R&D Carbon

CATHODE LINING PRODUCTS

SAMPLING AND TEST METHODS

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Version: **5**

Date : **14.11.2019**

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1 Introduction

Test methods for measuring the properties on lining materials were prepared within the international standardization group ISO SC7 TC47 since 1990.

Continuous standardization works are still performed on both the sampling and the different testing methods. Standardization is of up most importance in order to compare test results between suppliers and users of lining materials. In this document, recommended sampling procedures are given together with a short description on the test methods.

2 Sampling

2.1 Standard Sampling: ISO 8007

Two standards describe the sampling of electrodes used in the production of aluminum as shown below.

Standard Number	Designation
ISO 8007-1: 1999	Cathode Blocks
ISO 8007-3: 2003	Sidewall Blocks

2.2 Frequency: ISO 5022

The amount of sampled cores depends on the number of blocks to be characterized and is statistically calculated in the method ISO 5022. The following table shows an example taken from ISO 5022.

Consignment or Lot	Recommended Amount of Tested Blocks
< 100 Blocks	3
101 to 300 Blocks	4
301 to 600 Blocks	5
> 600 Blocks	6

2.3 Tools for the Sampling

Proper sampling with tight tolerances is the base for correct testing results. Therefore high attention is to be given to adequate selection of sampling equipment and to their correct use.

The drilling and cutting devices consist of drilling bits and cutting edges preferably coated with diamond or other extremely hard material. An appropriate drilling equipment is given in the figure below.

Figure 1: Example of a Core Drilling Machine (RDC 157)

Alternatively RDC can dedicate an experienced workforce for drilling cores in any direction by using a portable machine.

In order to cut on a routine basis the cylinders properly a diamond wheel saw is used. The next figure gives an example of equipment with minimum variation of the length of the samples.

Figure 2: Example of a Diamond Wheel Saw (RDC 148)

The required diameter of cores depends on the test to be performed. For testing mechanical properties at least three times the maximum grain size should be used. Cores of 50mm are drilled for these purposes; for the testing of the thermal conductivity and of the Rapoport swelling samples of 30mm diameter are prepared by lathing or drilling in a dedicated machine.

For the preparation of the samples used for the thermal conductivity testing plan and parallel surfaces of a 20mm disk are needed.

This is done by using a double saws grinding machine where the sample is clamped. The speed of sawing is automatically controlled.

Figure 3: Example of a Grinding Machine (RDC 149)

2.4 Drilling Schema

The cathode block is sampled in four different areas to take into account the anisotropy but also the fact that the cathode blocks are not homogenous. Six samples on each side “Front, side, Top and Bottom” are drilled to a 250 mm depth. A total of 24 samples will be tested according testing schedules depending on the orientation as shown in the chapter 3.

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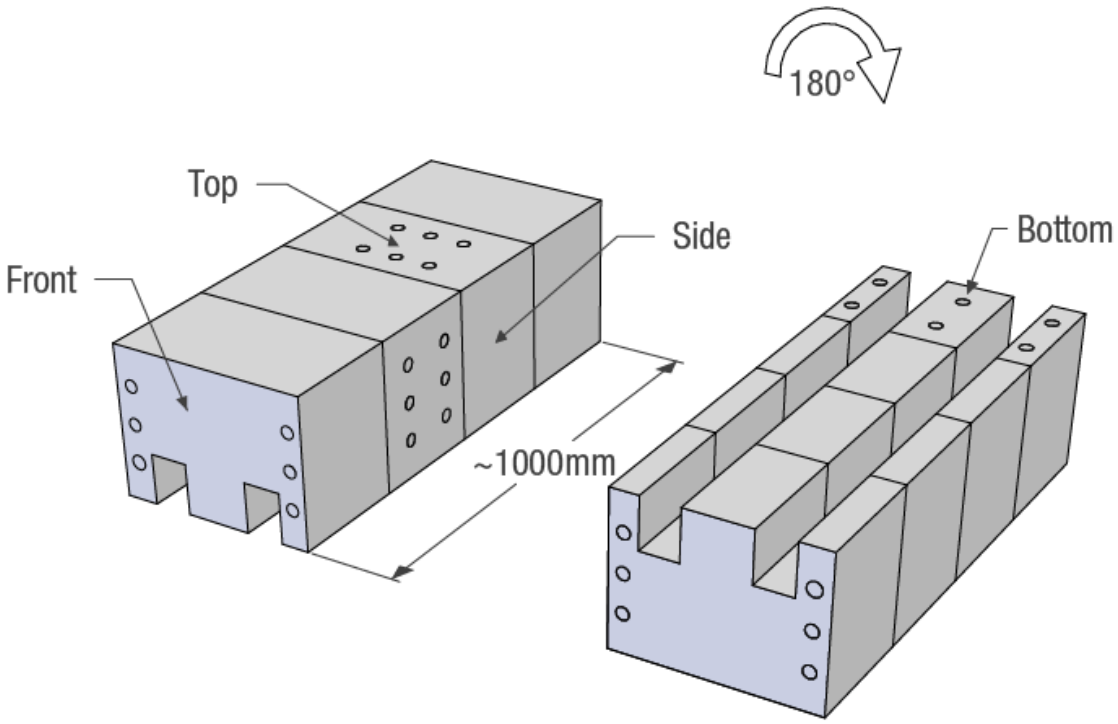
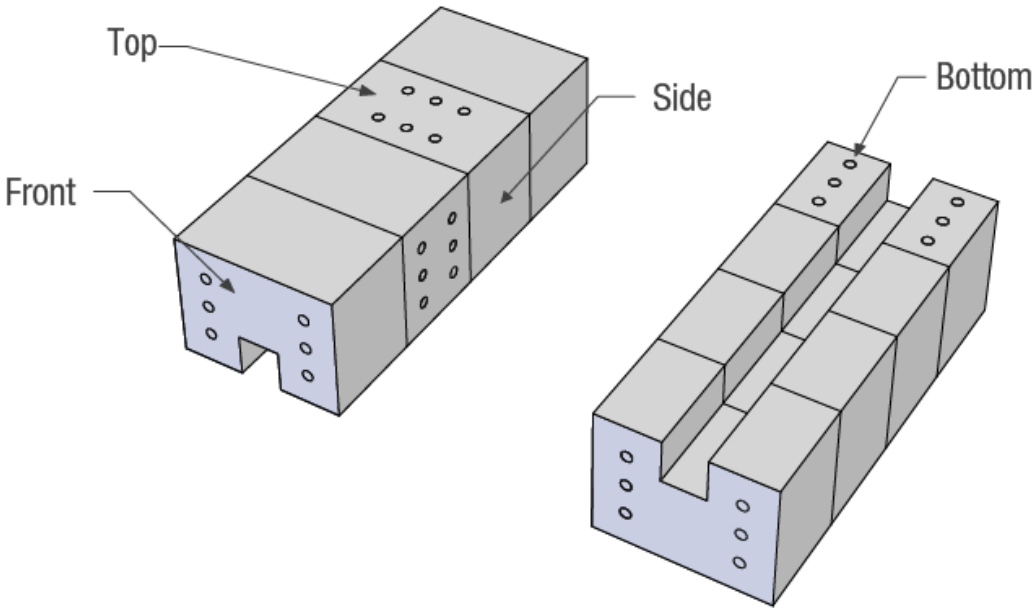
CATHODE DRILLING PLAN
SINGLE AND DOUBLE SLOT





2008/FD

3 Testing schedule

3.1 Front and side

Basically the swelling effects of the cathode occur along the two directions parallel to the front and to the vertical side of the cathode blocks. Therefore here the rapoport expansion and the Sodium vapour resistance are measured.

3.2 Top and bottom

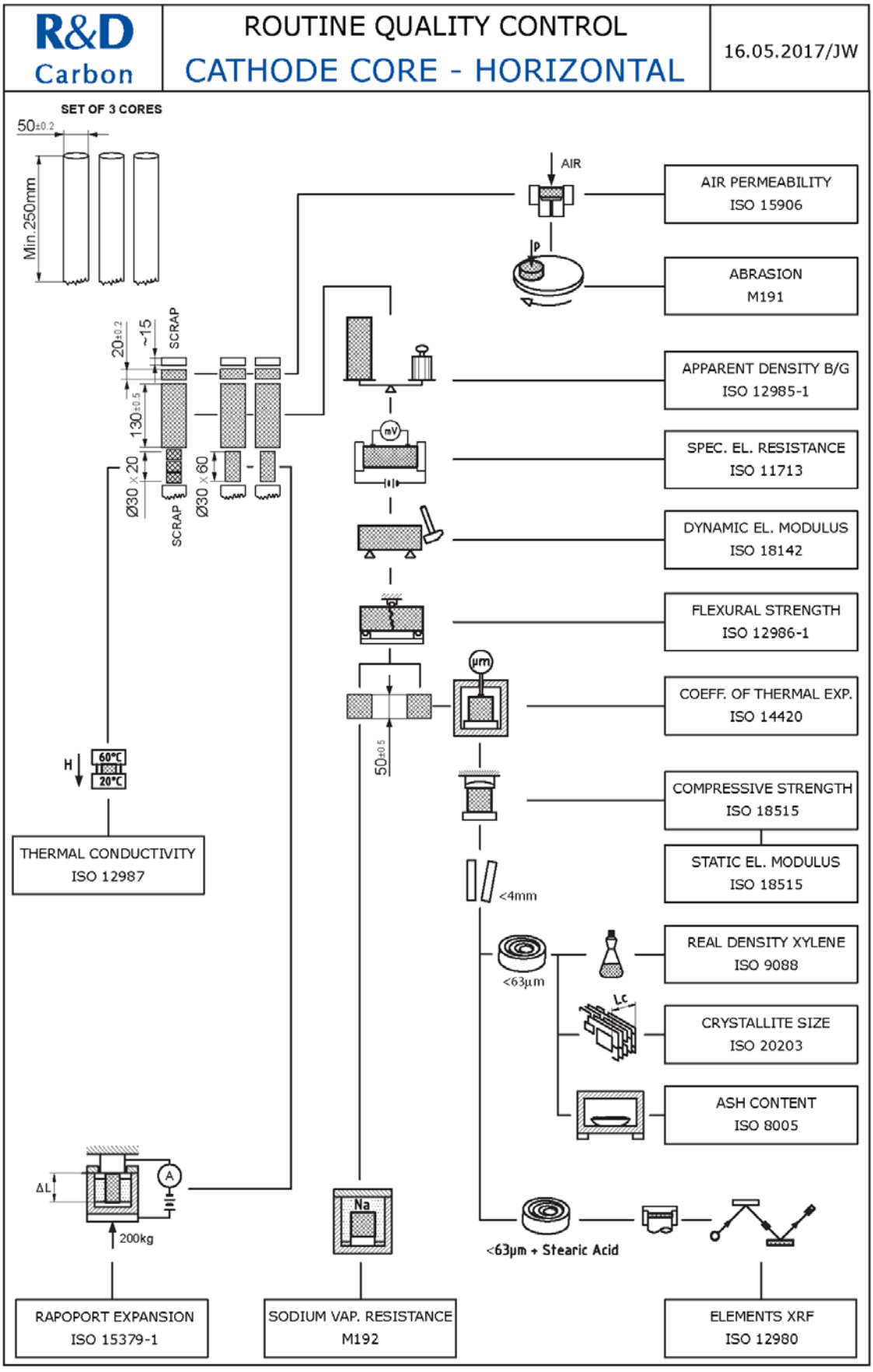
Here the abrasion resistance is rather an important property while the thermal conductivity and electrical resistance are relevant for the thermal loss and the voltage drop of the pot.

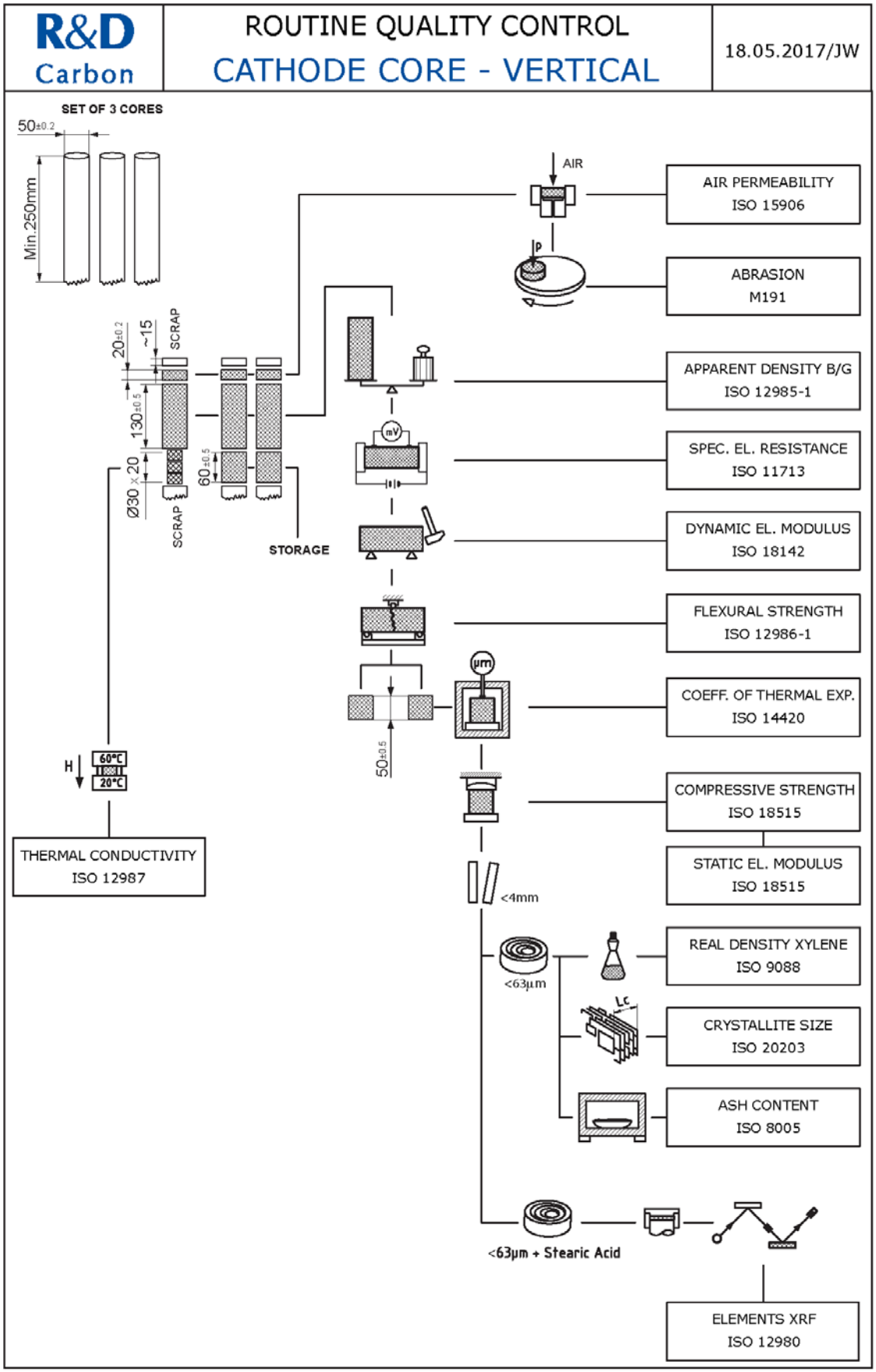
It is frequently referred to results found to the parallel and to the perpendicular direction of extrusion. This is coming from the fact that in the past most of the cathodes were extruded as graphite round electrodes are. The symbols used are // for parallel and for ⊥ perpendicular.

This terminology makes no sense when blocks are vibrated. Therefore the front side (or horizontal direction, corresponding to //) and the top/bottom sides (or vertical direction, corresponding to ⊥) are to be preferred when stipulating the direction.

As the bottom side shows lower density when the blocks are shaped with the slots and as the vertical sides of the cathode blocks is an important direction for the swelling effect in the pot it is important to characterize both additional directions.

The corresponding testing schedules are shown in the next two pages. For testing all properties relevant for cathodes a minimum of three samples is needed. With six samples each taken in the four mentioned sides the testing will be at least duplicated for each property.


R&D Carbon
ROUTINE QUALITY CONTROL
CATHODE CORE - HORIZONTAL
16.05.2017/JW
SET OF 3 CORES
50±0.2
Min.250mm
AIR
AIR PERMEABILITY ISO 15906
ABRASION M191
APPARENT DENSITY B/G ISO 12985-1
SPEC. EL. RESISTANCE ISO 11713
DYNAMIC EL. MODULUS ISO 18142
FLEXURAL STRENGTH ISO 12986-1
COEFF. OF THERMAL EXP. ISO 14420
COMPRESSIVE STRENGTH ISO 18515
STATIC EL. MODULUS ISO 18515
REAL DENSITY XYLENE ISO 9088
CRYSTALLITE SIZE ISO 20203
ASH CONTENT ISO 8005
20±0.2
~15
SCRAP
130±0.5
Ø30 X 20
Ø30 X 60
SCRAP
50±0.5
H
60°C
20°C
THERMAL CONDUCTIVITY ISO 12987
<4mm
<63µm
ΔL
A
200kg
Na
<63µm + Stearic Acid
RAPOPORT EXPANSION ISO 15379-1
SODIUM VAP. RESISTANCE M192
ELEMENTS XRF ISO 12980


R&D Carbon
ROUTINE QUALITY CONTROL
CATHODE CORE - VERTICAL
18.05.2017/JW
SET OF 3 CORES
50±0.2
Min.250mm
AIR
AIR PERMEABILITY ISO 15906
ABRASION M191
APPARENT DENSITY B/G ISO 12985-1
SPEC. EL. RESISTANCE ISO 11713
DYNAMIC EL. MODULUS ISO 18142
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STATIC EL. MODULUS ISO 18515
REAL DENSITY XYLENE ISO 9088
CRYSTALLITE SIZE ISO 20203
ASH CONTENT ISO 8005
ELEMENTS XRF ISO 12980
THERMAL CONDUCTIVITY ISO 12987
20±0.2
~15
SCRAP
130±0.5
Ø30 x 20
SCRAP
60±0.5
STORAGE
50±0.5
60°C
20°C
<4mm
<63µm
<63µm + Stearic Acid

4 Testing

Most of testing methods have been standardized by the ISO / TC 226 working on materials related to the Al-Industry. A description of each determination is given in the following pages together with an appropriate equipment.

4.1 Baked Apparent Density (BAD): ISO 12985-1

The BAD is determined by weighing a dried 130 mm long test specimen. The results are given in kg/dm^3. The BAD itself allows the calculation of the total porosity in combination with the real density in xylene.

4.2 Real Density Xylene (RDX): ISO 9088

The real density in xylene is measured in a pycnometer with xylene on a sample ground to <63µm particle size.

The xylene density of the amorphous cathode material depends mainly on the xylene density of the dry aggregate.

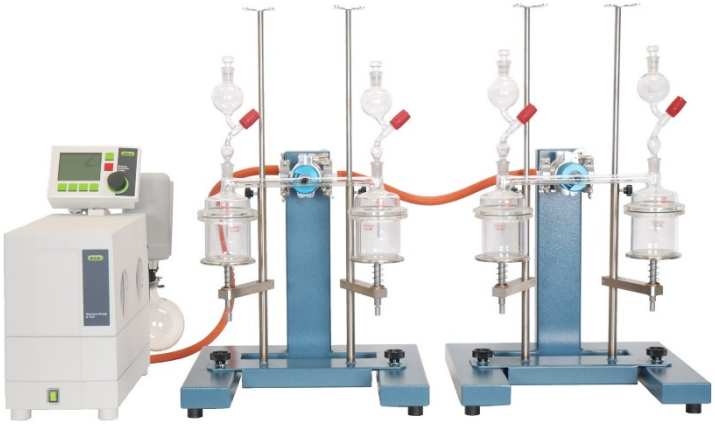

Figure 4: Real Density Determination Apparatus (RDC 152 / 186 / 198)

4.3 Total Porosity (TP)

The total porosity (TP) is calculated from the difference of the real to the apparent density according to the equation below:

$$TP\ [\%] = \frac{RDX - ADB}{RDX} \cdot 100$$

where

RDX: Real Density in Xylene in kg/dm^3

ADB: Baked Apparent Density in kg/dm^3

4.4 Air Permeability (AP): ISO 15906

The air permeability is determined by measuring the time taken for a certain volume of air to pass through a sample of 50 mm diameter and a length of 20 mm. The results are expressed in nanoperms.

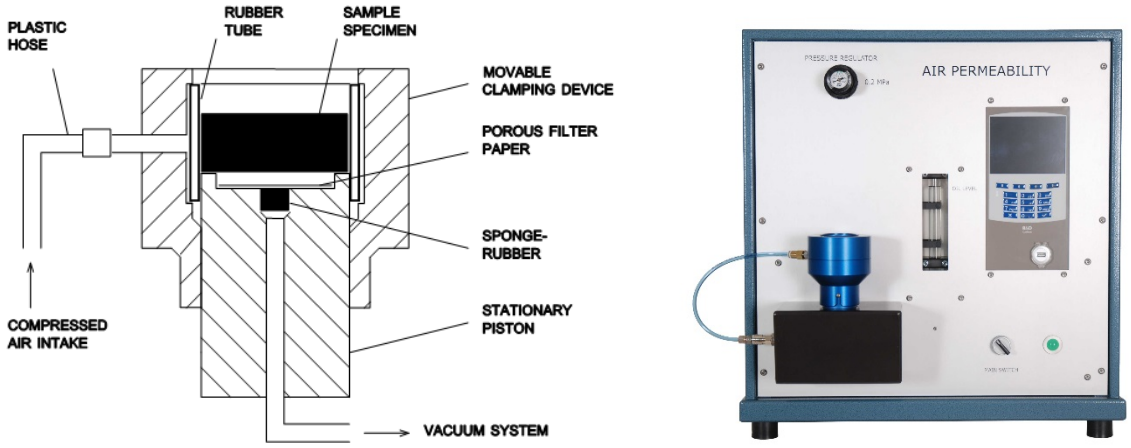

Figure 5: Air Permeability Apparatus (RDC 145)

4.5 Thermal Conductivity (TC): ISO 12987

The thermal conductivity is determined by a comparative method using samples with a diameter of 50 mm for amorphous (30 mm for graphitic and graphitized cathodes) and a length of 20 mm. The surfaces of the sample are to be plan parallel and very smooth. The use of a special grinding machine with two blades is mandatory (see figure 3 on page 5)

The heat flow is measured between electrically heated (60°C) and water-cooled (20°C) metallic measuring heads as shown in figure 6. The results are expressed in W/mK.

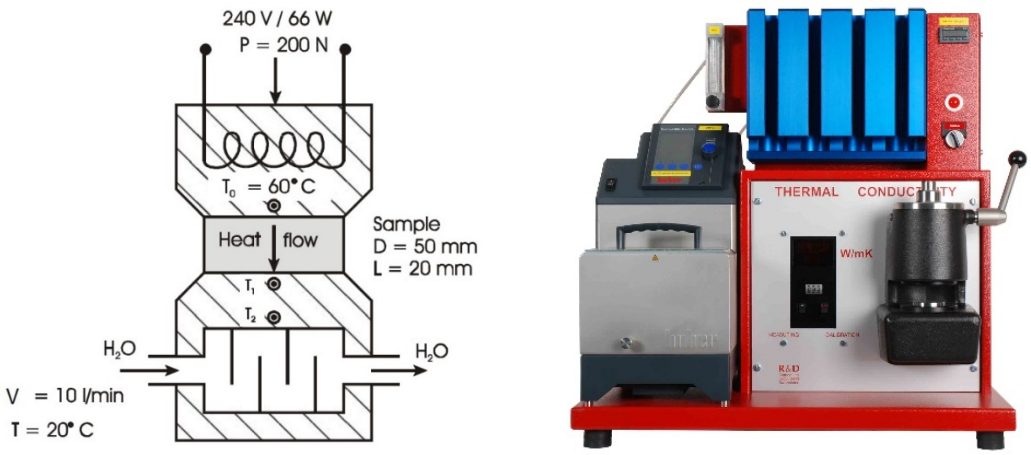

Figure 6: Test Arrangement of the Determination of the Thermal Conductivity (RDC 143)

The conductivity is mainly influenced by the nature of the dry aggregate, the porosity level and the baking (graphitizing) temperatures. The thermal conductivity of the cathodes strongly influences the cell heat-loss.

4.6 Specific Electrical Resistance (SER): ISO 11713

The specific electrical resistance is determined by measuring the voltage drop on a 50 mm diameter by 130 mm long sample at a constant current of 1.00 Ampere. The test arrangement is shown below. The results are expressed in µΩm.

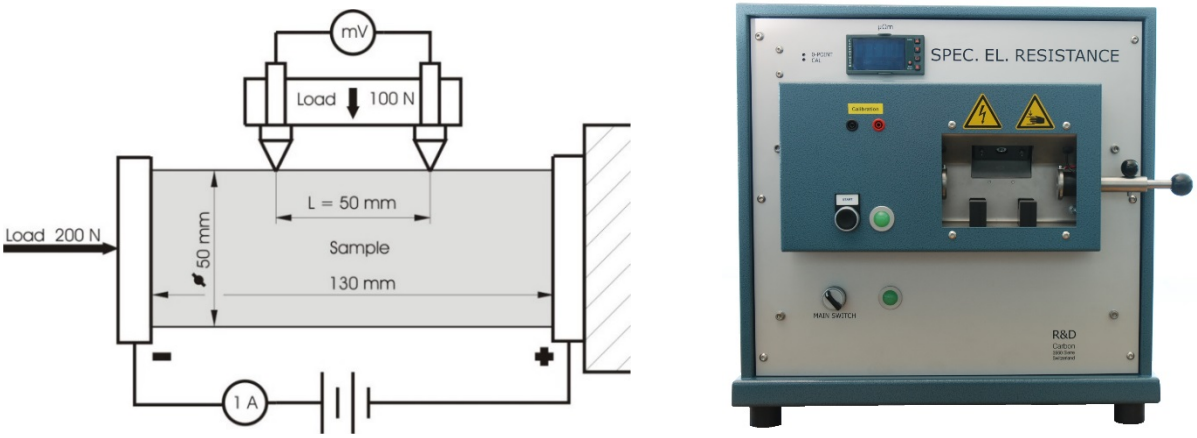

Figure 7: Test Arrangement for the Determination of the SER of anodes (RDC 150)

A strong variation of the SER indicates the presence of cracks due to poor forming and baking conditions.

4.7 Flexural Strength (FS): ISO 12986-1

The flexural strength is determined using three-point loading on a sample with a diameter of 50 mm and a length of 130 mm. The test arrangement is shown in Figure 8.

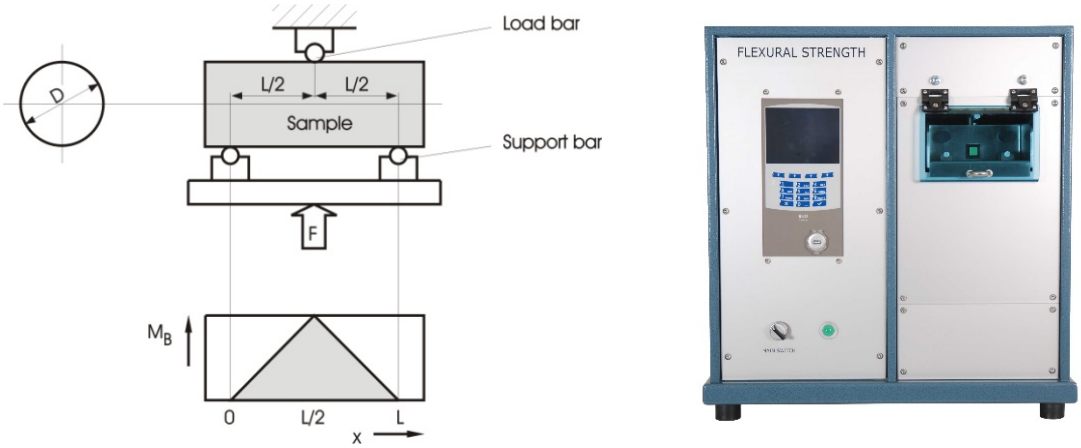

Figure 8: Test Arrangement for the Determination of the Flexural Strength (RDC 187)

The values are reported in MPa . The flexural strength is influenced by the amount of binder and fines as well as by the mixing, forming and baking conditions.

4.8 Comp. Strength and Stat. Elasticity Modulus (CS+SEM): ISO 18515

Compressive strength and static elasticity modulus are determined from the breaking load and the linear compression of a sample with a length of 50 mm. The values are reported in MPa for the compressive strength and in GPa for the static elasticity modulus. These parameters are important in considering the thermal shock resistance of cathode during the collector bar casting.

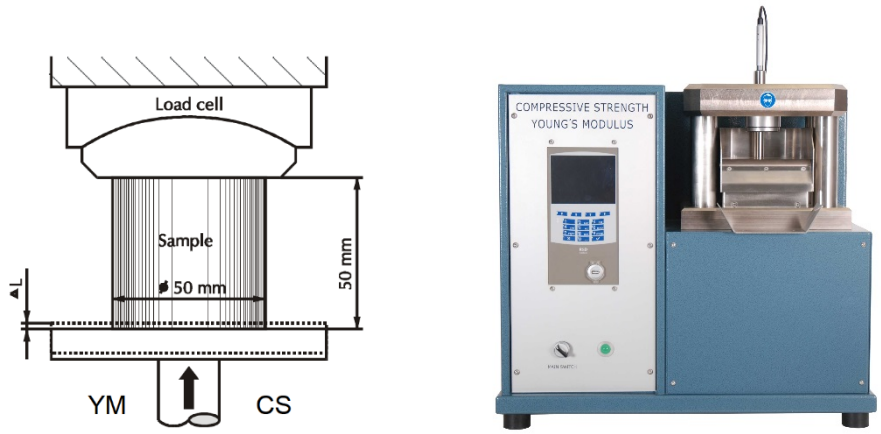

Figure 9: Test Arrangement for the Determination of the Compressive Strength and of the Static Elasticity Modulus (RDC 144)

4.9 Dynamic Elasticity modulus (DEM) : DIN 51915

It is determined by causing the specimen to vibrate by impulse exciting and measuring the frequency of the oscillation as shown below (taken from Grindosonic, Lemmens-Elektronika)

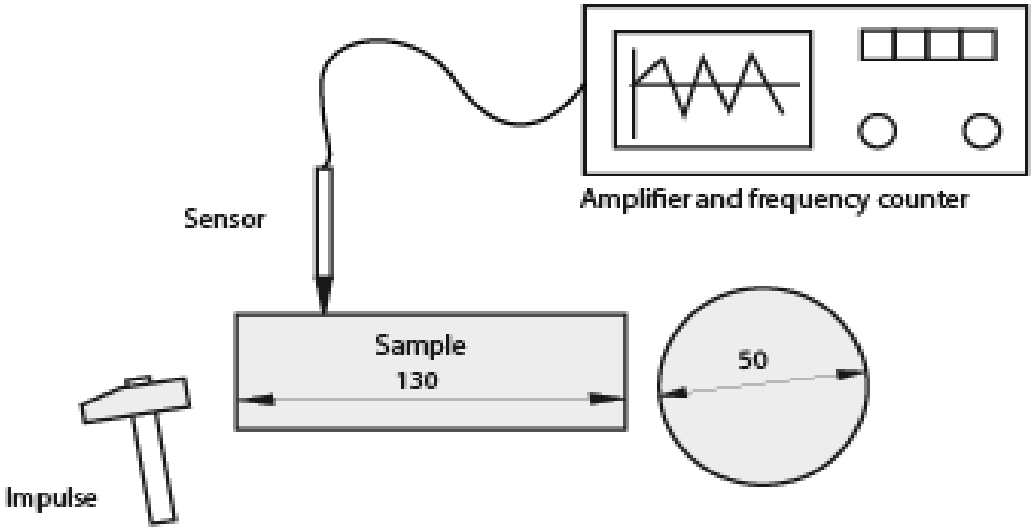

Figure 10: Test Arrangement for the Determination of the Dynamic Elasticity Modulus (EXT 110)

The dynamic elasticity modulus is than calculated from the frequency, taking into account the sample length and apparent density, as follows:

$$E_{dyn} = 4 \cdot ADB \cdot l^2 \cdot f^2 \cdot 10^{-12}$$

with

ADB: Baked Apparent Density in kg/dm^3

l: Length of the Ø 50mm core in mm

f: Resonant frequency in Hz

The elasticity modulus is expressed in GPa. Usually the dynamic elasticity modulus is about twice higher than the static elasticity modulus.

4.10 Thermal Expansion (CTE): ISO 14420

The coefficient of thermal expansion is measured between 25 and 300°C and reported as a mean coefficient having the unit 10^{-6} K^{-1}.

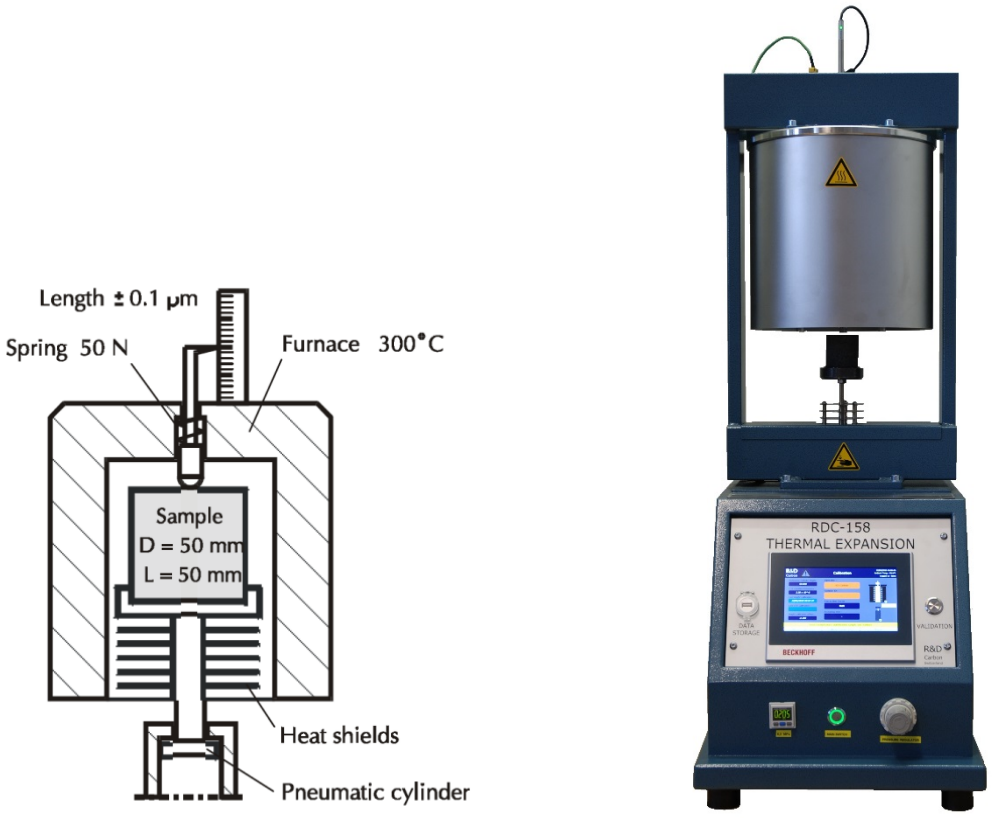

Figure 11: Test Arrangement for the Determination of the CTE (RDC 158)

4.11 Abrasion (ABR)

Abrasion of the cathode is due to the abrasive alumina sludge driven by the metal movements.

A high content in graphite material increases the abrasion rate value. A test where discs of 50 mm diameter and a length of 20 mm are ground under a load of 200 N on an abrasive paper with coarseness of 60 SiC was developed.

The heights of the 3 cylinders are measured before and after the test and the wear is calculated in percent. Each reported result is the mean of the three discs height decrease.

Sample Diameter	:	50 mm
Sample Length	:	20 mm
Wheel Speed	:	200 rpm
Sample Holder Speed	:	100 rpm
Load (3 samples)	:	150 N
Pressure on Sample	:	260 g/cm^2
Paper Coarseness	:	60 SiC
Time	:	60 sec

Figure 12: Test Arrangement for the Determination of the Abrasion (RDC 191)

4.12 Sodium Vapour Resistance (SVR)

A specimen of 50 mm diameter and 50 mm length is introduced in a stainless steel vessel together with a given weight of sodium. After evacuation to about 1 mbar the temperature is increased to 700°C. Samples are kept 2 hours at 700°C.

A sketch of the apparatus is shown below. The effect of sodium attack is quantitatively determined by comparing the compressive strength values measured on the cores after the test to the values obtained on the original material.

The sodium vapour resistance is defined as the ratio in percent of the compressive strength (CS) after the test to the original strength. Each reported result is the mean of 2x2 analysed cores.

$$SVR\,[\%] = \frac{CS_{aftertest}}{CS_{beforetest}} \cdot 100$$

Graphitic cathode shows better resistance towards sodium than pure amorphous cathode.

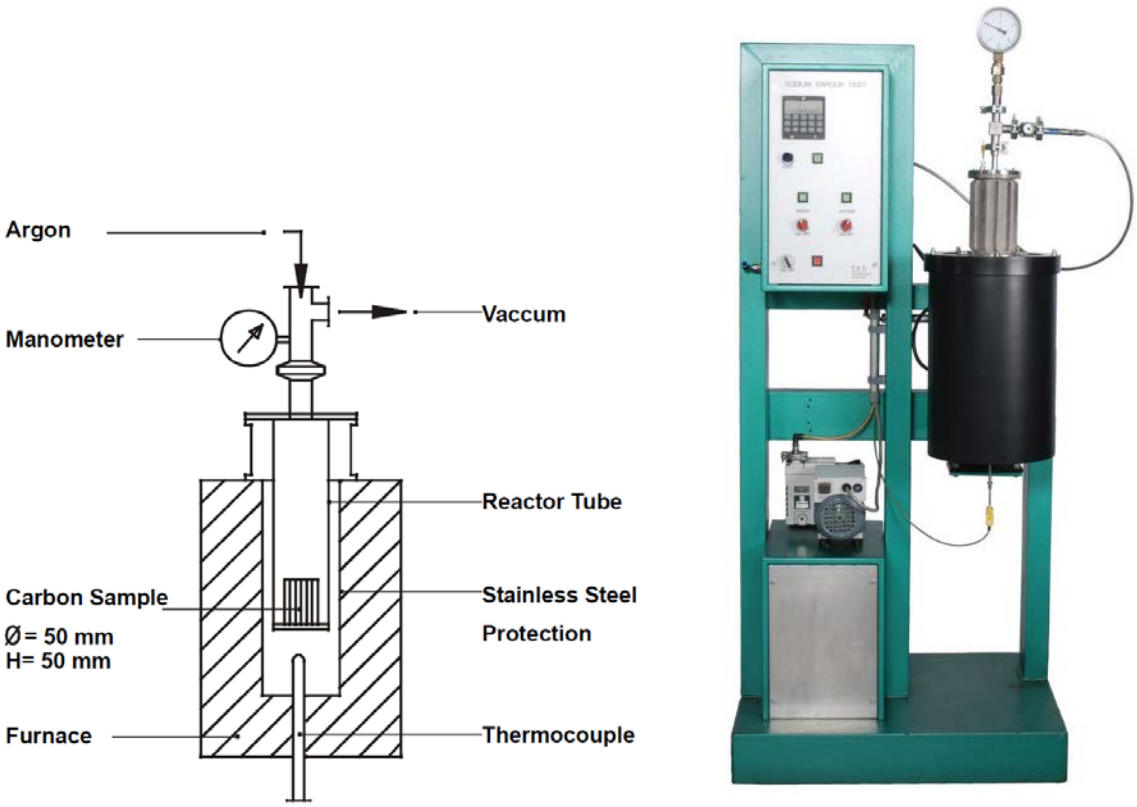

Figure 13: Test Arrangement for the Determination of the Sodium Vapour Resistance (RDC 192)

4.13 Rapoport Expansion (RE): ISO 15379-1

A cathode specimen is placed in a graphite crucible containing a basic bath. The assembly placed into a furnace at 980°C is pressed with 5 MPa pressure. A DC current (0.7 A/cm^2) will produce Al. Na components from the bath will penetrate into the cathode specimen and swelling will result.

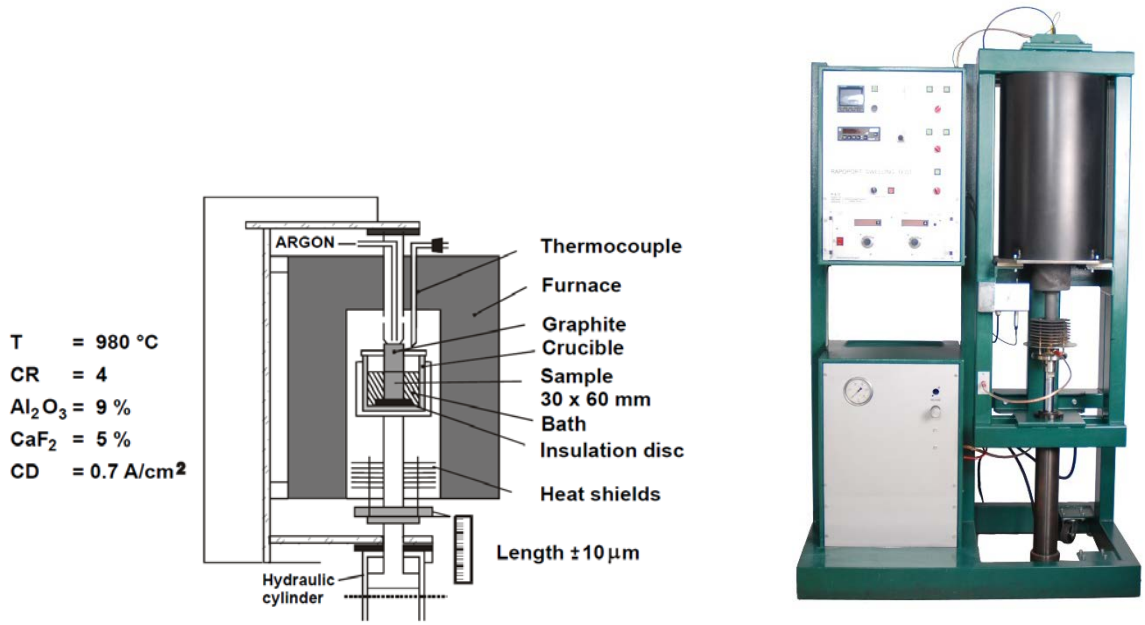

Figure 14: Test Arrangement for the Determination of the Rapoport Test (RDC 193)

The elongation of the specimen is followed by measuring the displacement of the hydraulic plunger system. The maximum elongation (e) in mm that occurs within 2 hours is used to calculate the Rapoport Expansion (RE) percentage for a 60 mm immersion depth.

$$RE\,[\%] = \frac{100 \cdot e}{60}$$

Amorphous cathodes show RE values around 0.8 % while graphitized cathodes practically do not swell (< 0.1 %).

4.14 Elements XRF (XRF): ISO 12980

The contaminants are determined by use of an X-ray spectrometer (see figure 15). The changes in the impurity levels give an indication of inconsistent raw materials quality.

Figure 15: XRF Spectrometer EXT 103

4.15 Ash Content: ISO 8005

The ash content is determined by burning at 700°C a sample of ground carbon (<63µm) in a porcelain dish. The remaining ash are weighed and expressed in %.

Figure 16: Furnace for Ash Content RDC 169

4.16 Interlayer Spacing (C/2)

The interlayer spacing is determined by x-ray diffraction (copper tube) made on a grounded sample <63µm. it is calculated from the determined diffraction angle θ [°2Θ] where the peak of x-ray intensity is recorded.

$$\frac{c}{2} = \frac{\lambda}{2 \cdot \sin\left(\frac{\theta}{2}\right)}$$

The wavelength λ of the source radiation is 1.54 Å.

Graphite shows an interlayer spacing of 3.354 Å while amorphous materials have a higher value close to 3.44 Å.

The graphitization degree (g) according Maire and Mehring can be calculated using the equation (0 < g < 1.00).

$$g = \frac{3.440 - \frac{c}{2}}{3.440 - 3.354} = \frac{3.440 - \frac{c}{2}}{0.086}$$

This test is normally made on graphitized cathodes only.

Figure 17: XRD Diffractometer EXT 104

5 Typical values

Based on specification values from the cathode suppliers and various measurements, the ranges of testing results on the next page could be assembled. The ranges were established for different cathode grades and for vertical and horizontal directions.

5.1 Typical Properties of Cathodes

Properties	Unit	Method	0% Graphite		30% Graphite		50 % Graphite		100% Graphite		Graphitized	
			Vertical	Horizontal	Vertical	Horizontal	Vertical	Horizontal	Vertical	Horizontal	Vertical	Horizontal
Baked Apparent Density	kg/dm^3	ISO 12985-1	1.52-1.58		1.52-1.60		1.54-1.64		1.62-1.70		1.60-1.68	
Total Porosity	%	M134	16.0-19.0		17.0-21.0		18.0-22.0		22.0-26.0		25.0-30.0	
Specific Electrical Resistance	µΩm	ISO 11713	40-65	32-50	30-48	24-44	26-42	21-36	16-24	13-20	10-14	9-12
Flexural Strength	MPa	ISO 12986-1	6.0-9.0	7.0-10.0	7.0-10.0	8.0-11.0	7.0-10.0	8.0-11.0	8.0-12.0	9.0-13.0	6.0-13.0	7.0-15.0
Compressive Strength	MPa	ISO 18515	22-40	25-42	22-38	25-40	21-37	24-38	20-34	22-34	15-34	18-36
Dynamic Elasticity Modulus	GPa	ISO 18142	5.0-8.0	6.0-9.0	5.0-8.0	6.0-9.0	5.0-8.0	6.0-9.0	5.0-9.0	6.0-10.0	5.0-9.0	5.0-10.0
Coeff. Of Thermal Expansion (25-300°C)	$10^{-6}/K$	ISO 14420	3.0-4.0	2.8-3.7	2.8-3.8	2.6-3.5	2.7-3.7	2.5-3.4	2.6-3.4	2.4-3.2	2.0-4.5	1.8-4.0
Thermal Conductivity	W/mK	ISO 12987	5-9	6-11	7-13	9-17	10-16	12-20	25-40	30-50	80-100	90-120
Real Density Xylene	kg/dm^3	ISO 9088	1.82-1.90		1.88-1.95		1.92-1.98		2.06-2.16		2.18-2.24	
Air Permeability	nPm	ISO 15906	1.0-5.0		1.0-5.0		0.5-4.0		0.5-3.0		0.2-3.0	
Abrasion	%	M191	1-3		1-4		2-6		15-30		30-70	
Sodium Vapour Resistance	%	M192	30-70		40-70		50-80		75-95		50-100	
Rapoport Expansion	%	ISO 15379-1	-	0.50-0.90	-	0.40-0.70	-	0.40-0.60	-	0.30-0.50	-	0.00-0.20
Ash Content	%	ISO 8005	4.00-8.00		3.00-6.00		2.00-4.00		0.30-1.50		0.10-0.60	

Figure 18 : Cathodes Typical Value