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# Compaction properties of carbon materials used for prebaked anodes in aluminum production plants

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ABSTRACT

The anodes used in aluminum production are formed by compaction of a paste composed of binder matrix and coarse particles of petroleum coke (aggregates). Binder matrix composed of a coal tar pitch and fine calcined petroleum coke is usually characterized by coke and/or pitch content and also by the fineness of the coke particles. Since the coke particles are rigid and assumed to be non-deformable during compaction, the deformation behavior of the binder matrix plays a crucial role in the anode paste compaction process. Compaction of binder matrix with different compositions in a rigid closed die was studied in this work. Binder matrix compositions were compacted to a maximum uniaxial pressure of 70 MPa at 150°C. Different strain rates of $2.9 \times 10^{-4}$ $s^{-1}$ and $2.9 \times 10^{-3}$ $s^{-1}$ enabled us to evaluate the contribution of viscous behavior of the material to the compaction of binder matrix as a function of its composition and deformation rate. A similar experimental compaction procedure with strain rates of $1.8 \times 10^{-4}$ $s^{-1}$ and $1.8 \times 10^{-3}$ $s^{-1}$ was applied on paste samples with different pitch contents. This study revealed that the compaction of binder matrix and anode paste with conventional compositions is not significantly a time dependent process. Viscous behavior may therefore not have a significant contribution to the compaction of the material.



## 1. Introduction

The anodes used in aluminium smelting process are made by mixing carbonaceous materials with coal tar pitch (binder) to form a paste with a doughy consistency. This material is most often vibro-compacted but in some plants pressed during which it is deformed and densified. The green anode is then sintered to increase its strength through decomposition and carbonization of the binder. Green density of anode depends on the compaction behavior of the paste and strongly correlates with final density, electrical [1] and mechanical [2] properties of the anode. The main target of anode makers is therefore to obtain high and homogeneous density through the anode in order to decrease its electrical resistivity and to increase its service life. This work was performed to study the compaction behavior of anode paste and to reveal the effect of its rheological behavior on its compaction during forming.

Two size ranges of coke are normally used to make anode paste: large aggregates (>0.15 mm and <9.5 mm) and fine particles (<0.15 mm), also called fine coke. During mixing, fine cokes are embedded into the liquid pitch resulting in a viscous material, which surrounds the large coke aggregates. This viscous material, also called binder matrix, acts to bond the aggregates together. It also deforms during compaction and fills the voids either between the large aggregates or inside them. The coke aggregate particles are considered as a non-deformable phase of the paste but being subjected to rearrangement during compaction. Coke aggregates and binder matrix are therefore the principal constituents of anode paste, which may influence its compaction properties, and consequently the green density obtained after compaction.

Since the binder matrix surrounds the coarse coke particles and deforms during compaction, its rheological parameters could be important in determining compaction behavior of paste. In turn, volume fraction and granulometry of fine coke could be considered as two major parameters affecting the rheological properties of the binder matrix and its capability in filling the voids. The research works on prebaked anode paste have been mostly focused on the effect of fine coke granulometry on the pore filling capability of binder matrix and on the properties of the final product. Hulse [3] reported that prebaked anode paste has a granulo-viscoelastic behavior which depends on temperature, pitch content and coke particle characteristics such as size distribution, shape and roughness. By increasing the pitch content and temperature the viscosity of paste decreases and viscosity has a larger contribution in the compaction. Higher coke content and coke fineness on the other hand enhance the elastic behavior. Figueiredo [4] showed that by using smaller particle size of the fine coke and optimizing the pitch content a larger density and lower electrical resistivity and air permeability can be obtained. Similar improvement was reported on the

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baked properties of binder matrix only, when the weight fraction of fine coke particles smaller than 96 μm was increased from 43% to 86% and optimum pitch content was used [5]. It has also been reported that the granulometry and the amount of fine coke influence the capability of the binder matrix in filling the voids between coke aggregates. Vidvei [6] found out that decreasing the particle size of the fine coke (60% smaller than 75 μm) led to an improvement in anode density and a decrease in electrical resistivity. However, behavior of paste during compaction was not reported in the literature.

Rheological properties of binder matrix have been extensively investigated for Soderberg anodes where the anode is not pre-formed but baked in-situ over the electrolysis cell. Gildebrandt et al. [7,8], Kravtsova et al. [9] and Vershinina [10] studied the effect of coke content, temperature, and particle size of fine coke on viscosity of binder matrix. Their experimental data showed that the viscosity of binder matrix decreases with increasing temperature and particle size of fine coke but it increases significantly when the amount of fine coke (<74 μm) exceeds over 50 wt% of binder matrix. The possible explanation for the effect of particle size on viscosity has been given by Hulse [3] and Kravtsova [9] who ascribed this effect to direct particle-particle interaction, number of contacts and thickness of pitch layer on the particle surface. Sakai [11,12] found that 50 wt% of fine coke in binder matrix is a critical point since its behavior changes from Newtonian to viscoelastic when coke amount exceeds this point. Again, the influence of binder matrix formulation on compaction behavior of paste and green density of anode has not been considered in these works since they have been mostly carried out on Soderberg anodes where the compaction of paste is not of great interest. There is thus a lack of information on the effect of binder matrix parameters on anode paste compaction behavior.

Anode forming process takes place within a relatively short period of time, typically one minute for vibro-forming and half a minute for pressing. Considering the viscous properties of binder matrix, at a first glance, one may expect that the compaction rate plays a significant role in paste compaction behavior. Strictly speaking, it is expected that the paste shows a time dependent behavior and the viscous phase, i.e. binder matrix, flows under pressure and fills the voids over time leading to a better densification at longer pressing times. On the other hand, at high coke volume fractions, a solid skeleton may form and the compaction behavior may be governed by the strength of the particle/particle contacts. This study aimed thus to reveal whether the binder matrix and paste exhibit a time-dependent behavior and whether this time dependency affects the compaction behavior of anode paste. However, in addition to rheological behavior, other phenomena such as air entrapment may affect the time dependency and compaction behavior of the material that can be studied in future works. In a first step, the compaction characteristics of binder matrix as a function of weight fraction and particle size of fine coke were studied. Then the compaction tests were performed on paste with different pitch contents and fine coke granulometries to better understand the viscous behavior and its importance in the compaction of paste with different formulations.

## 2. Materials and methods

A commercially available calcined petroleum coke with a real density of 2.057 g/cm$^3$ was milled in a laboratory ball mill to produce fine coke. Different milling times were used to obtain three different granulometries. Size distribution and Blaine number (BN) of the fine fractions were measured by sieve analysis and laser diffraction particle size analyzer (Malvern Mastersizer 2000), respectively. Blaine number is an indication of specific surface area (SSA) and is used to assess the fineness of the powder. Specific surface area of the fine cokes was measured using BET method (Micromeritics, TriStar II). Table 1 presents the milling parameters, particle size distribution and specific surface area of the prepared fine cokes.

Each fine coke with a given Blaine number was mixed with a coal tar pitch at different pitch to fine coke ratios (P/FC), indicated in Table 2, to produce a binder matrix. The pitch had a Mettler softening point of 109 °C and a quinoline insoluble (QI) content of 15.5%. Lower P/FC ratios were used for the samples with a Blaine number of 2300 since this Blaine number represents lower specific surface area to absorb the pitch. Fine coke and pitch were preheated at 178°C and mixed at 178°C for 10 minutes in a Hobart N50 mixer, installed in an oven. The total mass of fine coke and pitch was 274 g for all formulations.

The binder matrix compositions were compacted in a cylindrical steel mold with an inner diameter of 63 mm. The height of the samples was measured after putting the punch on the sample before compaction and the bulk density of each composition was calculated. Compaction tests were carried out at two constant displacement rates (DR) of 1 and 10 mm/min. Average deformation rates were calculated using the initial and final heights of the samples (Table 2). Uniaxial pressure was progressively increased to 70 MPa. The tests were performed at 150°C inside a three zone split-tube furnace mounted on a MTS Servohydraulic press. Force-displacement data were obtained from the machine using a 250 KN MTS load cell and a 150 mm position transducer (LVDT) of the press. Mass, diameter and height of the samples were measured and used to plot the compaction curves. Having the real time height of the sample inside the mold, geometrical density was calculated at each point of the force-displacement curve. Evolution of the relative density was then plotted as a function of applied pressure. Relative density is the ratio of geometrical density to the real (theoretical) density of the material. Real density of coke and pitch were used to calculate the real density of pitch/coke compositions. Each sample was repeated twice to ensure the repeatability of the test. The tests were repeatable thus the results of one test for each sample were used in this work.

For the second part of the tests, the influence of displacement rate on the compaction of anode pastes (including large aggregates) with different compositions was studied. Table 3 shows the size distribution of coke particles used to prepare the samples. Table 4 summarizes the formulations of paste samples and the compaction parameters used for each sample. Our preliminary experiments showed that when the Blaine number of the fine coke is 4000 the optimum pitch to coke ratio (P/C) is 16.2/100. This P/C ratio results in a maximum baked density of anode. Total mass of coke and pitch was 488 g for all compositions. The paste samples were made with the same mixing parameters as used to prepare the binder matrix. They were then compacted at 150°C to a maximum pressure of 60 MPa at different displacement rates of 0.1, 1 and 10 mm/min. Average strain rates are shown in Table 4. Two replicates of each sample were prepared to verify the test repeatability.

For further investigation of the viscous behavior of the paste during compaction, a creep test was performed on the paste samples. The paste samples were first compacted with a displacement rate of 10 mm/min

**Table 1**
Ball milling parameters, size distribution and specific surface area of the fine cokes.

| Ball milling parameters | | | Blaine number | Particle size distribution (wt%) | | | | | BET surface area (m$^2$/g) |
|---|---|---|---|---|---|---|---|---|---|
| Batch weight (kg) | Initial particle size (mm) | Milling time (min) | | +149 μm | −149 + 74 μm | −74 + 53 μm | −53 + 37 μm | −37 μm | |
| 4 | −2.38 + 1.41 | 60 | 2300 | 22.8 | 35.5 | 10.7 | 10 | 21 | 2.9 |
| 2 | −2.38 + 1.41 | 34.5 | 4000 | 1.6 | 26.4 | 20.2 | 16 | 35.8 | 4.1 |
| 2 | −2.38 + 1.41 | 49 | 6300 | 0 | 10.7 | 20.6 | 26.2 | 42.5 | 6.1 |