

ELECTRODE TESTS OF PURIFIED COKE FROM COAL IN ALUMINUM MANUFACTURE

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During the electrowinning of aluminum from aluminum oxide by the Hall process nearly 0.5 pounds of high grade carbon is consumed for each pound of aluminum produced. The raw materials making up this carbon must, of necessity, be of high purity because many metallic impurities in the carbon are transferred to the aluminum produced, and affect the metallurgical properties of the aluminum. For this reason raw materials used in anode manufacture for the aluminum industry have stringent purity specifications.

In addition to the specifications of purity, coke used in the manufacture of electrodes for aluminum production must be heat treated to temperatures of about 1300°C to insure the high temperature dimensional stability of the electrode. It must also contain about 25 percent of particles larger than 1/4 inch to allow for a graduated aggregate in electrode manufacture that is needed to prevent the propagation of stress cracks in large carbon masses.

Because petroleum coke represents a large volume source of relatively pure carbon, it is used almost exclusively for anode manufacture by the aluminum industry in the United States. Some coal tar pitch coke is used in Europe to supplement the supply of petroleum coke.

Coke derived from coal is not used in alumina reduction cell anodes because of the high ash content. Several investigators¹⁻⁶ have studied methods of removing the mineral matter from coal for the purpose of making purified coke for electrode use, and coke from purified coal has been used in Europe on a commercial scale in at least two cases.^{7,8} These were wartime uses, however, and were not competitive when adequate supplies of high grade petroleum coke were available.

Possible future shortages of electrode grade petroleum coke have encouraged the continued investigation of methods of producing high purity coke from coal as a substitute and competitive material for use in electrodes. This report will be concerned primarily with a performance test of electrodes made from a purified coke from coal in pilot plant and commercial alumina reduction cells.

Process Description

Figure 1 is a diagram of the major steps of a process for manufacturing high grade coke from coal. In a pilot plant operated by Reynolds Metals Company for the production of coke, a mixture of high volatile bituminous coal and a solvent oil was digested in a continuous pressure digester to a temperature slightly above the temperature of maximum solubility of the coal.⁹ The coal solution from the pressure digester was charged to centrifuges where the

suspended mineral matter and fusain were separated from the coal solution. This solution from the centrifuge was charged to a continuous distillation still where the solvent was separated and returned to the mixing cycle. The still bottoms which contained the purified coal were charged directly to a coke oven where a purified coal was converted to coke and heat treated to a temperature that would assure dimensional stability at the operating temperature of an alumina reduction cell.

Coal from two sources was run in the pilot plant — the Black Creek seam in North Alabama and the No. 9 seam in Western Kentucky. Typical analyses of these coals are shown in Table I. Typical properties of cokes made from these coals compared with an electrode grade petroleum coke are shown in Table II. Electrical resistivity was determined by the Great Lakes Carbon Company Method, C-12, and the Hardgrove grindability index was determined by ASTM Method No. D409-51. The coke prepared from these coals had a grey metallic luster and was more resistant to grinding than regular petroleum coke. The iron content was the only property of this coke that was inferior to electrode grade petroleum coke and did not meet specifications imposed by aluminum producers. Since the iron content of the coke produced in the pilot plant was about three times higher than coke produced from the same coals in laboratory scale equipment, it is believed that this difference represents iron pickup from the pilot plant processing equipment and is not an inherent limitation of the process.

Two types of carbon anodes are used in the aluminum process. In the prebaked anode type cell, electrode blocks are fabricated from a graded carbon aggregate and coal tar pitch. This mixture is pressed into blocks by large hydraulic presses, and the resulting blocks are heated in furnaces to about 1200°C. The baked block is suspended in the molten salt electrolyte by the electrical connection which is usually made with a steel pin held in a specially molded well in the carbon block by cast iron. In the other type of anode system, which is known as the continuous electrode or Soderberg system, heat from the electrolytic process is used to bake a carbonaceous paste prepared from a graded coke aggregate and coal tar pitch. This paste is added to the top of the anode casing as carbon is consumed by the process from the bottom of the anode. Electrical connections are made through steel pins embedded in the carbon.

Approximately 6000 pounds of coke from purified coal were processed into electrode blocks at the carbon plant of a commercial aluminum plant for tests in a 10,000 ampere scale alumina reduction cell. These blocks were 20 x 16 x 13 inches and each weighed about 200 pounds.

There are two major sources of anode carbon consumption in an alumina reduction cell. These are electrolytic reaction with oxygen released from the aluminum oxide at the working face of the anode and reaction with oxygen from the air on the sides and top of the anode in the area not wet by the molten salt electrolyte. To determine the amount of carbon lost to oxygen from each of these sources, a number of the anodes were capped with an alumina cap prepared from a tabular alumina castable refractory. The rest of the blocks were run without a cap to protect against air burning which is the normal practice in an alumina reduction plant. To provide experimental control and comparison against regular electrode materials, half of the anodes in the cell at any time were prepared from petroleum coke.

Each anode was weighed before being placed in the test cell. After seven days of electrolysis the unburned portion was removed from the cell and weighed. The difference between the initial and the final weights was taken to be equal to the carbon consumed during the test period. The anodes that were capped with an alumina refractory were weighed before capping and after test the remaining cap was broken from the block before the stub was weighed. Each individual anode position on the test cell was equipped with electrical shunts and the current passing through the block during the test period was recorded with integrating ammeters. Results of the test are summarized in Table III. Approximately 30 anode blocks made from the coke from purified coal were tested as were a like number of control blocks made from petroleum coke. This number of blocks was established by statistical treatment of data from previous experiments as being the number required to distinguish a carbon consumption difference of 0.5 gms. /amp. hr. in this type of test cell.

The anode stubs from the coke from coal blocks removed from the test cell were hard and dense and showed no tendency for coke particles to dust from the electrode surface.

In a second test, more than 20,000 pounds of coke made from purified coal were made into a carbon paste and tested in a 45,000 ampere Soderberg type reduction cell. Mechanical properties of electrode specimens prepared from samples of the carbon paste that were baked to about 1,000°C in a laboratory furnace are shown in Table IV with the mechanical properties of specimens from comparable paste made from electrode grade petroleum coke. One notable characteristic of the paste prepared from coke from purified coal was that about two percent less pitch was required than was normally used to prepare paste of comparable viscosity from petroleum coke.

Midway through the test the anode was raised from the electrolyte and inspected. The working face of the anode was flat and smooth and the anode was free of large cracks indicating that the coke from the pilot plant was thermally stable for use at the anode operating temperatures. Cell operation was smooth and efficient and the anode generally could not be distinguished from anodes made from petroleum coke.

Discussion

Examination of the test results summarized in Table III indicate that the consumption of carbon blocks was nearly the same for the coke from coal anodes as it was for the petroleum coke anodes. The difference in consumption between capped and uncapped anodes shows that 20 percent of the carbon in the petroleum coke anodes was lost to air burning compared to 16 percent for the anodes made with coke from coal. This is an indication that the coke from coal electrodes were less susceptible to attack by oxygen in the air. This indication is supported by observations made while determining the ash content that the cokes made from coal required considerably longer time to burn away than did petroleum cokes.

The performance testing of electrodes made from coke from purified coal in both prebaked and Soderberg type anodes indicated that the coke was satisfactory and could meet the specifications for anode grade coke for the aluminum industry.

ACKNOWLEDGMENT

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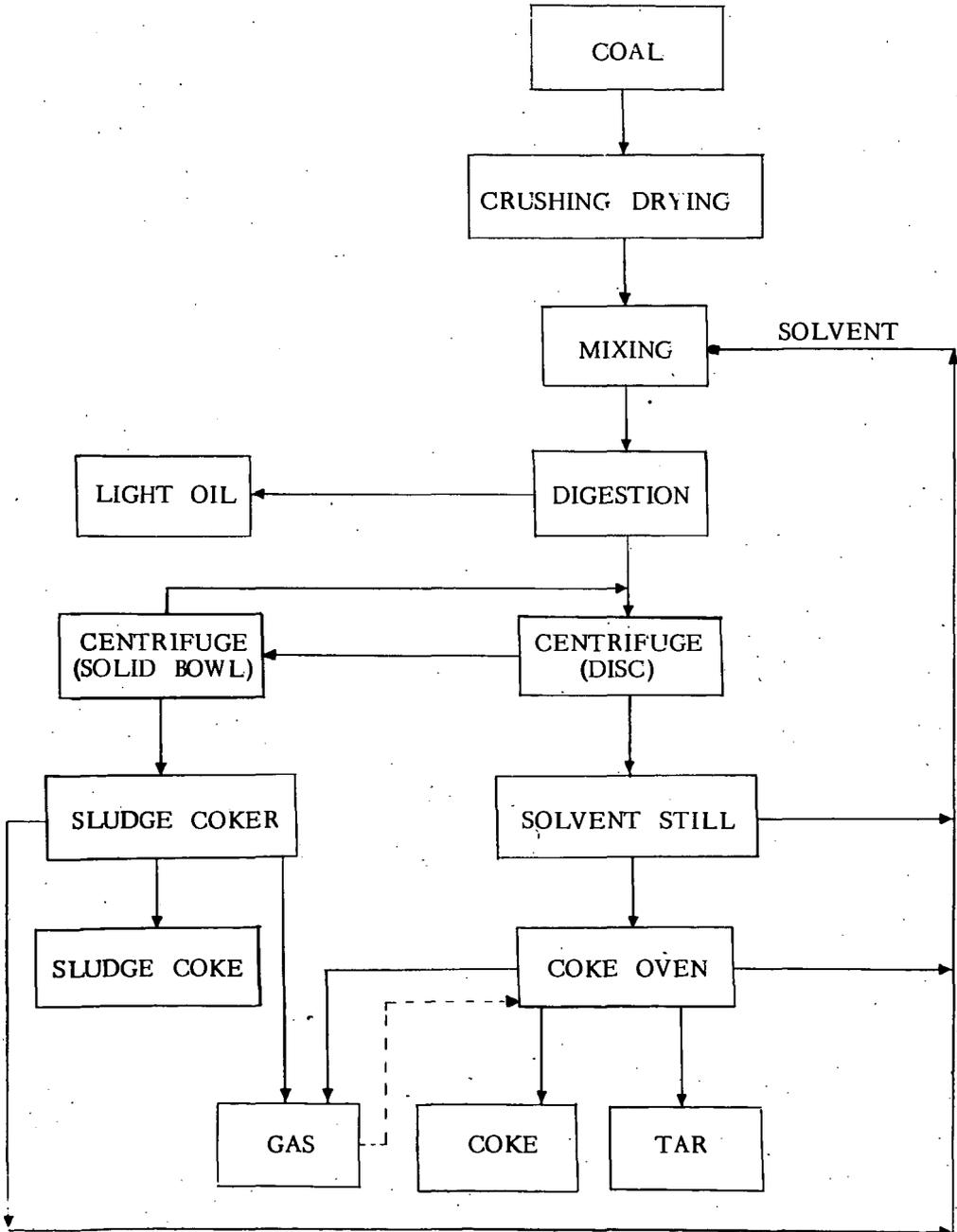


FIGURE 1. DIAGRAM OF A COKE-FROM-COAL PROCESS

TABLE I
ANALYSES OF COALS USED IN INVESTIGATION
OF ELECTRODE COKE FROM COAL.

	Black Creek Coal Seam		Kentucky No. 9 Coal Seam	
	As Received %	Dry Ash-free %	As Received %	Dry Ash-free %
Moisture	2.7	----	----	----
V. M.	35.4	37.4	40.5	45.0
Ash	2.8	----	9.9	----
H ₂	5.4	5.7	5.1	5.6
C	79.8	84.4	72.5	80.5
N ₂	1.7	1.8	1.5	1.7
O ₂	9.5	7.6	7.9	8.8
S	.8	.8	3.1	3.4

TABLE II

PROPERTIES OF COKES FROM KENTUCKY COAL AND
ALABAMA COAL AFTER CALCINING TO 1340°C

	Alabama Coke	Kentucky Coke	Typical Petroleum Coke
Specific Gravity	2.02	2.01	2.03
Electrical Resistivity, ohm-in.	0.029	0.034	0.034
Hardgrove Grindability Index	22	22.5	37
Sulfur, Percent	0.46	0.67	0.8 - 1.65
Silicon, Percent	0.04	0.09	0.03
Iron, Percent	0.07	0.08	0.05
Aluminum, Percent	0.09	0.09	0.02
Ash, Percent	0.58	0.76	0.34

TABLE III
 CONSUMPTION OF CARBON IN A 10,000
 AMPERE PREBAKE ALUMINUM CELL

	Electrode Consumption, gms. /amp. hr.			
	Coal Coke		Petroleum Coke	
	Result	σ	Result	σ
Capped Carbons	0.121	± 0.002	0.118	± 0.003
Uncapped Carbons	0.144	± 0.004	0.147	± 0.004

TABLE IV
 PHYSICAL PROPERTIES TEST RESULTS OF
 SODERBERG ELECTRODE SPECIMENS WITH
 COKE-FROM-COAL AGGREGATE

	Aggregate			
	Coke-From-Coal		Petroleum Coke	
	Result*	σ	Result*	σ
Apparent Density, gms. /cm. ³	1.58	$\pm .03$	1.56	$\pm .02$
Electrical Resistivity, ohms/m/mm ²	53	± 2.2	60	± 1.6
Compression Strength, Kg. /cm. ²	601	± 56	436	± 35

* Average of eight determinations.