R&D Carbon

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EVALUATION OF SÖDERBERG PASTE FOR ALUMINIUM APPLICATION

SAMPLE PREPARATION AND TEST METHODS

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Table of contents

1 Introduction

The quality of Söderberg paste for the Aluminium industry is determined by measuring different properties on the green paste and then by preparing baked electrode specimen which are eventually tested.

For the green paste the following properties are determined:

- Water content
- Green Apparent Density
- Flowability

After baking and core drilling the following properties on the baked specimen:

- Baked Apparent Density baked
- Specific electrical resistance
- Thermal conductivity
- Flexural strength
- Compressive strength
- Air and CO_2 reactivities
- Air Permeability
- Real Density
- Impurities

The interpretation of these different test results allows a good prediction of the behavior of the paste in the electrolysis pots.

In this document the testing conditions and methodology are first described followed by the preparation of the baked electrode and cores for property testing .The test schedule and the corresponding equipment and test arrangement are reviewed. Typical values for wet and dry paste are eventually listed and the relevance of each property for the anode behavior in the pots are commented.

2 Green Paste Testing

2.1 Sample Preparation

Approximately 500 grams of Söderberg paste are placed in two porcelain dishes and heated in the RDC 185 air forced cabinet (Figure 1) to 170°C. The temperature of the paste is measured with a thermometer.

Figure 1: RDC185 air forced cabinet for paste preparation and testing isometric cylindrical samples of 50 mm

Two molds are preheated in the same cabinet. To prevent sticking, the molds are slightly treated with oil. When the paste temperature each 170°C (~`1 to 1h30heating) the hot paste dish is weighed to determine the water content. The hot paste is then added in three or four steps to each mold (see Figure 2).Tamping with the stopper using the nylon hammer after each paste addition is performed to guarantee a uniform densification. Excess paste on the mold top is removed with a steel spatula

After the molds are cooled with water, the test specimens are removed, dried with a cloth and then weighed. The difference between the weights of the two test specimens should not exceed 2 grams.

The operations are repeated twice to obtain a total of 4 green paste samples.

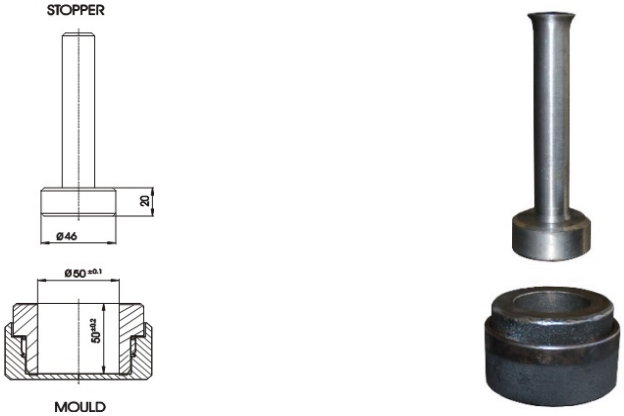

Figure 2: RDC 190 mould and stopper for the green paste cylinder preparation

2.2 Water Content (WC)

The water content is determined prior the preparation of the test specimen by measuring the weight loss (0.01g scale precision) between the ambient temperature and the heated (170°C) Söderberg paste sample.

The calculation is made according the following equation:

$$WC = \frac{m_b - m_a}{m_b} \cdot 100$$

where

WC:	Water content [%]
m_b:	Mass of the cold sample [g]
m_a:	Mass of the heated sample[g]

The mean value of the two determinations is rounded to the first decimal.

2.3 Green Apparent Density (GAD)

The green apparent density is determined on each cylinder from their weight (0.01 g precision balance) at the end of the sample preparation. Their volume is constant as isometric sample of 50 mm are automatically prepared

The calculation on each cylinder is made according the following equation:

$$GAD = \frac{m_{green}}{98.17}$$

where

GAD:	Green Apparent Density [kg/dm^3]
m_{green}:	Mass of the sample [g]

The mean value of the four determinations is rounded to the second decimal.

2.4 Flowability (F, FL)

Two different procedures for the determination of the paste are available, depending on the flowability of the paste. For wet pastes (high flowability), the method without load is applied (2.4.1). For dry pastes (low flowability), the method with load is applied (2.4.2), in order to increase the sensitivity of the analysis. If the kind of paste is unknown or has intermediate flowability value, both methods can be applied. The first test to be applied is the one without load

2.4.1 Flowability without load (F)

The RDC 185 forced air oven is preheated to 170±3°C. The PTFE coated plate is placed on the middle shelf of the oven. Two cold test specimens are placed in a predetermined position on the hot plate. After 30 minutes, the plate is taken out of the oven and immediately cooled with water. The diameter of the deformed sample is measured four times (4 times with a 45 degree angle progression from an arbitrary diameter position) and the average calculated.

The flowability is calculated from the ratio of the diameters (after and before the test) according the following equation:

$$F = \frac{d_{after}}{50}$$

where

F: Flowability without load [-]

d_{after}: Mean diameter after test [mm]

The mean value of the two determinations is rounded with two decimals.

2.4.2 Flowability with load (FL)

The forced air oven is preheated to 170±3°C. The PTFE coated plate is placed on the middle shelf of the oven. Two cold test specimens are placed on the hot plate and the steel cylinders mounted on the furnace (2 kg each) are placed on the top of the samples. After 30 minutes, the plate is taken out of the oven and immediately cooled with water. The diameter of the deformed sample is measured four times (4 times with a 45 degree angle progression from an arbitrary diameter position)and the average calculated.

The flowability is calculated from the ratio of diameters (after and before the test) according the following equation:

$$F_L = \frac{d_{after}}{50}$$

where

F_L: Flowability with load [-]

d_{after}: Mean diameter after test [mm]

The mean value of the two determinations is rounded with two decimals.

3 Preparation of Test Electrodes

Two Söderberg paste samples (10 kg each) are weighed in two 20 l metallic buckets that will be placed in a forced air oven heated to about 180°C with a cover to minimize the risk of pitch fumes loss.

After 6 hours, the hot paste is filled in two 5 liters buckets (28.5 /30 cm diameter and 34 cm height) used as molds. To prevent sticking, they are lined with a heavy weight brown wrapping paper, so that there is a 100 mm overlap, and the paper extends 150 mm beyond the top of the bucket. The buckets are filled in 5 portions. The paste is tamped manually after each addition with a piston of Ø80 mm. The buckets are filled until the tamped paste is 20 mm underneath the top of the basket. When the paste has cooled down, the excess paper on the top of the bucket is folded down over the paste.The bucket containing the paste is placed in the furnace RDC 165 Söderberg baking furnace BF12S and positioned under the pressure rod. A pressure of 50 kPa (4.2 bar) is applied to the top of the electrode sample by means of a pneumatic pressure device and lifted automatically when the temperature reaches 600°C. The automatically controlled heating rates for the baking procedures are:

- 100°C/h from 20°C to 200°C
- 15°C/h from 200°C to 600°C
- 50°C/h from 600°C to 1000°C

The heat soaking time by 1000°C is 5 hours.

Figure 3: RDC 165 Söderberg baking furnace BF12S

Under these conditions, the baked test electrode samples have physical and chemical properties close to those of industrial anodes.

4 Preparation of the testing cores

After cooling, five test cylinders of 50 mm diameter are drilled from each baked electrode using the RDC 179 core drilling machine The top 20 mm of the cores is discarded by using the RDC 148 diamond wheel saw machine and eventually a 130 mm long cylinder is cut, as shown on the testing schedule shown on the next page. A grinding machine (RDC 149) is also used to prepare 20 mm plan parallel discs for the measurement of the thermal conductivity and air permeability. The samples are dried over a period of 6 hours at a temperature of 120°C.

Figure 4: RDC 179 Pilot core drilling machine

Figure 5: RDC 148 Diamond wheel saw

Figure 6: RDC 149 Grinding machine

5 Baked Cores Testing

The properties of the baked cores are determined according the test schedule below. Most of testing methods are ISO standards. A description of each determination is given in the following pages together with the corresponding RDC equipment.

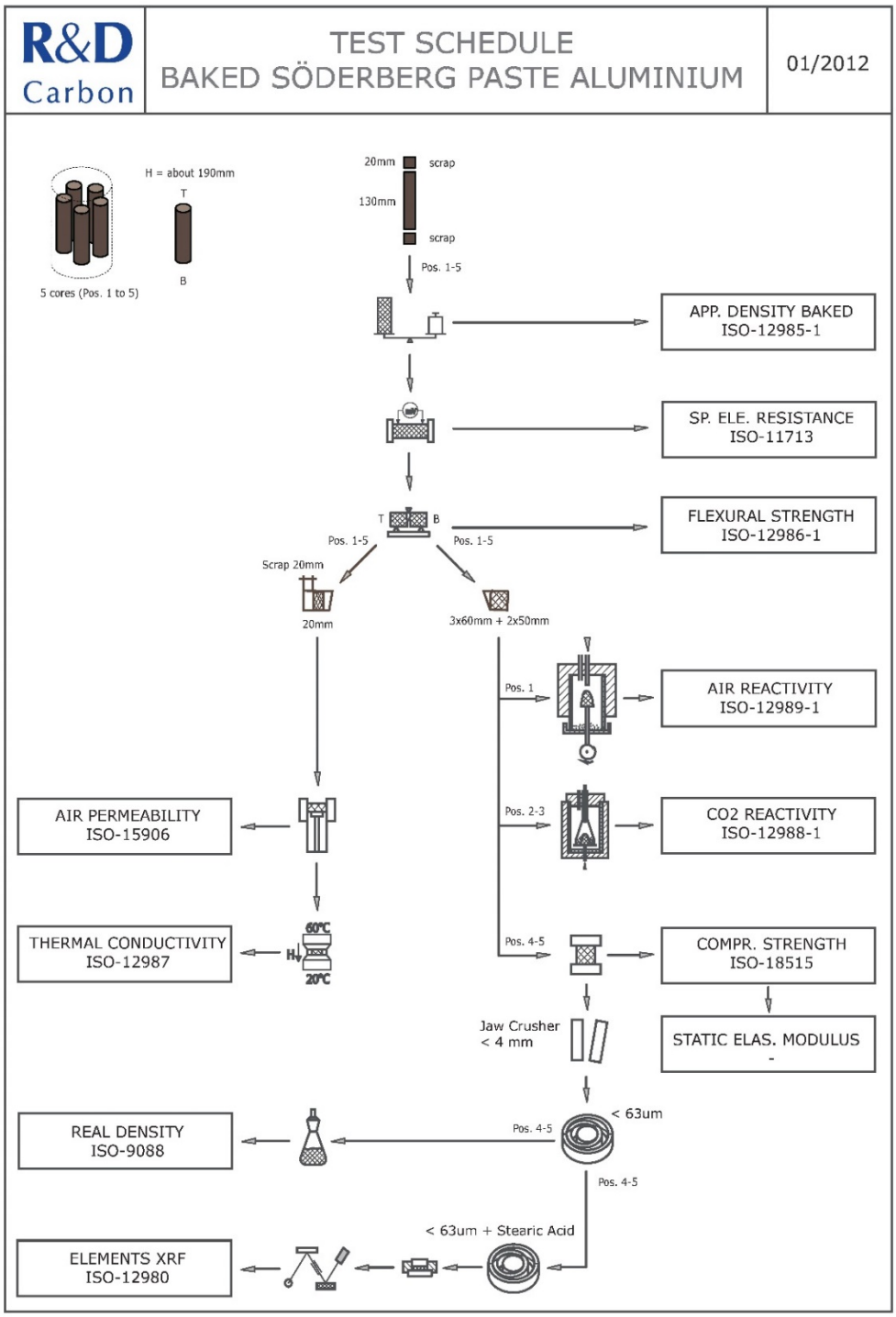

Figure 7: Test Schedule

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

The BAD is determined by weighing and measuring the dimensions of a dried 130 mm long test specimen. The results are given in kg/dm³.

The apparent density of baked anodes is an important quality figure to characterize the anode performance in the cell. Most of the physical properties are strongly influenced by the apparent density of the material.

5.2 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].

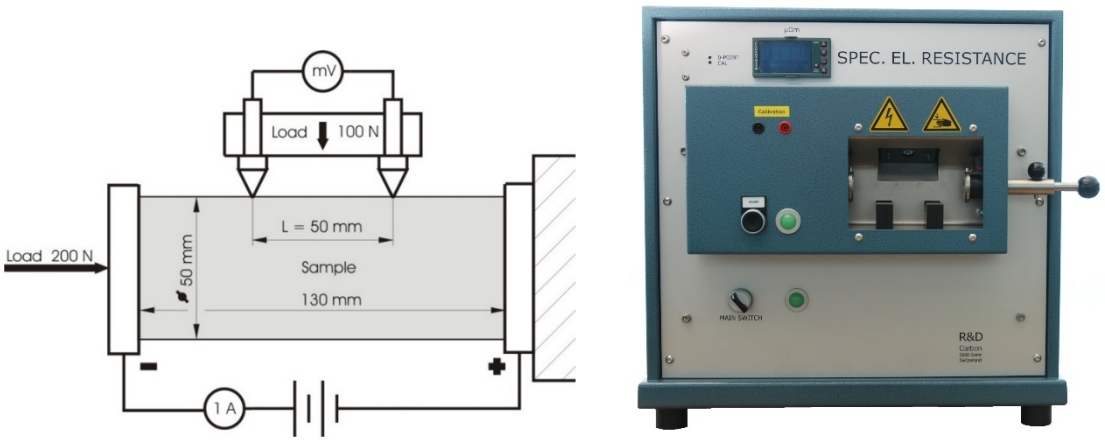

Figure 8: Test arrangement for the determination of the SER (RDC 150)

The specific electrical resistance is strongly influenced by the density of the anode. A high density results in a low specific electrical resistance. Generally, a low resistivity is desired, with the restriction that the other anode properties will thereby not be influenced negatively

The measurement of the specific electrical resistance is also used to detect microcracks in the material.

5.3 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 below.

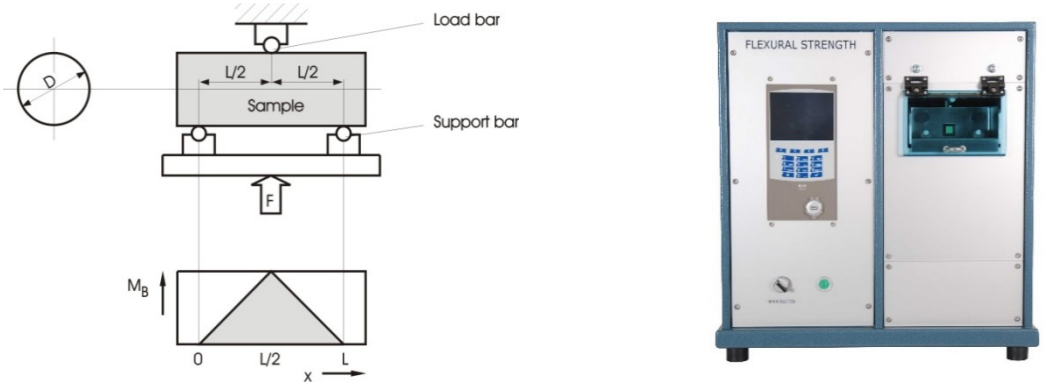

Figure 9: Test arrangement for the determination of the flexural strength (RDC 187)

The values are reported in MPa (10^6 N/m^2). The flexural strength is mainly influenced by the raw materials quality (QI of the binder, grain stability of the coke) as well as by the intensity of the paste mixing.

5.4 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 disc of 50mm diameter and a height of 20 mm. The results are expressed in nanoperms (nPm).

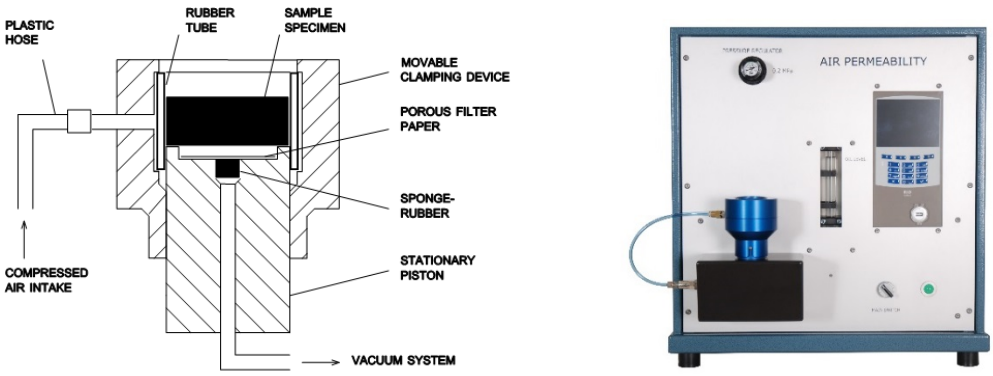

Figure 10: Test arrangement for the determination of air permeability (RDC 145)

The air permeability of the material has a great influence on CO_2 and Air anode burning reactions. A high gas permeability leads to an internal attack of the baked anodes bottom material eventually to an increased excess anode consumption and to carbon foam accumulation in the bath related to the binder matrix selective burning.

5.5 Thermal Conductivity (TC): ISO 12987

The thermal conductivity is determined by a comparative method using sample discs with a diameter of 50 mm and a length of 20 mm. The surfaces of the sample have to be plan parallel and very smooth to guarantee a defined thermal transfer to the metallic cells. The use of a special grinding machine with two blades is mandatory (see figure 6 on page 9). The heat flow is measured between electrically heated (60°C) and water-cooled (20°C) metallic measuring heads as shown below. The results are expressed in W/mK.

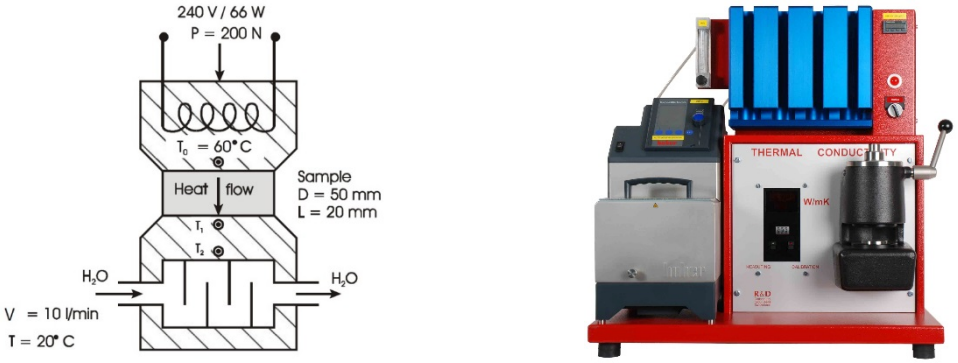

Figure 11: Test arrangement for the determination of the thermal conductivity (RDC 143)

The thermal conductivity is mainly a function of the density of the anode and of the calcining degree of the coke. A high density generally leads to a high thermal conductivity as well. The anode top temperature and therefore the paste flowability target has to be therefore adapted to its thermal conductivity level.

5.6 Air Reactivity: ISO 12989-1

The air reactivity is measured by the RDC 151 apparatus. An anode sample core with a diameter of 50 mm and a length of 60±0.1 mm is preheated in an inert atmosphere at 550°C and then cooled with a gradient of 15°C/h to 400° in an air flow of 200 l/h. In order to collect the dust in a cold area, the sample is cyclically tapped and the dust collected on a plate underneath the furnace.

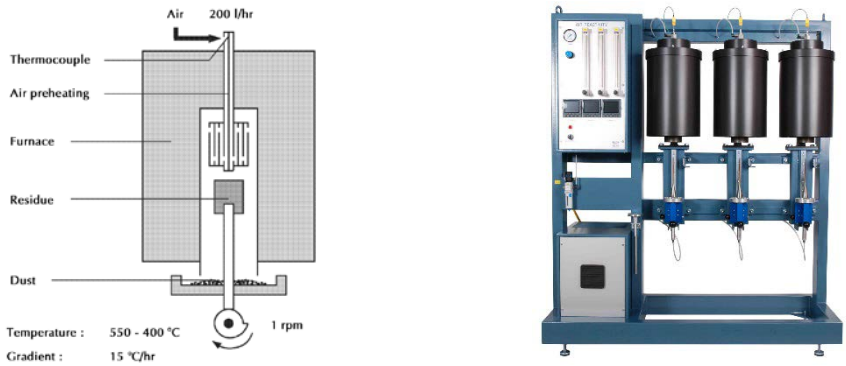

Figure 12: Test arrangement for the determination of the air reactivity of anodes (RDC 151)

After cooling and weighting, the sample is mechanically tumbled with steel balls in a separate piece of equipment (RDC 181) for 20 minutes to remove any loosely-bound particles. The total weight loss can be divided into two components: the loss due to burning and the loss due to dusting.

Figure 13: Tumbling apparatus (RDC 181)

The air reactivity behavior is characterized by three results:

- Air reactivity residue: residual sample
- Air reactivity dust: removed grains and dust
- Air reactivity loss: loss due to air burn

The air reactivity of the anode is primarily influenced by the reactivity of the coke as well as by excess sodium that might be present in the binder. The level of porosity is also relevant so that denser baked paste shows better air reactivity figure.

5.7 CO_2 Reactivity: ISO 12988-1

The CO_2 reactivity is measured by the RDC 146 apparatus. An anode sample core with a diameter of 50 mm and a length of 60±0.1 mm is exposed to a carbon dioxide atmosphere at 960°C for 7 hours.

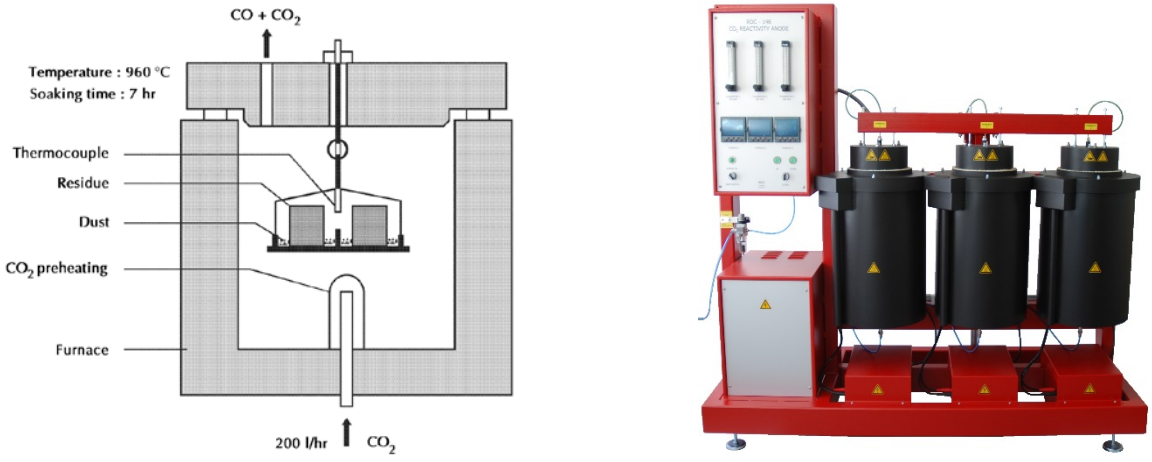

Figure 14: Test arrangement for the determination of CO_2 reactivity of anodes (RDC 146)

After cooling and weighting, the sample is mechanically tumbled with steel balls in a separate piece of equipment (RDC 181, see figure 13) for 20 minutes to remove any loosely-bound particles. The total weight loss is divided into two components: the loss due to burning and the loss due to dusting.

The CO_2 reactivity characterized by three results:

- CO_2 reactivity residue: residual sample
- CO_2 reactivity dust: removed grains and dust
- CO_2 reactivity loss: loss due to air burn

The ratio carboxy reactivity dust vs loss gives an indication of the selective CO_2 burn of the binder matrix. The selective carbon dioxide burn is strongly influenced by the CO_2 reactivity of the coke and by the catalytic effects of sodium present in the binder.

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

Compressive strength and static elasticity modulus are determined from the breaking load and from the deformation (strain) under load 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.

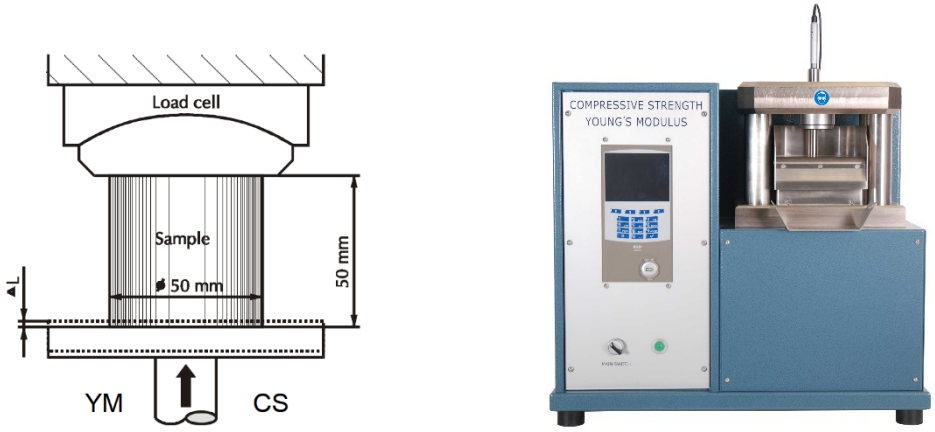

Figure 15: Test arrangement for the determination of the compressive strength and of the static elasticity modulus (RDC 144)

5.9 Real Density (RD): ISO 9088

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

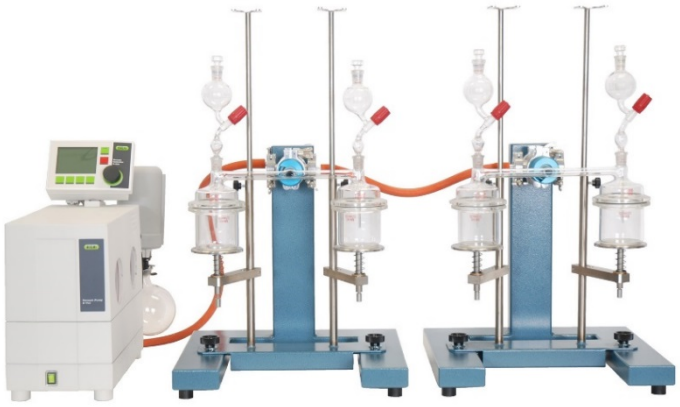

Figure 16: Real density determination apparatus (RDC 152 / 186 / 198)

The real density depends on the real density of the petroleum coke.

5.10 Elements XRF (XRF): ISO 12980

The contaminants are determined by use of an X-Ray fluorescence apparatus (see figure below). The changes in the impurity levels give an indication of inconsistent raw materials quality. The results are expressed in % for the sulfur and in ppm for the other impurities.

Figure 17: XRF spectrometer EXT 103

For the metal purity the Iron and Silicon in baked paste are important. For good anode burning behavior the concentration of catalytic elements like Vanadium, Calcium and Sodium have to be minimized through appropriate raw material selection.