Apart from its hardness and the problem of cathode block machining, we could not state that TiO_2-doped blocks had an advantage over undoped and graphitized test bodies. The reduction of ZrO_2 to ZrC turned out to be more difficult. When the abundant zircon mineral $ZrSiO_4$ was added to cathode carbon test bodies, a nice mixture of ZrC and SiC crystals was obtained in the matrix after graphitization. The embedded carbide crystals are believed to improve the abrasion resistance of graphite cathode blocks but they may represent a severe problem with respect to machinability. Other commercially available, brittle and grindable alloys are Cr-Si, Fe-Cr-Si and Fe-Zr-Si.

Such metallic powders were also tried as additives. The Rapoport expansion curves did not indicate any improvement.

From our experiments with blast furnace blocks, we also learned that the dissolution of carbon in pig iron can be stopped by the addition of a refractory oxide like alumina. The loss of carbon in aluminium takes place via the formation of aluminium carbide, Al_4C_3. To restrict or minimize the reaction between aluminium and carbon, especially graphite, we selected zirconia in the form of the purified, natural mineral baddeleyite as a prospective additive. Other reasons for choosing ZrO_2 were: thermodynamically, it is hardly reduced by aluminium and it has a very low solubility in cryolite melts. As shown in Figure 8, zirconia has a beneficial effect on cathode expansion. With a proportion of up to 10 % ZrO_2 in the dry aggregate, the electrical resistivity of the cathode block remains almost unaffected.
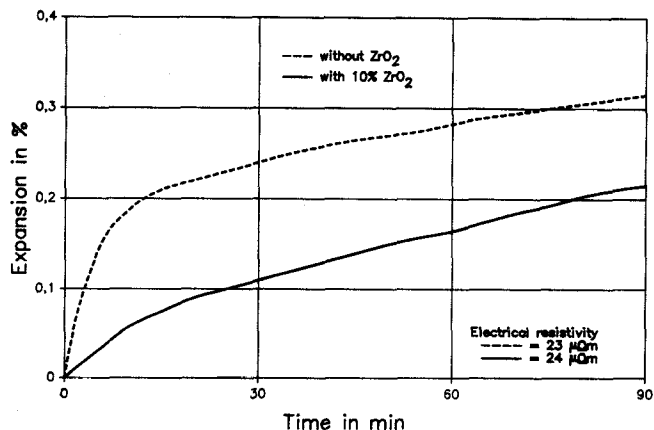
Figure 8   Rapoport expansion of a bench-scale
cathode block with the addition
of 10 % ZrO₂

Graphite cathode block

The essential properties of graphite cathode blocks can best be understood in comparison to the more conventional, baked cathode block types which contain ECA and electro-graphite as filler materials (see Table IV).

Table IV.   Basic Types of Currently Applied Cathode Blocks and their Characteristic Data

Group	Basis of the carbon raw materials	Resist-ivity $\mu\Omega m$	Rapoport Test Expansion %	Thermal conduc-tivity W/mK
I	100 % of electrically calcined anthracite (ECA)	45 - 55	0.9 - 1.1	6 - 7
II	ECA with additions of electro-graphite up to approx. 50 %	25 - 40	0.3 - 0.8	8 - 20
III	85 - 100 % of electro-graphite (Designations: semi-graphite, graphitic, partially graphitized	16 - 20	0.2 - 0.3	24 - 36
IV	Fully graphitized up to 2500 °C (Raw materials: graphitizable petroleum coke, pitch coke,	10 - 13	≤ 0.1	100 -120

The discussion whether to use graphite cathode blocks or not started in the sixties. At that time we applied a primitive cup test (see Figure 9) to demonstrate the excellent sodium resistance of graphite. In the seventies and eighties there were still strong arguments against the use of graphite cathode blocks. The main reasons are given in Table V. In the nineties, i.e. at present, the argumentation has changed in favour of graphite (see Table VI). At a symposium in 1987 the author made the following comment on graphite blocks: "Pure graphite blocks may offer advantages for high amperage cells but the technology around their installation has to be improved to make them profitable". It is hoped that this quotation is no longer valid.
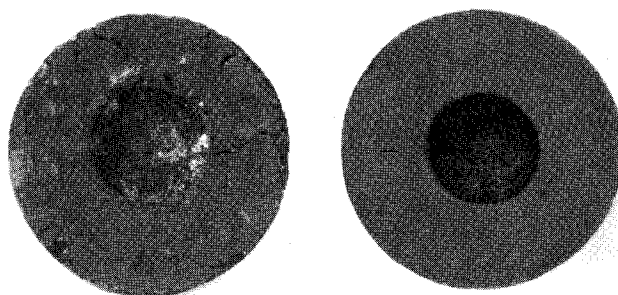

ECA   Graphite

Figure 9   Early cup test for examining sodium resistance (Reaction mixture in the bore hole: NaF + Al)

Table V.   Status of Graphite Cathode Blocks in the Seventies and Eighties

- Trouble with high abrasion rate and formation of "potholes"
- Only slight advantage in energy saving and cell voltage
- Saving of energy does not offset higher cathode block price
- No clear opinion on the prolongation of cathode life

In Table VI a dozen favourable and unfavourable features of graphite blocks have been collated. Long ago a few experiments were performed to shed light on the particular behaviour of graphite with regard to abrasion resistance, sodium diffusion and aluminium carbide formation (see Table VII).

The crucial properties of graphite blocks require modified and suitably adjusted measures to be taken during lining and operation. Some possible measures are listed in Table VIII in connection with the topics abrasion resistance, thermal conductivity and sodium penetration. The fundamental issues surrounding graphite cathodes still await satisfactory solutions.

Table VI.   Favourable and Unfavourable Features of Graphite Cathode Blocks

Favourable features	Unfavourable feature
• Unaffected by sodium infiltration, practically no expansion	• Insufficient resistance to mechanical abrasion
• Low electrical resistivity	• Undesirably high thermal conductivity
• Relatively low modulus of elasticity	• Problems with thermal back insulation
• Low coefficient of thermal expansion	• Comparatively high porosity (6 - 10 % higher)
• Relatively high resistance to thermal shock	• Fast sodium permeation
• Low ash content, therefore no reactions with ash constituents	• Strong propensity to formation of aluminium carbide
• No nitrogen, therefore no formation of sodium cyanide	• Relatively low wettability by cryolite and aluminium
• Very low sulphur content, therefore negligible formation of sodium sulphate	• Weak or poor bond to ramming paste
• No or only slight increase in cathode voltage drop	• Sensitivity of spalling during start-up
• Almost no adverse effects at high current densities	• Displacement of current flow to the sides
• Highly uniform cathode bottom temperature, i.e. excellent temperature equalization	• Unduly high heat flux to the pot shell side walls with risk of deformation
• Relieving heat dissipation under high current load	• Quite expensive, high lining costs

Table VII.   Orientation Tests to Compare Particular Properties of Carbon Materials

Property	Type of Carbon	Unit	Value
Relative abrasion resistance (special test)	Gas-calc. anthracite Electr. calc. anthracite Semigraphite Impregnated graphite Standard graphite	wear in mm in 5 min	0.15 0.27 13 30 48
Relative sodium absorption	Metallurgical coke Petroleum coke Gas-calc. anthracite Electro-graphite	Na content in %	6.4 3.4 2.9 0.3
Rel. penetration rate	Gas-calc. anthracite 100 % graphite	% Na in Pb	1.7 4.3
Rel. diffusion rate	100 % graphite	mm/h	10-20
Relative propensity to Al carbide formation	Metallurgical coke Gas-calc. anthracite Petroleum coke 100 % graphite	%	37 43 90 100
Relative wettability	Gas-calc. anthracite 100 % graphite		high low

Barriers

From high-temperature laboratory experiments we learned that sodium as well as liquid fluorides and chlorides of sodium and aluminium diffuse through gas-tight ceramics based on sintered alumina and alumina silicates. Silicates and also the dense, low-softening magma, consisting of silicates and cryolite-melt constituents, are oxygen-ion conductors at elevated temperatures. Hence, sodium and oxygen can meet and interact inside the gas-tight magma. Temperature is the limiting parameter of such reactions.

Barriers in the form of coatings or thick layers may be provided along the top or bottom face of the cathode blocks. On the top face, one has to primarily deal with the quadruple attack of aluminium and sodium in their metallic state and in the form of their fluorides. On the bottom face, the corrosive impact is eased by the fact that the aggressive dissolution capability of liquid aluminium is missing and that the corrosion rate may be slightly diminished by a somewhat lower temperature. Thus, it seems to be more meaningful to concentrate the necessary effort on the bottom face of the cathode blocks.

In various tests we found that, if exotic materials are excluded, cast iron and silicon metal are the most suitable barrier materials. There are, however, specific prerequisites to be met before the system works successfully.

The cast iron must be in very tight contact with the graphite cathode block. Any access given to an oxidizing gas, such as air or carbon dioxide, into the interface must be prevented, otherwise corrosion occurs. Cast iron is impermeable to sodium vapour as well as to aluminium fluoride. Detrimental swelling

reactions are also not observed as long as a highly reducing atmosphere is maintained. Besides, it is advisable to protect the external surface of the cast iron layer against oxidation.

If the cast iron cover, which is closely attached to the bottom of the cathode blocks, fulfills its function as a corrosion-resistant and tight barrier, one may return to an effective bottom insulation with bulk alumina compacted by vibration. The thermal conductivities of the insulating materials are drastically changed by an intense infiltration of the electrolyte melt. This change is moderate for chamotte bricks, namely from initially 1-1.2 W/mK up to about 3 W/mK, i.e. an increase by the factor of approximately 3. For bulk alumina, the rise in thermal conductivity is dramatic. It may move upward from about 0.3 W/mK to soaring values of 5-6 W/mK. It is therefore an absolute necessity that the alumina pad is shielded against bath impregnation. The combination of graphite cathode blocks with a protected alumina bottom insulation would alleviate the handling and treatment of spent potlining enormously. Both could be passed through the autogenous mill together with the bath material and recycled to the pots in well-balanced doses.

Silicon is, like cast iron, inert to sodium because binary alloys are practically non-existent. Moreover, silicon does not react with NaF or AlF_3 to form SiF_4. It is solely the oxidized silicon metal, namely silica, which reacts vehemently with aluminium fluoride.

$$3\ SiO_2 + 4\ AlF_3 \rightarrow 3\ SiF_4 + 2\ Al_2O_3 \qquad (1)$$

This reaction is mainly driven by the formation of Al_2O_3. A reaction between SiO_2 and NaF is less likely because the bond energy between oxygen and sodium is far lower than between aluminium and oxygen. The SiO_2 skin on silicon is very thin. If SiO_2 is volatilized via the compound SiF_4, it will be replaced by a new coating where alumina and NaF prevail. Silicon can be cast into tiles which can be placed underneath the cathode blocks.

Conclusions

Over the last four decades, hundreds of useful experiments have formed the solid base for fostering a successful cathode block development. Recent years have been characterized by an increasing application of electro-graphite which has ultimately led to a more intensified use of fully graphitized products. Nevertheless, the utilisation of graphite cathode blocks in electrolytic reduction cells cannot yet be considered a perfect achievement. The definite advantages of graphite cathode blocks are offset by a few drawbacks. The pros and cons of graphite block properties have been outlined. Tests were made to identify graphite block deficiencies, and measures were devised to overcome these problems.