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Quality of Calcined Petroleum Coke and Its Influence on Aluminium Smelting

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Abstract

This paper reports a study on the structure and porosity of calcined petroleum coke (CPC), the impact on mechanical properties of the corresponding baked anodes; and their behaviour in electrolytic reduction cells, especially the susceptibility towards thermal shock. This work was supported by characterization techniques used by CVG Venalum and PDVSA (Venezuela), such as mercury porosimetry, physisorption, and image analysis by optical microscopy (OM). The results indicated that good CPC quality is reflected by good mechanical anode properties as long as the anode manufacturing process is stable. The anode properties are related to the OTI (optical texture index). It is therefore possible to predict the anode behaviour from the CPC structure and porosity, take appropriate action, and decrease the net carbon consumption (NCC).

Introduction

The primary aluminium industry in Venezuela is represented by CVG Venalum, Alcasa, and Carbonorca, importing some 400t calcined petroleum coke (CPC) annually.

The CPC demand by the aluminium industry grows faster than the supply. The CPC market is therefore short, which is reflected by a global CPC quality deterioration. This has been the focus of numerous studies, for example on the adaptation of the anode manufacture processes and the use of "non traditional" cokes. Previously, these cokes were considered not suitable for anode manufacture.

CPC procurement has been affected by the shortage of crudes suitable for the production of anode-grade coke. This resulted in increasing prices and more use of CPCs with higher impurity content and varying textures such as increasing concentrations of isotropic coke. These changes are reflected by increased impurity levels in the produced aluminium, higher anode porosity, and a higher coefficient of thermal expansion (CTE). The higher CTE increases the susceptibility towards thermal shock cracking.

Texture
The CPC texture mainly depends on the nature of the coker feedstock. Aromatic oils yield anisotropic cokes, whereas isotropic cokes originate from paraffinic and asphaltic oils.

Porosity:
Coke porosity influences the required binder level, the bulk density, and the mechanical properties of the baked anode. The pore size has a significant impact on the gas reactivity, as the pitch binder penetrates into the pores larger than 15 microns, while gas diffusion in pores narrower than 0.5 microns is very slow. Therefore, the concentration of pores between 0.5 and 15 microns should be as small as possible. Pores are classified according to their size [1]:

- Macropores (15µm-50µm), small influence on the permeability and surface area.
- Micropores (0.5µm-15µm), influences the CPC CO_2 reactivity.
- Submicropores (<0.5 microns), due to the small diffusion coefficient of CO_2, very small impact on CPC CO_2 reactivity.

Mercury intrusion porosimetry:
This technique is widely used to determine the pore size distribution and the pore volume. It is applicable when the material is sufficiently rigid to resist high compressive forces and does not amalgamate. Pore diameters between about 360 and 0.003 microns can be evaluated.

Nitrogen adsorption
Nitrogen adsorption at its boiling temperature (-196 ºC) represents the most widely used technique to determine total surface area and the volume and dimensions of micro and mesopores. Nitrogen adsorption is complimentary to mercury porosimetry which is better suited for marcopores.

Optical microscopy:
Information on the coke texture can be obtained by optical microscopy. An approach to quantify this information is the optical texture index (OTI) [2]. The observed textures are classified according to Table 1 and the OTI is calculated following Eq. (1).

$$OTI = \sum_{i}^{n} f_i x OTI_i \qquad (1)$$

where f_i: fraction of the optical texture, OTI_i: corresponding factor shown in Table I.

The OTI can be considered as a measure of carbon anisotropy. A high OTI corresponds to highly anisotropic coke. According to ref. [3], the OTI values for petroleum cokes range from 2.7 to 22.4. Anode-grade cokes have OTI values between 3.2 and 12.3. The OTI correlates with other properties, such as the electrical conductivity and the CO_2 reactivity.

Table I. Nomenclature to describe optical textures in cokes [2]			
Texture		Size	OTI_i
Isotropic	I	No optical activity	0
Fine-grained mosaics	Mf	<1.5 µm	1
Medium-grained mosaics	Mm	1.5-5 µm	3
Coarse-grained mosaics	Mc	5-10 µm	7
Medium-flow anisotropy	MFA	<30 µm length, <5 µm width	7
Supra mosaics	Ms	Aligned mosaics	10
Small domains	SD	10-60 µm	20
Coarse-flow anisotropy	CFA	30-60 µm length, 5-10 µm width	20
Domains	SD	>60 µm	30
Flow-domain anisotropy	FD	>60 µm length, >10 µm width	30

Experimental Procedures

For this study, four CPC samples from traditional suppliers, identified as A, B, C, and D as well as 136 cores of baked anodes manufactured by Venalum from these cokes were characterised.

The following characterization methods were used:

- ASTM D5061-92 (Reapproved 2004), coke texture by optical microscopy.
- COVENIN 2231-85, sieve analysis of petroleum coke.
- ASTM D 4222-03, specific surface area by nitrogen adsorption.

Baked anode cores were prepared for analysis following R&D Carbon procedures [4]. The heat transfer coefficient for the baked anodes was determined according to Eq, (2):

$$h = \frac{\left(-\ln\left(\frac{T-T_\infty}{T_i-T_\infty}\right).\rho.V.c\right)}{A_s.t} \qquad (2)$$

where: h: heat transfer coefficient, T: sample temperature; Ti: initial temperature, T_∞: Temperature around, As: Surface Area. ρ: density, V: volume, c: heat capacity, t: time

The thermal shock resistance (TSR) factor was calculated according to Eq. (3) [5].

$$TSR = \sqrt{\frac{2G\left(\frac{V_{muestra}}{V_{anodo}}\right)^{1/m}}{\pi.a.E}}.\frac{2.\lambda(1-2\nu)}{\alpha.L.h.Y.\Delta T} \qquad (3)$$

where G: fracture energy, V_{sample}: sample volume, V_{anode}: anode volume, m: Weibull modulus, a: characteristic crack dimension, E: static modulus of elasticity, λ: thermal conductivity, ν: Poisson ratio, α: thermal expansion coefficient, L: immersion depth, h: heat transfer coefficient, Y: geometry factor, ΔT: temperature difference bath anode.

Porosity Analysis

Mercury (Hg) porosity analysis was conducted with an AutoPore IV 9500 instrument from Micromeritics. CPC samples were ground, moisture was removed by applying vacuum (50 torr), afterwards the sample was immersed in Hg and subjected to pressures from 0.5 to 45psi.

Anode Porosity was determined according to Eq. (3):

$$\%\ Porosty_{baked\ anode} = (1-BAD/RD)*100 \qquad (3)$$

where: BAD: baked anode density, RD: Real density in CPCs.

Nitrogen adsorption

The adsorption tests were performed with a TRSITAR 3000 – ASAP 2010 instrument from Micromeritics. Prior to the experiments, samples of 0.5 to 1 g CPC were degassed at 200°C. Nitrogen isotherms were recorded at -196 °C for reduced relative pressures (P/P_0) between 0.025 and 0.99.

Optical Texture Index (OTI) Measurement

CPC samples (20g) were embedded in 1¼ inch Bühler molds, using resins and fast curing epoxy hardener (for about 1 hour), de-molded, and polished with alumina of 1, 0.3, and 0.05 microns. Between each sequence of grinding (with 320, 400, 600, and 800 grit sandpaper) and polishing, the specimens were washed with soap and water, before they were placed in a beaker with alcohol and exposed to ultrasound for 10 min. Grayscale micrographs were recorded with a Olympus BX-51 microscopy equipped with 50X SLMP objective using cross polarized light. The boundaries of regions with the same crystalline orientation were established by assuming that they correspond to variations of the grayscale between adjacent pixels larger than 60%. The OTI for these regions was determined according to the dimensions listed in Table I.

Results and Discussion

Average properties of the four CPCs used between 2006 and 2009 are presented in Table II. There were only moderate differences between the physicochemical properties of the CPCs.

Table II. Physicochemical Evaluation of petroleum cokes used in CVG Venalum						
Property	Unit	Spec.	A	B	C	D
Moisture	%	0.20 max	0.03	0.02	0.02	0.01
Volatile	%	0.30max.	0.3	0.28	0.29	0.29
Ash	%	0.50max.	0.21	0.17	0.15	0.2
Fixed carbon	%	99.00max.	99.47	99.54	99.55	99.5
S	%	1.9 - 2.8	2.57	2.25	2.17	2.6
Fe	ppm	300max.	199	177	131	181
Si	ppm	200max.	190	122	139	190
Ni	ppm	220max.	166	157	189	206
V	ppm	270max.	253	223	215	146
Ni+V	ppm	450max.	419	380	404	352
Na	ppm	150max.	71	57	30	57
Ca	ppm	150max.	95	89	30	69
Ti	ppm	30max.	n.d	n.d	n.d	n.d
L_c	Å	-	32.97	31.17	31.07	31.08
Physical Properties						
Real Density	g/cc	2.06–2.09	2.066	2.071	2.07	2.066
Bulk Vibrated Density	g/cc	0.87	0.879	0.877	0.883	0.870
Electrical resistivity	µohm-m	460 -520	452	459	474	443
CO_2 Reactivity	%	10max.	6.5	7.94	4.9	6.28
O_2 Reactivity 600°C	%	0.15max.	0.11	0.10	0.11	0.14

Surface Area and Porosity

Morphological characteristics of the CPC were determined by nitrogen adsorption and mercury porosimetry.

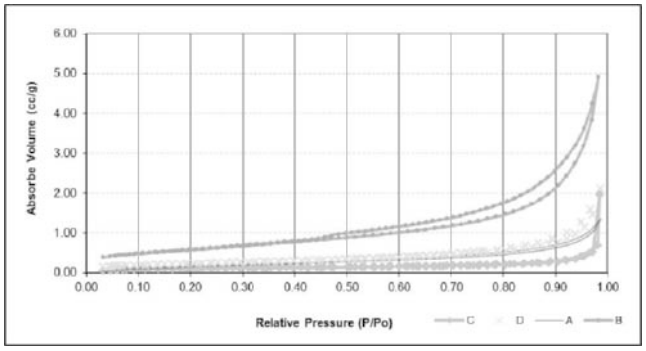

Figure 1. CPCs nitrogen adsorption isotherms

The isotherms of all four CPCs showed H3-type isotherms (Figure 1). This type is typical for solids with slit-shaped mesopores and no microporosity [6]. The absence (very small volume) of micropores was also confirmed by t-plot analysis of the adsorption data (Table III). The BET surface areas of the four CPCs were relatively small and did not differ too much.

Table III. CPC surface area and micropore volume ranges by nitrogen adsorption				
Samples	A	B	C	D
Superficial Area BET (m^2/g)	0.64 -2.09	0.85-2.11	0.40-0.55	0.33-0.85
Micropores Area (m^2/g)	0-0.45	-0.11*	0.16-0.19	0.04-0.20
Micropores Volume (cm^3/g)	0.000237	-0.000066*	0.000080	0.000006

* Apparent negative value, most probably due experimental uncertainty associated with very small volumes of adsorbed nitrogen

The Hg porosimetry data showed very similar pore size distributions for all the CPC samples (Figure 2). The pore volumes and sizes were also similar (Table IV). Pore diameter ranged from 10 to 173µm. The average surface area was about $3m^2/g$, which is characteristic of macroporous solids.

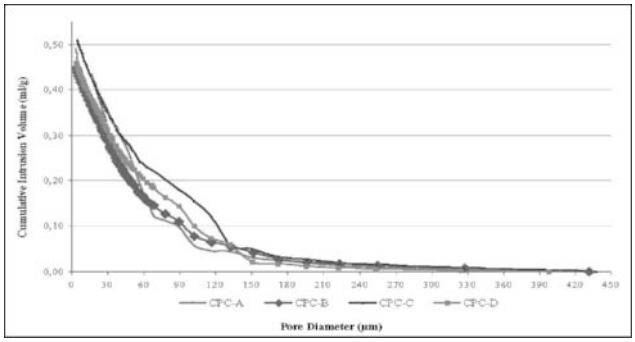

Figure 2. Cumulative CPC pore volumes by Hg porosimetry

Table IV CPC pore characteristics by Hg porosimetry				
CPC	Pore Volume (cc/g)	Pore Diameter distribution (µm)	Average Pore Diameter (µm)	Surface area(m^2/g)
A	0.51	10 - 173	100	3.0
B	0.45	63 - 172	101	3.4
C	0.51	66 - 171	109	2.9
D	0.46	66 - 151	96	2.9

CPC Texture

The concentrations of the different textures identified in the CPCs are presented in Figure 3. The most prevalent textures were small, medium, and coarse mosaics. These textures have small OTI factors (Table I). Only small concentrations of anisotropic textures were found. An example for such a texture is presented in (Figure 4, coke A).

The concentrations of the different textures in CPCs A, C, and D were similar. As compared to these CPCs, CPC B had a higher concentration of fine mosaics and lower concentrations textures with high OTI factors. It is reasonable to assume that coke B was produced from feedstocks containing significant amounts of asphaltenes, which favoured isotropic textures.

CPCs A, C, and D had OTI values in the range of typical anode-grade cokes (3.2 - 12.3); whereas the OTI of CPC B was lower than this range (Table V).

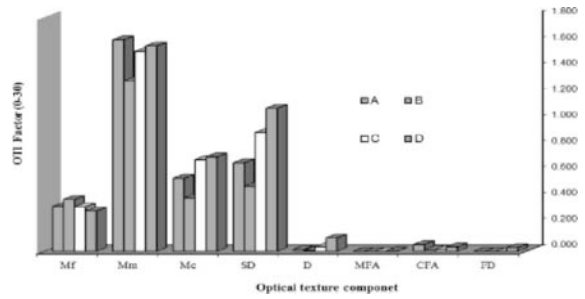

Figure 3. Concentration of textures identified in the CPCs

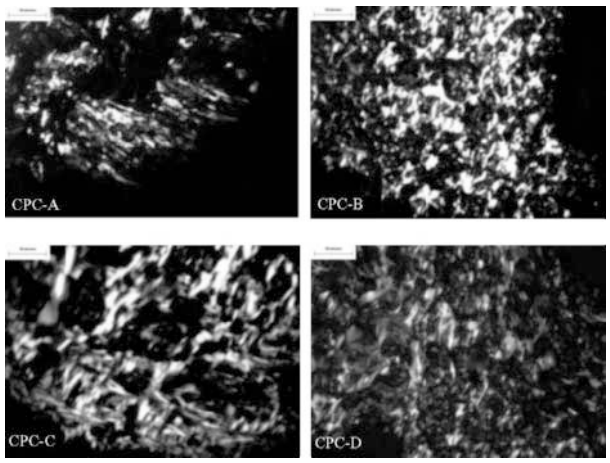

Figure 4. Optical micrographs of the different CPCs. Black zones are isotropic areas.

Anode Porosity

As compared to the other anodes, anodes manufactured with CPCs A and D had lower porosities, reflecting the low porosities of these CPCs (Tab V).

Anode made with CPC D also had a low permeability. The lowest permeability, however, was observed for anodes made with CPC B, which had a higher porosity. This observation is explained by operational stability in the carbon plant during usage of this coke.

Table V. CPC OTI, CPC porosity, and porosity of the corresponding anodes

Sample	Real Density$_{CPC}$ (g/cc)	Baked Anode Density (g/cc)	Pm (nPm)	Theoretical Porosity (%)	Exp. Porosity$_{CPC}$ (%)	OTI
A	2,066	1,538	2,432	25,6	7,11	3,28
B	2,071	1,530	1,670	26,1	11,34	2,64
C	2,070	1,531	4,662	26,0	11,09	3,54
D	2,066	1,550	1,962	25,0	7,17	3,89

Susceptibility Towards Thermal Shock

As compared to the other anodes, anodes made with CPC B had a lower TSR value, indicating a high susceptibility towards thermal cracking (Figure 5). Its TSR value (0.65 ± 0.17) is characteristic for isotropic cokes and in agreement with the low OTI value reported in Table V.

Anodes made with CPC C had better mechanical properties as evidenced by a higher TSR value (1.11 ± 0.05) and good performance in reduction pots. The corresponding anodes had a lower carbon consumption (0.423 ± 0.07 t/tAl) as compared to anodes made with the other cokes studied.

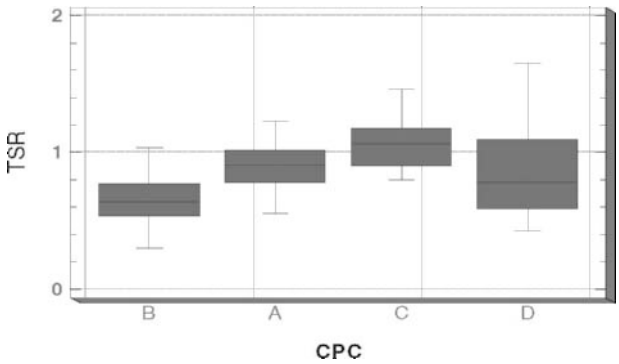

Figure 5. TSR factor statistical analysis

Conclusions

Coke texture and porosity and anode quality correlate well. Thus, data from coke optical microscopy and Hg porosimetry allow prediction of anode performance, especially when comparing cokes with otherwise similar properties.

The study confirmed that the CPCs used by CVG Venalum from 2006 to 2009 were in general of high quality. Anodes made with the best performing among the CPC studied (CPC C) had a low net carbon consumption of 0.42 t/tAl, and high resistance towards thermal shock.

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