PILOT SCALE ANODE EVALUATION OF CALCINED COKE USED FOR PREBAKED ANODES

PREPARATION AND TEST METHODS

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1 Summary

A pilot scale standard procedure was developed to manufacture pilot anodes (Ø 146 mm, l ~200 mm) using an intensive impeller mixer, an hydraulic press and a pilot baking furnace.

Batches of dry aggregate coke are mixed with four different pitch contents in the range of 13% to 16%. After forming and baking in an electrical furnace, the pilot anodes are core drilled and cylinders of 50 mm diameter are tested according ISO standard methods.

Worldwide cokes were tested and typical ranges of the anode properties for the different pitching levels were defined but up-dated on a continuous basis to follow the evolution of the available anode grade cokes on the market.

A precise determination of the pitch requirement and valuable information on the suitability of a given coke candidate for prebaked anodes are provided. The evaluation of the results covers the fields of the anode consumption related to the burning behavior properties and also of the anode thermal shock resistance linked to the mechanical and thermal properties.
2 Introduction

This document described the procedure and the corresponding equipments used in the RDC pilot plant at Sierre, Switzerland, for the evaluation of the suitability of calcined coke as anode grade material.

The preparation of the dry aggregate, the mixing with the binder, the forming and baking conditions are defined. The testing schedule of the baked anode cores are given along with the typical ranges of the worldwide coke anodes that are represented graphically.

3 Experimental

The coke material is sieved in a pilot continuous sieving machine and the material larger than 8 mm is crushed in a jaw crusher and sieved again.

The fines is prepared out of the intermediate coke fractions 2 to 0 mm by using an air jet collision mill where the dust fineness can be adjusted to a 3500 Blaine level corresponding to a \( d_{50%} \) of 50 µm.

Six different fractions are weighed to form a 5.5 kg dry aggregate according to the following straight line formulation for the grains:

- 8-4 mm: 14%
- 4-2 mm: 14%
- 2-1 mm: 14%
- 1-0.5 mm: 14%
- 0.5-25 mm: 14%
- Fines 3500 Blaine: 30%

![Figure 1: Dry aggregate preparation: crusher, sieving machine, air jet collision mill](image-url)
3.1 Binder Characteristics

A modern coal tar pitch showing a relatively low QI content with a typical 113°C Mettler Softening Point (SP) is used as a binder. The binder was crushed to < 4 mm and is used in the solid state in the mixing step.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Method</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Point Mettler</td>
<td>ISO 5940-2</td>
<td>°C</td>
<td>113.0</td>
</tr>
<tr>
<td>Viscosity at 160°C</td>
<td>ASTM D5018</td>
<td>cP</td>
<td>1'550</td>
</tr>
<tr>
<td>Quinoline Insoluble</td>
<td>ISO 6791</td>
<td>%</td>
<td>8.4</td>
</tr>
<tr>
<td>Toluene Insoluble</td>
<td>ISO 6376</td>
<td>%</td>
<td>28.0</td>
</tr>
<tr>
<td>Real Density in Helium</td>
<td>ISO 21687</td>
<td>kg/dm³</td>
<td>1.31</td>
</tr>
<tr>
<td>Ash Content</td>
<td>ISO 8006</td>
<td>%</td>
<td>0.25</td>
</tr>
<tr>
<td>Elements XRF</td>
<td>ISO 12980</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td>ppm</td>
<td>202</td>
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<tr>
<td>Ca</td>
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<td>ppm</td>
<td>311</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>ppm</td>
<td>232</td>
</tr>
</tbody>
</table>

Table 1: Binder Properties

4 Production of the pilot anodes

4.1 Mixing

For each of the four pitch content levels, four pilot anodes are prepared. The 5.5 kg dry aggregates are placed into steel containers for the overnight heating at 200°C in a drying cabinet.

An intensive Eirich impeller mixer of 10 liters capacity is used. The hot dry aggregate is transferred to the mixer and the corresponding cold crushed binder is added. The mixing time is 10 minutes and the paste temperature controlled to be 173°C ±1°C (60°C above pitch SP).

The paste is cooled to 150°C ±2°C by adding 1% of water prior forming.
4.2 Forming

A pilot press having a mould of 146 mm diameter and a maximum pressure of 400 bars is used for forming cylindrical anodes of 200 mm maximum height.

The batch of mixed paste is transferred to the mould and a specific pressure of 200 bars is applied for 1 minute. After unmolding, the anode is cooled to ambient temperature and the dimensions and weight are measured.

A total of 16 pilot anodes are prepared (four pilot anodes for the four pitch content levels).

![Figure 3: RDC 160 Pilot Press](image)

4.3 Baking

A pilot electrically heated bake furnace is used which can accommodate 8 pilot anodes. The 16 pilot electrodes are baked in two different baking runs. Packing material <4mm is used to protect the anodes against oxidation.

![Figure 4: RDC 167 Pilot Baking Furnace](image)
The following heat treatment is followed:

- RT – 200°C: 200°C/h
- 200°C – 800°C: 30°C/h
- 800°C – 1’100°C: 50°C/h
- Soaking time at 1’100°C: 20 hours

### 4.4 Anode Testing

After cooling, the pilot anodes are unloaded and weighted with the possible packing material stuck on their surface. After mechanical cleaning of the surfaces, their cleaned weights are measured. The baking loss and the percentage of sticking of packing material, which is an indicator of excess pitch, can be calculated.

The baked electrodes are core drilled vertically in order to collect 3 cores for each pilot anode, i.e. 12 cores per pitch content tested or 48 cores for the four different pitch levels.

![Figure 5: RDC 179 Pilot Core Drilling Machine](image-url)
The cores for each pitch content level are then tested according to the typical testing schedule shown in the figure below.

Figure 6: Test Schedule Pilot Anodes
4.5 Presentation of the Results

The test results are presented in the forms shown on the next pages. The ranges of results obtained on a worldwide basis for typical prebaked anode coke are shown as grey zones.

The positive effect of increasing the pitch content can be observed up to a given critical percentage where overpitching results in lower shrinkage level (expansion during the devolatilization of pitch) together with reduced baked apparent density and increased permeability. The other properties like the coefficient of thermal expansion and reactivities are less influenced by the pitching as they are simply coke dependent.

A coke candidate giving anodes with properties lying in the grey zone shows a typical performance. When one curve is outside the grey zone this means that the coke shows an inferior or a better performance than typical cokes.

The binder requirement to get

- a maximum baked anode density,
- a minimum sp. el. resistance,
- a given level of mechanical strength,
- or optimum electrical and thermal conductivities,

on the under pitch percentage side can be easily accessed and also compared when several candidates are evaluated.

The maximum percentage of binder guaranteeing no sticking of packing material as well as a given tolerable expansion (less shrinkage) during baking can be determined too.

The levels of the CO₂ and air reactivity residue and dust give valuable information on the burning behavior and on the dusting propensity of the prebaked anodes.

The levels of the flexural strength and elasticity modulus along with the thermal expansion and conductivity allow the prediction of the thermal shock resistance potential of the full size prebaked anodes in the pots.
### PILOT ANODE RESULTS

#### Physical / Electrical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PITCH</td>
<td>B/900</td>
</tr>
<tr>
<td>COKE</td>
<td>C/------------</td>
</tr>
<tr>
<td>BUTTS</td>
<td>No</td>
</tr>
<tr>
<td>REF.</td>
<td>PAB/------------</td>
</tr>
</tbody>
</table>

#### Graphs

1. **Green App. Density** (kg/dm³)
   - Range of Cokes
2. **Shrinkage (Vol.)** (%)
3. **Baked App. Density** (kg/dm³)
4. **Spec. El. Resistance** (µOhm)
5. **Flexural Strength** (MPa)
6. **Compr. Strength** (MPa)
7. **Thermal Expansion** (10⁻⁶K⁻¹)
8. **Elasticity Modulus** (GPa)

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PILOT ANODE RESULTS

Burning Behaviour Properties

PITCH : B/900
COKE : C/-------------
BUTTS : No
REF. : PAB/-------------

PERMEABILITY (nPm)

THERMAL CONDUCTIVITY (W/mK)

RANGE OF COKES

CO₂ REACTIVITY RESIDUE

AIR REACTIVITY RESIDUE

CO₂ REACTIVITY DUST (%)

AIR REACTIVITY DUST (%)

CO₂ REACTIVITY LOSS (%)

AIR REACTIVITY LOSS (%)

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5 Conclusions

The pilot procedure delivers anode results allowing to answer to the question “is a candidate coke anode grade?” and to pinpoint on its strength and weakness.

For refiners and calciners, this pilot study will be the base of an improvement program when needed and for the end-users in the carbon plant it can provide the green light for full size trials. The precious information resulting from the pilot evaluation can guide any process adaptations in the carbon plant as well.