# Ageing of Carbon Materials during Electrolysis, Experience from Operation and Laboratory Tests

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## Abstract



Carbon materials (C-materials) are important lining materials in aluminium electrolysis. They undergo significant changes during operation that might affect the stability and the performance of the cell. In this paper, we describe the development of an aging test in lab scale for C-materials simulating operational conditions during aluminium electrolysis. We further present the behaviour of different materials during the test compared with real life experience. Possible ageing mechanisms are discussed in light of experimental findings and characterization methods.

**Keywords:** Aluminium electrolysis, Carbon materials, Lining material, Testing.

## 1. Introduction

Carbon materials constitute important parts of the lining in an aluminium electrolysis cell. Carbon is normally used in the cathode blocks, the rammed joints and in the sidewall as pre-shaped blocks [1]. There are different properties desired for the different usages in the lining. The cathode blocks should have low electrical resistance and high wear resistance. In the most productive lines, only graphitized materials are used as cathode blocks. Between and around the cathode block, ramming paste is used. The ramming paste consists of mainly calcined anthracite with a carbonaceous binder, either pitch- or sugar-based types. The primary purpose of the ramming paste is to seal the area around the cathode blocks to prevent bath and/or metal to leak into the lining.

The ramming paste can also be used in the sidewalls of a cell. The thermal conductivity of the sidewall material is an important property in designing the thermal balance of the cell. Instead of using ramming paste in the sidewalls, many smelters are using pre-baked side blocks. This simplifies the installation and provide a more erosion resistant material. The pre-baked side blocks are normally made of calcined anthracite with addition of 0-30 % graphite. The amount of graphite and the calcination degree of the anthracite determine the final thermal conductivity of the side block. In general, the thermal conductivity of a pre-baked side block is higher than that of a corresponding baked ramming paste.

In designing low energy cells, a low thermal conductivity material in the sidewall is desired. However, the exposure to the electrolysis conditions in a cell is known to change the properties of carbon material [1]. The present paper shows that the change in properties can be rapid and significant. Thus, a lab test with the aim of being able to screen carbon materials with respect to their aging properties has been developed.

## 2. Ageing of Carbon Materials in Industrial Cells

### 2.1 Sampling/Characterization

Larger samples or chunks of ramming paste, side- and cathode blocks were taken out during autopsies of shut-down cells of different ages, see Figure 1 for the location of the different materials in the cell. Smaller samples for analysis were then core-drilled from the large samples in dry condition. The main ageing property of interest in this work is the thermal conductivity. The thermal conductivity is measured at room temperature by the hot disk method [2]. Electrical resistivity is also measured at room temperature according to ISO method 11713:2000.

Samples of virgin materials were core-drilled out of regular deliveries to the plants and analysed in the same way as used materials.

The lattice parameters of the carbon structure as determined by XRD based on ISO 20203:2005, were analysed for selected samples.

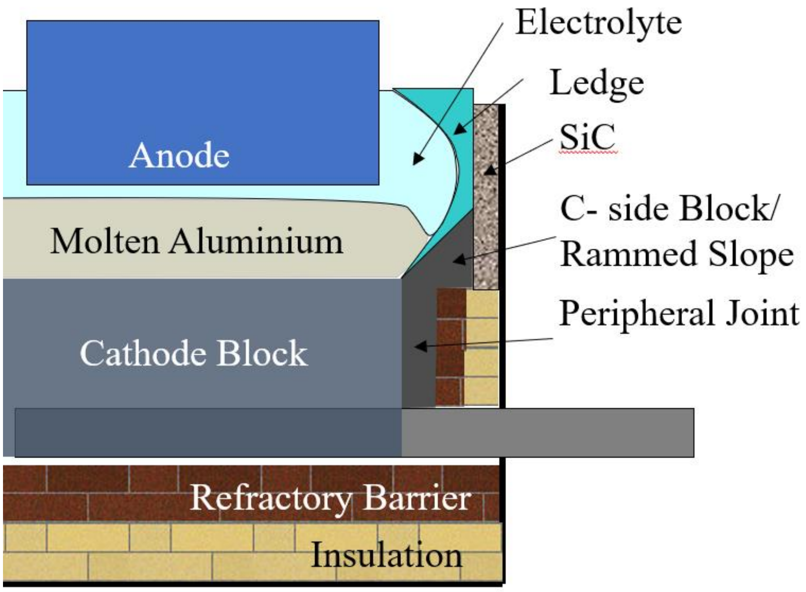


**Figure 1. Sketch of one half of a cross-section of a Hall-Hérault electrolysis cell showing the location of the different materials.**

## 2.2 Ramming Paste

Measured values of thermal conductivities of ramming paste in virgin and used conditions are shown in Table 1. Table 1 further gives the position in the cell where the paste is taken from as well as the binder type in the ramming paste. All pastes are based on anthracite as the aggregate phase. Several samples taken from the same pot, and the range of values are given in this table. The thermal conductivities of all the samples taken from only the narrow joints (between the long side of the blocks) are shown in Figure 2. Virgin baked samples of ramming paste were prepared according to ISO 20202:2004, rammed with 50 strokes.

The thermal conductivities of baked virgin ramming paste are in the range 4-7 W/mK. In operation, the thermal conductivity values increase several times and values above 50 W/mK are seen. Even after a few days in operation an increase is seen. The variation within a cell is also large. The narrow joints seem to have the largest increase, and the rammed slope and peripheral joint have normally lower thermal conductivity values than the narrow joints.

It is not possible to differentiate between the different pastes. Given the fact that anthracite is the main component in the ramming paste, it seems that the nature of the binder does not influence the aging of the ramming paste.

identified, however remaining intercalated Na in the lattice might increase the electronic component of the thermal conductivity.

Further, the results show that operational conditions are important for the ageing of carbon materials in the cell. Exposure to Na at high chemical activity, either dissolved in molten metal/bath or gas will rapidly increase the thermal conductivity of the anthracitic C-materials. This behaviour can be reproduced in a lab test in a relativity short time scale. The results show the differences between the materials; however, more data is needed to be able to screen materials with respect to ageing behaviour. One complicating factor is inhomogeneities in the virgin material from commercial sources, and care should be taken in selecting materials for testing.

## 5. Conclusions

The present study on primarily anthracitic carbon materials has shown that these materials undergo significant ageing during operation, where up to 10 times increase in thermal conductivity is observed. A laboratory test has been developed to study this behaviour, and ageing effect can be studied in the timescale of a few days. Although the tests results show a quite different behaviour for different materials, more data is needed to use the test for a material screening purpose. The results also show that the increase in thermal conductivity during operation/exposure is accompanied by a higher interplanar spacing and lower crystallite width of the carbon crystallites. This is the opposite response compared to increasing thermal conductivity of carbon materials during a normal graphitization process.

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