LABORATORY TESTING OF CARBON CATHODE MATERIALS AT OPERATIONAL TEMPERATURES

Morten Sørlie[1] and Harald A. Øye [2]

[1] Elkem Carbon R&D
N-4602 KRISTIANSAND S, Norway.
[2] Institute of Inorganic Chemistry
Norwegian Institute of Technology
University of Trondheim
N-7034 TRONDHEIM, Norway

It is important to have a good understanding of materials properties of cathode carbon under actual preheating, start-up and electrolysis conditions. Towards this goal we have adapted, improved or developed the following test methods at elevated temperatures which we consider important as design tools as well as quality control of the materials. 1) Expansion due to sodium penetration. 2) Rate of sodium penetration. 3) Chemical resistance towards sodium. 4) Abrasion resistance during electrolysis. 5) Thermal expansion/contraction. 6) Thermal conductivity.

The relevance of different test methods as part of a smelter quality assurance system is discussed.

INTRODUCTION

The producers of carbon cathode materials (carbon blocks and ramming paste) characterize routinely their materials with respect to room temperature properties. The following room temperature properties are usually given: Density (real and apparent), Porosity (total and apparent), Cold crushing strength, Flexural strength, Spesific electric resistance, Thermal conductivity 20°C, Coefficient of thermal expansion (20-200°C). These properties are useful quality criteria, but do not characterize the materials behaviour during start-up and operation and their resistance towards chemical and physical forces during a possible cell-life of up to 10 years.

In order to obtain a better description of the actual behaviour of the carbon materials in the cell environment we have adapted, improved or developed a series of test methods. The application of these methods has also borne out that materials that are nominally the same and have room temperature properties within spesifications may behave radically different in the physical/chemical environment of the cell. Regular and realistic testing of the applied carbon materials by the aluminium producers is hence an important part of a quality assurance system. The properties we wished to describe, are the action of metallic sodium, abrasive forces, thermal expansion/contraction and thermal conductivity.

EXPANSION DUE TO SODIUM PENETRATION

Sodium is formed by the reaction

$$Al(l) + 3NaF(\text{in cryolite}) = 3Na(\text{in C}) + AlF_3 (\text{in cryolite})$$
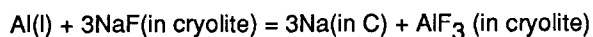
which then leads to expansion of the intercalated carbon material. This expansion has been measured by the socalled Rapoport method [1], but by discussions with different laboratories it became clear that the classical Rapoport test does not function well, and therefore is not often used. In order to avoid some of the problems inherent in the Rapoport test, we chose to monitor the expansion in an open system under argon atmosphere, using a transducer/ pushrod system as our expansion measuring device. Using this technique we were able to show the effect of cryolite ratio, extrusion direction and choice of cathode material on expansion during electrolysis.

A schematic diagram of the apparatus is shown in Figure 1 [2]. The cathode is a vertical cylinder of carbon material, with a hole through its centre parallel to the long axis. A boron nitride rod, slighty thinner than the diameter of the hole and attached to the centre of a boron nitride disk, is then inserted into the cylindrical cathode making the bottom face of the cathode rest on the boron nitride disk. Surrounding the boron nitride rod and resting on the upper surface of the cathode is a hollow stainless steel tube. This tube becomes an extension of the cylindrical cathode and conducts current from the power supply to the cathode. The upper part of the tube supports the position metering probe, which acts as a pushrod and measures the difference between the height of the upper edge of the tube and the upper surface of the boron nitride rod. This difference gives the expansion or contraction of the cathode. The probe is, through an A/D converter, connected to a computer for data aquisition and handling.

The electrolysis configuration is, in effect, perpendicular to the usual industrial configuration because electrolysis occurs on the cylindrical surface of the cathode and the inside surface of the crucible-anode walls.

A cryolite ratio (CR = mole NaF/mole AlF3) of 4 (basic) was used for most of our experiments, mainly in order to better differentiate between various carbons. Other cryolite ratios (basic, neutral and acidic) were also used to measure the effect of cryolite ratio on the cathodic expansion.

The reproducibility of the test is good, considering the inhomogeneity in the carbon materials. Figure 2 shows a deviation less than 10 % of the expansion for an amorphous carbon.
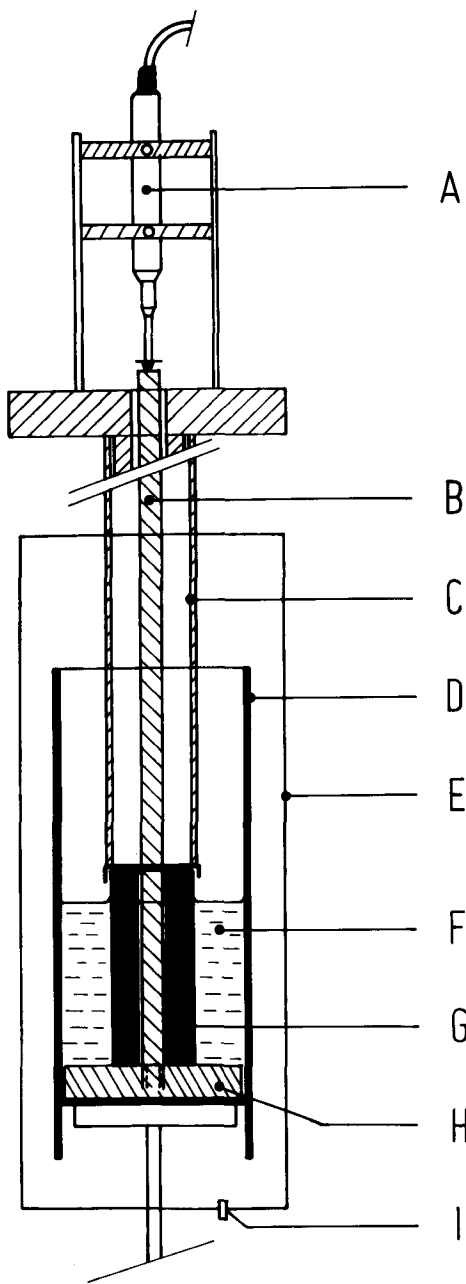
Figure 1. Apparatus for a modified Rapoport test.
A: Transducer; B: Boron nitride rod; C: Inconel steel cathode extension; D: Graphite crucible (anode); E: Furnace; F: Cryolite melt; G: Test specimen (cathode); H: Boron nitride disk; I: Gas inlet.

RATE OF SODIUM PENETRATION

The experimental set-up for determination of the rate of sodium penetration has been reported earlier [3]. The carbon specimens were about 70 mm long and machined to a diameter of 25 mm. Similar to the sodium expansion test, the carbon specimen served as the cathode but was rotated at 200 rpm during the electrolysis with only 2 mm of the cylinder submerged in the electrolyte (Figure 3). This gave satisfactory stirring of the electrolyte. The rate of
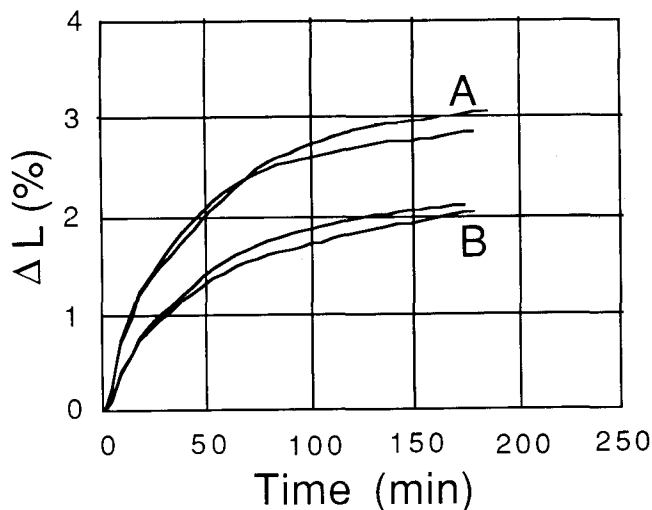

Figure 2. Sodium expansion of two amorphous carbon materials during aluminium electrolysis showing the reproducibility of the test.

sodium and bath penetration into the cathode is a function of current density, CR and time of electrolysis. Due to the rapid sodium migration most experiments are performed at short electrolysis time ($\leq$ 4 hours). All experiments are performed at 1000°C.

After removal of excess electrolyte or cathodic deposits from the cathode surface, the specimen was cut into disks, ranging in thickness from 3 to 5 mm. One surface of each disk was then analyzed for Na, Al and F by means of X-ray fluorescence spectroscopy.

A quick method for penetration studies is to cut this laboratory cathode along its long axis and measure the penetration depth of sodium metal by pressing the exposed surface against a paper wetted with phenolphtalein acid/base indicator [4]. It proved to be a quite accurate way of determining the diffusion depth of Na-metal (at a cut-off concentration) into anthracitic materials. Remeasurements by means of X-ray fluorescence techniques of the same carbon materials gave nearly identical curves at a cut-off concentration of 3 weight% Na.

Table 1. Time calculated for sodium (3 weight% cut-off concentration) to penetrate 30 cm deep into a carbon block at 1000°C (reversed polarity apparatus).

CD	CR	Time (days)					
(A/cm²)		M-I	M-II	M-IV	M-V	B-III	B-VIII
0.15	1.5	67	67		47		>200
	4	26	12	20	35	27	109
0.50	4		6				

Table 1 gives some results and illustrates the rate of sodium penetration dependent on the carbon materials, cryolite ratio and current density (CD).

CHEMICAL RESISTANCE TOWARDS SODIUM

The reactor for testing the sodium resistance of baked carbon specimens consists of the stainless steel vessel shown in Figure 4. A lid (A) fits a container (B), with a gold gasket (C) in between. The lid is secured to the container with screws. The container has room for four specimens (D). A stainless steel spacer (E) separates the samples from a pool of liquid sodium metal.

A manometer is placed at the top of the vessel, which is outside the hot zone of the furnace. Both the pressure in the vessel and the temperature can be controlled and measured.

Test specimens and sodium metal are transferred to the steel vessel in an argon atmosphere drybox, where the levels of O_2 and H_2O were kept below 5 ppm. The closed vessel is placed in a vertical Marshall furnace and the

Figure 4. Apparatus for the sodium vapour test.
A: Lid; B: Container, C: Gold gasket; D: Carbon specimen; E: Sample holder; F: Sodium metal (liquid); G: Furnace; H: To manometer.

vessel evacuated to 100 Torr. The temperature is over a period of 1.5 hours increased to 800°C, making the pressure increase from 100 to 500 Torr. The samples are kept at 800°C for 4-4.5 hours before they are allowed to cool overnight. The pressure has then decreased to its initial value, 100 Torr.

Figure 5 pictures the result of a vapour resistance test for two different materials tested. Of the three specimens, the one to the left is a reference not exposed to sodium vapour, while the two others have been exposed as described above.
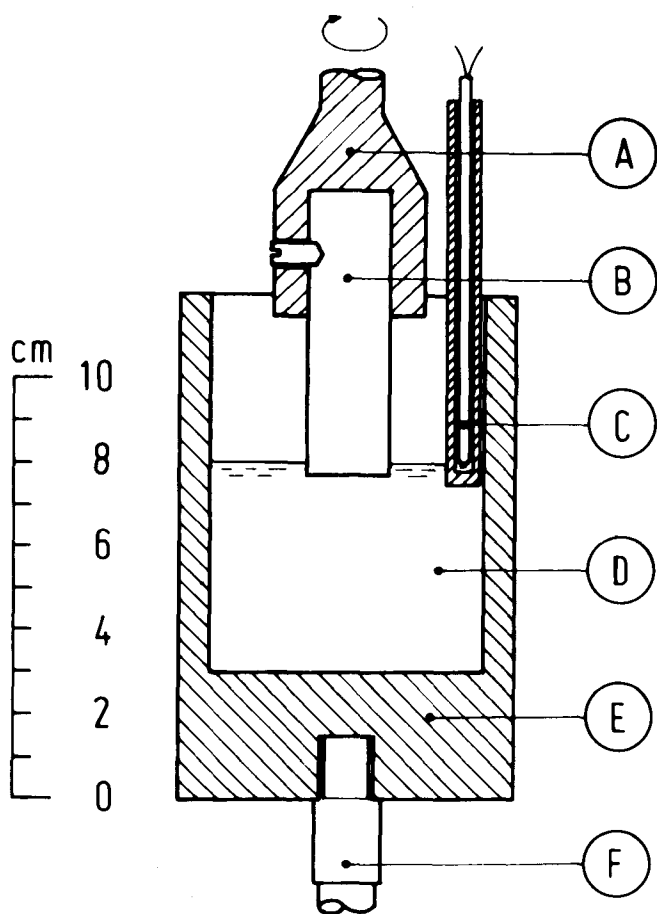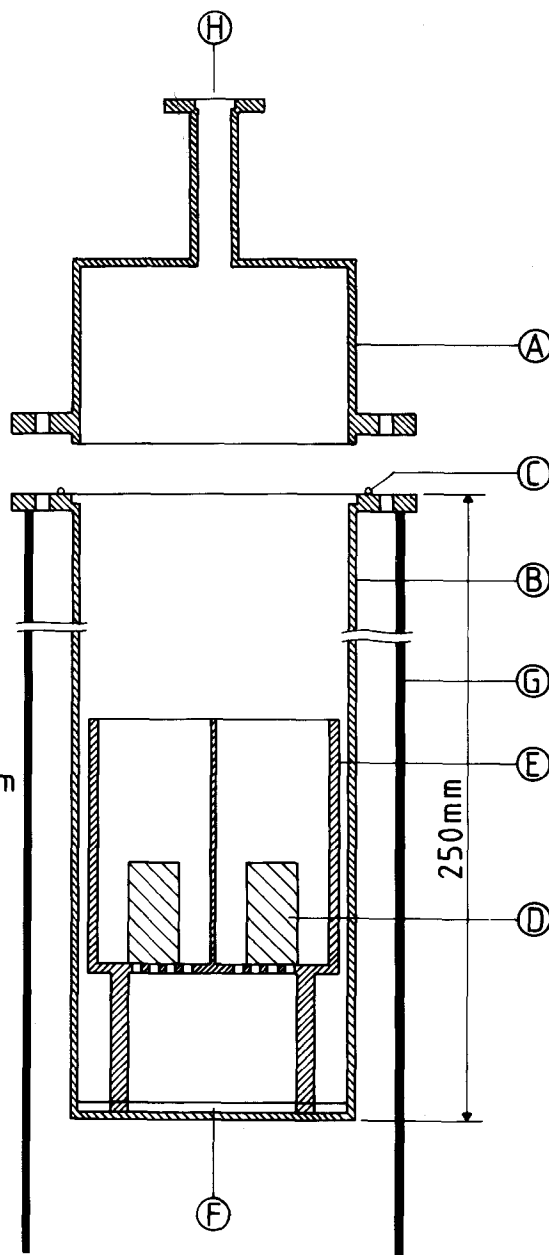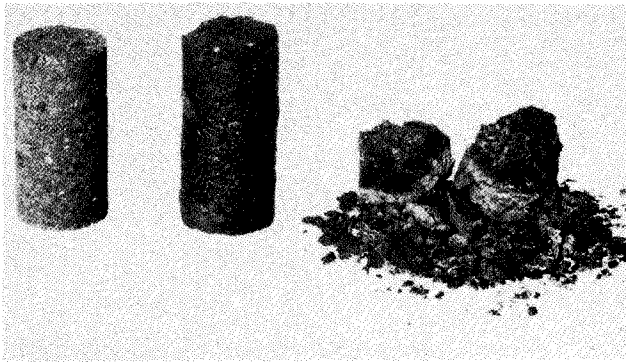

Figure 3. Reversed polarity apparatus for measuring rate of sodium and bath penetration.
A: Graphite supporter; B) Test specimen (cathode); C) Thermocouple; D) Cryolite melt; E) Graphite crucible (anode); F) Graphite supporter.

When unbaked samples are investigated, the diameter/height ratio is kept close to unity in order to minimize slumping in the plastic temperature range.

Figure 5. Two baked cathode carbon specimens exposed to sodium vapour (middle and right). The sample on the left is an unexposed reference.

ABRASION RESISTANCE DURING ELECTROLYSIS

It is of interest to evaluate cathode materials under electrolysis conditions being subject to a combination of chemical and physical forces. In order to simulate this the following set-up and procedure were arrived at [4].

A cylindrical sample (diameter 30 mm, height 20 mm with a 6 mm hole which was wider at the bottom) was mounted on a stainless steel rod connected to an electrical jig saw. The sample was immersed in a fluoride melt with suspended alumina (CR = 2.5, 5 mass% CaF_2, 30 mass% Al_2O_3) at 1020°C under inert atmosphere. The sample was oscillated with frequency 16 Hz and amplitude 26 mm for 3 x 1 hour. During the middle period an electrolysis with current density 0.3 A/cm^2 was also performed. The alternate oscillation and oscillation with electrolysis was necessary in order to better distinguish between the materials. Oscillation alone had little effect and continuous electrolysis led to the deposit of a protective carbide coating [5]. The samples were photographed afterwards and classified from the wear of the lower edge. Figure 7 shows a sample before and after the test.

Significant differences in wear resistance are observed, but the differences are less than obtained with dry SiC-abrasion at room temperature. Contradictive to the dry abrasion tests, where erosion on graphite is found to be 15-40 times faster than for anthracitic materials, no uniform correlation between the degree of graphitization and abrasion is observed from our simulated *in situ* measurements. The results did, however, correlate with industrial studies of the same materials.

THERMAL EXPANSION/CONTRACTION

Thermal expansion/contraction of baked carbon specimens, ramming paste, refractories and insulation materials were determined using the quartz glass dilatometer shown in Figure 8. The temperature control and programming system is versatile, but the standard heating rate is 3°C/min. from ambient temperature to about 1000°C. A transducer picks up the thermal movements of the sample and feeds the data into a computer.
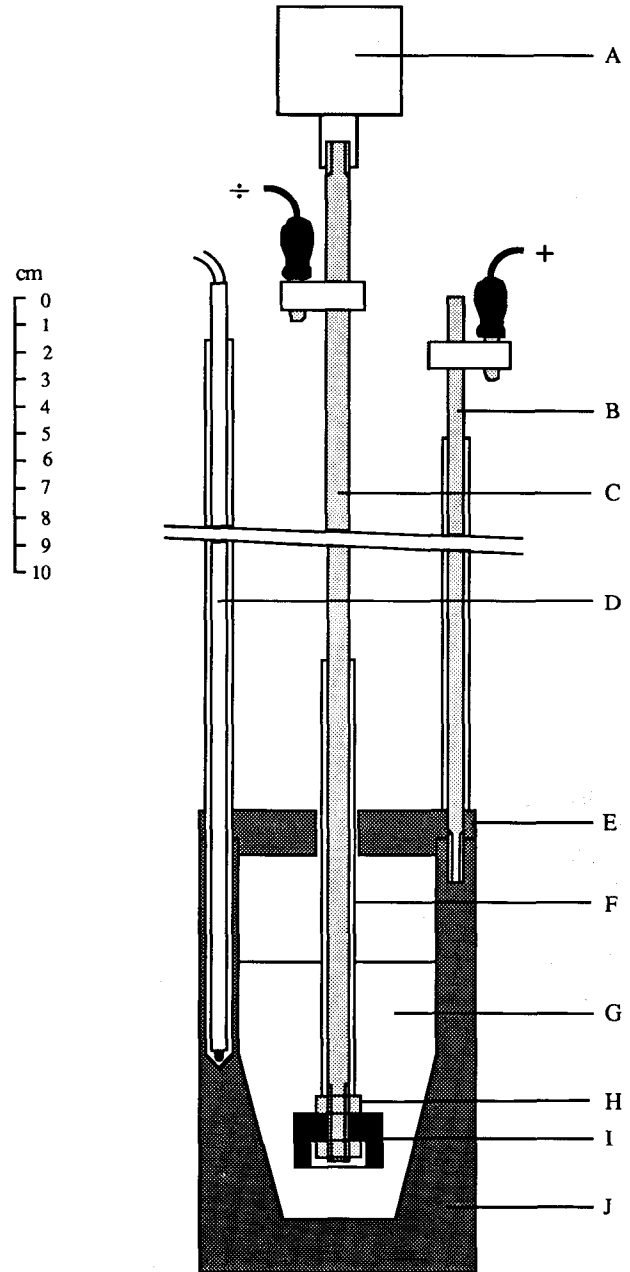

Figure 6. Apparatus for the abrasion test:
A: Electrical jig saw; B: Thermocouple (Pt/Pt10%Rh);
C: Rod of stainless steel (connection to the cathode);
D: Rod of stainless steel (connection to the anode);
E: Graphite lid; F: Alumina tube; G: Bath; H: Stainless steel nuts; I: Sample (cathode); J: Graphite crucible (anode).
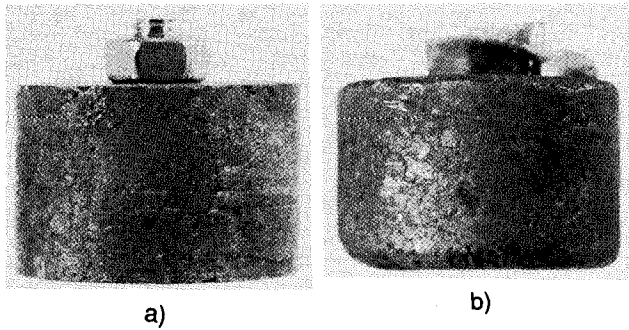
Figure 7. Abrasion test specimens.
a) Before test. b) After test.

THERMAL CONDUCTIVITY

Stationary methods for measurements of thermal conductivity at elevated temperatures are cumbersome and prone to errors. The standard transient hot wire technique is, however, not applicable for electrically conducting carbon materials. In order to overcome the difficulties we have developed a method using an electrically insulated strip [6].

A 25 μm iron foil as shown on Figure 9 was insulated on both sides with 25-30 μm natural mica foils and clamped between two carbon cylinders (diameter 50 mm) of the material to be studied. Typical dimensions of the foil were $2h = 40$ mm and $2d = 6$ mm. The assembly was placed in a furnace with inert atmosphere and equilibrated. A known constant current was passed through the foil and the temperature rise in the foil was monitored by measurement of the resistance between the two side leads. The current pulse lasted about 7 seconds and the current was high enough to give between 0.5 and 1 % rise of the resistance in the iron foil. *The resistance of the iron as function of temperature had been determined in earlier calibration experiments. The presence of the mica did not introduce errors in the measurements. The geometry of the foil was* optimized to avoid unwanted heat losses. Figure 10 shows some results for commercial cathode blocks and a baked Søderberg electrode paste.
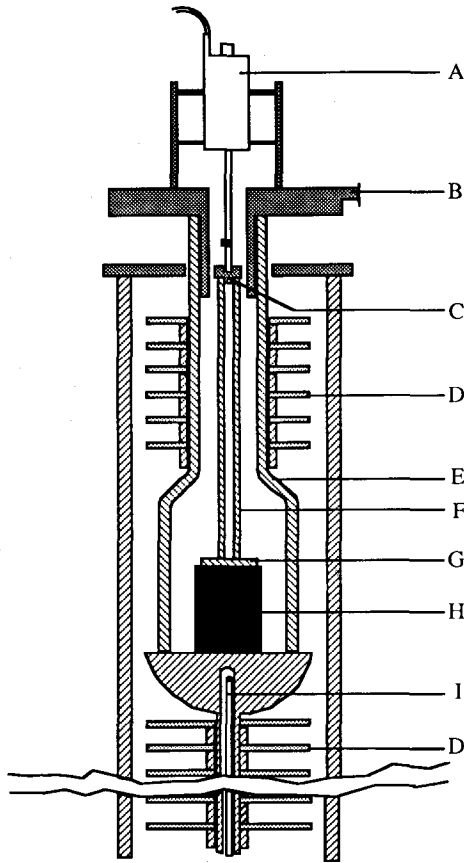

Figure 8. Experimental set-up for thermal dilation of cathode lining materials.
A: Transducer; B: Transducer support (brass); C: Quartz lid; D: Radiation shields; E: Transducer support (quartz); F: Inner quartz tube; G: Quartz plate; H: Specimen; I: Thermocouple.
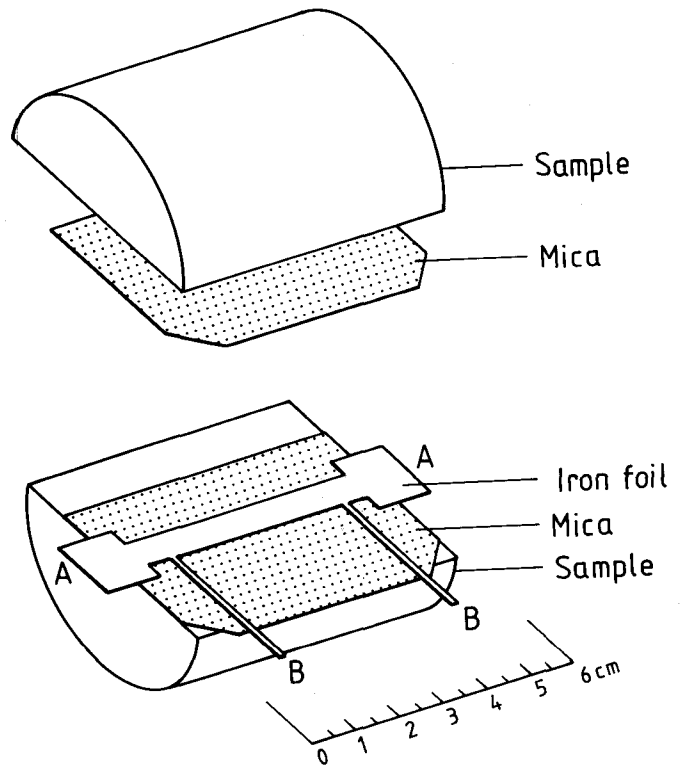

Figure 9. Experimental set-up for the hot strip thermal conductivity measurements.
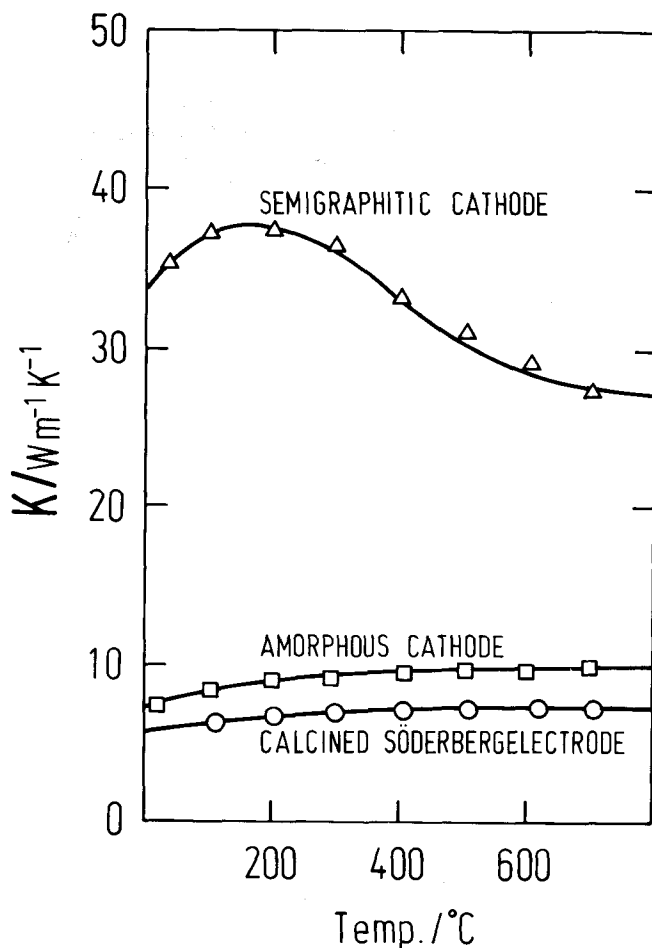
Figure 10. Thermal conductivity of some baked carbon materials obtained with the hot strip method.

QUALITY ASSURANCE SYSTEM FOR CARBON MATERIALS USED IN CATHODES

Proper lining design and workmanship during installation, as well as start-up and operation of an aluminium electrolysis cell are decisive for a satisfactory cell-life. If, however, inadvertently inferior or unsuitable materials are used, the best design and workmanship may still lead to early cell failure of the cell. When a proper design and operational procedure are arrived at, it is hence important to either keep the spesifications within given boundaries or know fully the consequences of changed materials properties. A common problem in smelters are also variations in properties of received materials with time even for nominally identical qualities. Such variations are often realized in after-time when early pot-failure start to appear. Large expenses can be saved if potential problems are spotted before the materials are utilized and in the following we will comment on what elements should be part of a smelter quality assurance system. The book by Sørlie and Øye [7] is referred to for test methods not discussed in detail here.

Dimensional tolerances should be checked regularly as part of a quality assurance system. This includes parallelity of faces, arching, twisting and details of the collector bar slot.

Mechanical faults. Blocks with visible mechanical faults (cracks) are usually screened out by the manufacturer, but a check by ultra-sound to detect hidden faults should be part of the users quality assurance system.

Apparent density can quickly be calculated by weighing the block and by measuring a few dimensional parameters. This method is not particularly accurate, but often good enough to monitor changes in aggregate materials formulation, or blocks that differ significantly from the average with respect to compaction.

Strength. Usually mechanical strength will be no problem with blocks, but some ramming pastes may be so mechanically weak after baking that they crumble by light handling. Although the baked ramming paste do not need to be mechanically strong, it is believed that very weak materials are inferior.

Young's modulus. High elasticity, *i.e.* a low value of Young's modulus is an important quality parameter. This value is, however, often strongly coupled to the strength.

Electrical resistivity is an important quality indicator and discrepancies from average values are signs of improper baking or unwanted materials.

Thermal conductivity is an important design parameter, and one should especially be aware of the different temperature variations for different materials (Figure 10) and that the thermal conductivity of amorphous bottom blocks increases during the first couple of years. It should, however, not be necessary for the user to measure it on a regular basis.

Oxidation resistance. CO_2 reactivity is not in itself a relevant property for cathode blocks. The test is, however, routinely carried out for anodes and it is easy to test some cathode samples as well. Increased reactivity may then be an indicator of inferior materials or improper baking (too low temperature). Low O_2 reactivity (airburn) is important for sidewall carbon.

Expansion due to sodium penetration is an important design parameter for heaving and expansion of bottom blocks during start-up. The test is, however, elaborate and not suitable for routine checking.

Chemical sodium resistance is suitable for routine checking and is not only a direct indicator of resistance to chemical attack, but low resistance will usually give increased expansion, heaving and spalling.

Thermal expansion/shrinkage. A lowest possible thermal expansion is an important quality parameter for bottom blocks. Shrinkage is usually not a problem for blocks if they are not underbaked, but shrinkage of ramming paste from 500 to 1000°C is a very critical parameter and should be checked by the user on a regular basis. Many early pot failures have been attributed to crack formation and aluminium penetration in the peripheral seam due to shrinkage.

Compaction tests of ramming paste give information of evenness in quality and the proper application temperature [8]. Penetrometer measurements of density of rammed seams should be used as a quality control of the actual ramming [9].

ACKNOWLEDGEMENT

REFERENCES

1. M.B. Rapoport and V.N. Samoilenko: "Deformation of Cathode Blocks in Aluminium Baths during Process of Electrolysis", *Tsvet Met.* **30 (2)** (1957) 44-51.

2. A. Støre, P. Lossius. P.A. Skjølsvik, W. Sørgård and H.A. Øye: "Sodium Expansion Testing of Cathode Materials for Aluminium Electrolysis." *Proc. Int. Conf. Carbon (Carbon '88)*, Newcastle upon Tyne, U K (1988) 531-533.

3. A. Støre, M. Ystenes and H.A. Øye. To be published.

4. C. Krohn, M. Sørlie and H.A. Øye: "Penetration of Sodium and Bath Constituents into Cathode Carbon Materials Used in Industrial Cells". *Light Metals* (1982) 311-324.

5. O. Herstad, C. Krohn and H.A. Øye: "Precipitation of Solid Compounds During Electrolysis of Cryolite-Alumina Melts." *Aluminium* **59** (1983) 200-206.

6. T. Log and H.A. Øye: "A Hot-Strip Method for Determination of Thermal Conductivity in Solid Carbon Materials at Elevated Temperatures". *Proc. 18th Bienn. Conf. Carbon,* Worchester, MA (1987), 521-522.

7. M. Sørlie and H.A. Øye: *"Cathodes in Aluminium Electrolysis"*. Aluminium Verlag 1989.

8. M. Sørlie and H.A. Øye: "Compaction of Room Temperature Ramming Paste." *Light Metals* (1987) 571-580.

9. M. Sørlie, B.M. Faaness, J.A.S. Belmonte, "Densification of Ramming Paste in Cathodes", *Light Metals* (1988) 269-275.