STUDIES OF ELECTRODIC SODERBERG PASTE

W. A. G. Oliveira, M. M. Coser, A. G. Cunha, K. M. B. Alves, E. J. Lourenço and F. G. Emmerich*
Departamento de Física, Universidade Federal do Espírito Santo, 29060-900 Vitória, ES, Brazil
**Carboindustrial S.A., Rua Atalydes M. de Souza, 245, 29168-060 Serra, ES, Brazil*

Introduction

The Soderberg paste is employed to form the Soderberg electrode that conducts the electric current in reduction furnaces; it is prepared by a hot mixture of a dry carbonaceous material with a binder. Usually the dry carbonaceous material is anthracite or calcined petroleum coke and the binder is a coal tar pitch. The quality of the final paste depends on the raw materials and their mixture procedure. The objective of the present study is to investigate important physical properties of the raw materials and of the final product and for that we have made measurements of apparent and true densities, hardgrove grindability index-HGI, electrical resistivity, BET surface area, dynamic elasticity modulus, proximate analysis and Mössbauer spectroscopy.

Experimental

The samples were collected and prepared according to the ASTM methods; the measurements of true density were made using the picnometer method with helium as the displacement fluid, in a Quantachrome multipicnometer (model MVP-1), and the BET surface area was determined with an automatic analyser (Quantachrome model Quantasorb) with N_2 adsorption at 77 K.

The dynamic elasticity modulus was obtained through the room temperature measurement of the fundamental resonant frequencies of a slender bar of rectangular cross section. In this method, transverse vibrations are generated and received by two mechanical transducers placed at the middle of the specimen length, one acting as transmitter and the other as receiver. The pulse generator and the transducer combination are connected to an FFT (Fast Fourier Transform) analyser.

The test apparatus for electrical resistivity measurements consists of a Keithley electrometer (model 617) with internal source of precision of 50 mV and a Keithley nanovoltmeter (model 197 A). The samples of green and calcined anthracites were prepared in the form of rectangular parallelepipeds and the samples of coke were powdered. The grindability of anthracite and coke was determined with the "Hardgrove Grindability Test", which has been adopted as a standard procedure (e. g. ASTM). All the samples were submitted to the same grinding conditions in a miniature pulverizer for reduction of the particle size. The measurements of Mössbauer spectroscopy were made at room temperature on powder samples of the raw materials and of the final product, with a radioactive source of Co^{57} in a conventional transmission spectrometer.

Results and Discussion

The results of proximate analysis, true and apparent densities, porosity and BET surface area for the raw materials before and after heat treatment and for the final product are reported in Table 1. We observe that the value of the true density of the calcined petroleum coke is close to that of graphite (2,26g/cm^3), which shows that the calcination process has produced an accessible microporosity for the displacement fluid (helium). This behaviour of the microporosity can also be noted in the results of BET surface area because this measurement is dominated by the fine pore structure of the material.

The dynamic elastic modulus of the Soderberg paste was obtained for any grain orientation, and the results are shown in Table 2 for samples collected at different positions along the paste, a cylindrical rod with 70 cm of lenght. A comparison with the results of the static elastic modulus shows that these values are close, but an advantage of the dynamic test is that it is non-destructive. In this same table the values of the apparent density of the paste are given: our measurements show that there is a linear relation between the dynamic elastic modulus and the apparent density, according to other results in the literature [1].

Ours results for the variation of electrical resistivity of green anthracites with the temperature are shown in Figure 1. In the interval of temperature considered the data are satisfactorily adjusted to an exponential curve. This behaviour was also found by Inokuchi, Schuyer and Van Krevelen [2] and it is related with a percolation transition characterised by an increase of the conducting phase of the materials [3]. The electrical resistivities of the green and calcined petroleum cokes were measured at room temperature and the results show that there is a decrease of eight orders of magnitude after calcination [4].

The hardgrove grindability index-HGI of anthracites does not show significant modification after heat treatment, but the HGI of calcined petroleum cokes presents a reduction of 50% in comparison to the values of green cokes. The HGI is an important parameter to select raw petroleum cokes and coals that are compatible with each other when milled together in a blend, so that segregation of the blend does not occur during particle size reduction.

The Mössbauer spectrum of green anthracite has indicated that the sample does not contain iron sites submitted to hyperfine magnetic fields, but only lines typical of electric quadrupole interaction. However the calcined anthracite presents substances with atoms of iron in magnetic sites; which can be explained by the addition of new materials in the sample due to the fusion of the metallic cylindrical wall that surrounds the arc furnace electrode.

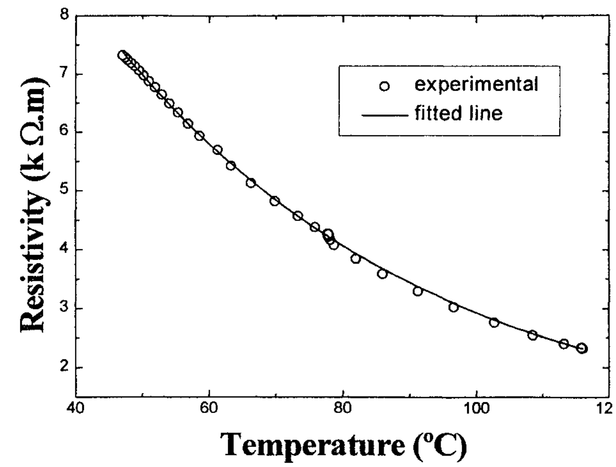

Fig. 1 - Electrical resistivity of green anthracite as a function of the temperature.

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Table 1 - Results of the measured physical properties.

Properties	green anthracite	calcined anthracite	green petroleum coke	calcined petroleum coke	Soderberg paste
Volatile Matter (%)	**5,4**	**0,4**	**8,80**	**2,60**	**15,9**
Ash (%)	**6,7**	**6,3**	**0,71**	**0,34**	**4,65**
Fixed Carbon (%)	**87,9**	**93,3**	**90,49**	**97,06**	**79,45**
Apparent Density (g/cm³)	**1,48**	**1,73**	**0,79**	**-**	**1,392**
True Density (g/cm³)	**1,59**	**1,93**	**1,44**	**2,19**	**1,782**
Porosity (%)	**6,92**	**10,36**	**45,1**	**-**	**21,8**
BET Surface Area (m²/g)	**8,90**	**8,96**	**2,5**	**4,94**	**-**

Table 2 - Results of the dynamics elastic modulus and of the apparent density for three regions of the Soderberg paste.

Regions	Dynamic Elastic Modulus (GPa)	Apparent Density(g/cm³)
Top	**1,5**	**1,359**
Middle	**1,9**	**1,376**
Bottom	**2,4**	**1,423**

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