

CARBON BODIES PREPARED FROM DEMINERALIZED ANTHRACITE— A COMPARATIVE STUDY WITH DELAYED PETROLEUM COKE

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Abstract—With the carbon electrode market for the aluminum industry in mind, bodies were prepared from low ash anthracite and their properties compared with bodies prepared from a typical calcined delayed petroleum coke. To reduce the ash content, anthracite was heated in one atmosphere of chlorine at 2000°C. In 20 min, the ash content of 100×150 mesh material was reduced from 9.0 to 0.28%, with amounts of the individual elements reduced sufficiently to meet specifications set by the aluminum industry. Properties measured on the fabricated bodies were density, electrical resistivity, crushing strength and reactivity to carbon dioxide. Additional results are presented for bodies, first fabricated from anthracite calcined at 1400°C, and then heat treated between 1750 and 2250°C in chlorine. It is concluded that bodies fabricated from anthracite, as described above, are not competitive with those prepared from calcined delayed petroleum coke, when the bodies are to be used as electrodes for aluminum production.

1. INTRODUCTION

ANTHRACITE is currently being utilized to some extent as a filler in the manufacture of electrodes and pot liners for selected electrolytic and electro-thermal processes, where the high ash content imparted to the bodies by the anthracite can be tolerated. However, the high ash contents of Pennsylvania anthracites have excluded their use in a very sizeable market—that is, as a filler material in carbon electrodes used in aluminum production. Specifications for the total ash content and its major constituents in filler materials used for electrodes in aluminium production are reported to be: ash, <0.80%; Si, <0.08%; Fe, <0.06%; Ca, <0.12%; and Ti, <0.01%. Typical values for calcined delayed petroleum cokes used as fillers in aluminium electrodes are reported to be: ash, 0.45%; Si, 0.04%; Fe, 0.04%; Ca, 0.03%; and Ti, 0.0008%.

The removal of mineral matter from Pennsyl-

vania anthracites has been studied for some time. GELLER and WALKER found that when anthracites were heated in an inert atmosphere for a reasonable soak time, a temperature of ca. 2800°C was required to reduce their ash contents to a level acceptable to the aluminum industry.⁽¹⁾ Obviously, such a costly process would not be competitive with the conventional calcining of raw petroleum cokes at 1300°–1400°C, despite some differences in cost of raw materials.

Recently, IMPERIAL studied the removal of mineral matter from anthracite by calcining at temperatures between 1000° and 1400°C in one atmosphere of flowing chlorine.⁽²⁾ At these temperatures the oxides in the mineral matter, upon their reaction with carbon in the anthracite, are reduced to the metals, which in turn react with chlorine to produce volatile metal chlorides. IMPERIAL found that the discrete mineral matter in anthracite was rapidly removed at 1400°C, but that the inherent mineral matter, which is located in closed pores and within crystallites, was removed only very slowly by this treatment. The ash contents of samples chlorinated at 1400°C

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were still too high for the samples to meet the specifications for use as an electrode material in the aluminum industry.

Consequently, it was decided to investigate the chlorination of anthracite above 1400°C to find temperatures where the ash content could be reduced to acceptable levels using reasonable chlorination times. It was apparent that operation at such temperatures would be more costly than those now used commercially for the calcining of petroleum cokes. However, it was thought possible that these higher temperature calcining conditions would result in the anthracite having some superior properties to calcined petroleum cokes (such as lower electrical resistivity, higher density, and greater strength) which would more than offset the additional calcining expense. This paper presents these studies.

2. EXPERIMENTAL

(a) Fillers used

Two raw Pennsylvania anthracites of medium volatile matter content, A-1 and A-2, and one delayed petroleum coke, P.C., calcined at ca. 1400°C, were used in this program. The P.C. was being used commercially in the production of carbon electrodes at the time of this study. It had an ash content of 0.1%. Proximate analyses of the raw anthracites are given in Table 1. Major constituents in the anthracite ash are silica, alumina, and iron oxides roughly in the amount 55, 36, and 5%, respectively.⁽³⁾ The major constituents of the mineral matter from which these impurities are derived are quartz, kaolinite, pyrite, and biotite.⁽⁴⁾

TABLE 1. PROXIMATE ANALYSES OF RAW ANTHRACITES

Anthracite	Fixed carbon (%)	Volatile matter (%)	Ash (%)
A-1	86.8	4.2	9.0
A-2	85.4	5.6	8.8

Carbon bodies were prepared from 100×150 mesh size fractions of the filler materials. This size fraction of the P.C. was obtained by grinding and sieving the as-received calcined material. Anthracite fillers were prepared by calcining 100×150 mesh raw anthracite in a helium atmosphere at 1400°C. For anthracite A-1, additional filler was prepared by subsequently heating a portion of the

calcined sample for 20 min in one atmosphere of flowing chlorine at 2000°C.

(b) Preparation of carbon bodies

For the anthracites, 82.5 parts of filler to 17.5 parts of coal tar pitch were used as the mix. For the P.C., 80.0 parts of filler to 20.0 parts of pitch were used. The pitch was a conventional medium melting point material, sample 22805, information on which has been published previously.⁽⁵⁾ These formulations were decided upon after experimentation on obtaining mixes of desirable fluidity. Mixing was performed in a sigma blade mixer at 130°C for 30 min. Following mixing, the material was allowed to cool and then crushed to -20 mesh. Green samples of $\frac{1}{2}$ in. dia. and either 1 or 2 in. long were formed by molding at 110°C.*

The green bodies containing the anthracite fillers calcined at 1400°C, were then baked at 850°C for 2.5 hr in nitrogen, having been brought up to this maximum temperature at a rate of 5°C/min. The baked bodies were further heated at temperatures between 1750° and 2250°C in one atmosphere of flowing chlorine, by inserting them into a resistance furnace, while it was maintained at the desired temperature within $\pm 20^\circ\text{C}$. Following a fixed chlorination time, the samples were removed from the furnace and cooled to room temperature in nitrogen.

The green bodies, containing either the calcined P.C. or the anthracite A-1 which was chlorinated at 2000°C, were baked at 900°C for 2.5 hr in nitrogen, following a heating rate to maximum temperature of 5°C/min.

(c) Methods and apparatus for sample testing

Measurements were made, in some cases, on both the bodies and filler materials used in body preparation.

1. *Ash analyses.* Ash analyses were obtained by emission spectroscopy, as described previously.⁽⁶⁾

2. *Electrical resistivity* Electrical resistivities of the bodies were obtained by comparing the potential drop across a known resistance with that across a fixed sample length as previously described.⁽⁷⁾ Electrical resistivities of the filler materials were

*For bodies fabricated from the calcined anthracite, a molding pressure of 3000 psi was used. For bodies fabricated from calcined P.C. and chlorinated anthracite, various molding pressures were used, as indicated in the appropriate tables.

measured by confining a 2 g sample between brass tipped steel pistons in a glazed steatite ceramic cell which was $\frac{1}{2}$ in. I.D. and 2 in. long. The cell, constituting one arm of a Kelvin bridge, was mounted in a Carver hydraulic press, which produced the desired compacting pressure.

3. *Densities.* Densities were determined on the bodies by dividing their weight by their volume. Helium densities of the fillers were determined in a constant pressure apparatus thermostated to a constant temperature within $\pm 0.02^\circ\text{C}$. Particle densities of the fillers were measured by the displacement of mercury at a pressure of 50 psi. At this pressure, penetration of mercury into the voids between 100×150 mesh particles is virtually complete, with penetration of mercury into pores within the particles still negligible.

4. *Strengths.* Flexural strengths were measured on cylindrical samples of $\frac{1}{2}$ in. dia. by 1 in. long using a testing machine produced by K. Frank, Weinheim, West Germany. Crushing strengths were measured on cylindrical samples of $\frac{1}{2}$ in. dia. by $\frac{3}{4}$ in. long, using a Carver laboratory press.

5. *X-ray diffraction studies.* A G. E. XRD-3 instrument was used in diffraction studies. From the (002) diffraction profile, interlayer spacings, crystallite heights, and relative crystallite alignments were determined, using procedures previously described.^(8,9)

6. *Reactivity.* Measurement of reactivities of bodies of $\frac{1}{2}$ in. dia. and 1 in. long at 950°C in one atmosphere of flowing CO_2 was conducted in an apparatus previously described.⁽¹⁰⁾

3. RESULTS AND DISCUSSION

The results of this research can logically be presented under three main sections: those concerned with the anthracite bodies chlorinated between 1750 and 2250°C , those concerned with fillers, anthracite A-1 chlorinated at 2000°C and P.C. calcined at 1400°C , and those concerned with baked bodies formed from the above fillers.

(a) Chlorinated anthracite bodies

Bodies of $\frac{1}{2}$ in. dia. by 1 in. long were chlorinated. Figure 1 summarizes the results for the decrease in ash content with chlorination time, for bodies formed from calcined anthracite A-2. There was an initial rapid decrease in ash content, followed by an extended period of slow decrease.

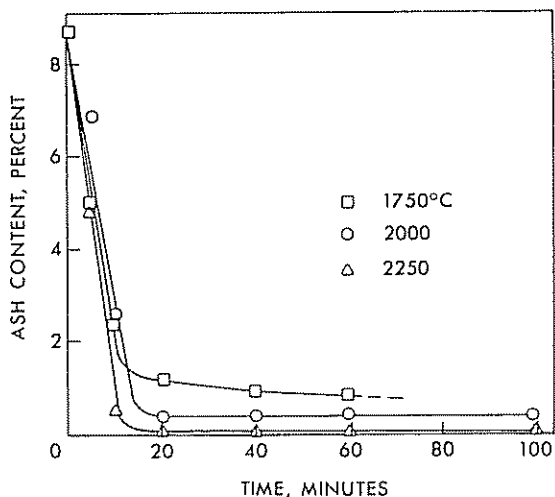


FIG. 1. Ash removal from bodies formed from calcined anthracite A-2 upon chlorination between 1750° and 2250°C .

The rapid decrease in ash content is primarily a result of the removal of metals derived from the discrete mineral matter in the anthracite. This discrete mineral matter, which constitutes roughly 70–80% of the total mineral matter, is accessible to the chlorine through relatively large macropores and cracks. Superimposed on this very rapid decrease in ash content, derived from this discrete mineral matter, is the slower decrease in ash content, derived from the inherent mineral matter. The rate of removal of this ash is determined by the combination of the rates of activated diffusion of metals from within crystallites to the surfaces of pores and of metal chlorides through pores of molecular size. After one hour chlorination time at 1750°C , the total ash remaining was still 0.81%, with the silicon content of 0.25%, considerably above specifications for electrodes for aluminum production. After one hour chlorination at 2000°C , the total ash remaining was decreased to ca. 0.3%, with the silicon content down to 0.05%, which is close to meeting specifications. For a chlorination temperature of 2250°C , the total ash was decreased to 0.17% in 15 min and all constituents of the ash were reduced below specifications.

On the basis of chlorination results for bodies from anthracite A-2, bodies formed from calcined anthracite A-1 were chlorinated at temperatures of 2000 , 2100 and 2250°C . Table 2 presents detailed

TABLE 2. ASH ANALYSES OF CHLORINATED BODIES FORMED FROM CALCINED ANTHRACITE A-1

Chlorination temp. (°C)	Time (min)	Ash content (%)	Individual elements in ash (%)			
			Si	Fe	Ca	Ti
2000	5	3.44	1.05	0.20	0.015	0.065
	10	0.71	0.22	0.03	0.002	0.01
	20	0.35	0.08	0.015	<0.001	<0.001
	40	0.17	0.04	0.009	<0.001	<0.001
	60	0.078	0.018	0.005	<0.001	<0.001
	100	0.015	0.002	<0.001	<0.001	<0.001
2100	5	2.0	0.60	0.10	0.009	0.035
	10	0.38	0.10	0.02	0.001	0.003
	20	0.20	0.05	0.01	<0.001	0.001
	40	0.11	0.03	0.005	<0.001	0.001
	60	0.058	0.015	0.003	<0.001	<0.001
	100	0.007	<0.001	<0.001	<0.001	<0.001
2250	5	0.89	0.25	0.03	0.003	0.01
	10	0.13	0.03	0.005	<0.001	<0.001
	20	0.046	0.009	0.003	<0.001	<0.001
	40	0.009	0.001	<0.001	<0.001	<0.001
	60	0.018	0.002	<0.001	<0.001	<0.001
	100	0.007	<0.001	<0.001	<0.001	<0.001

results for the decrease in total ash content and individual elements, as a result of these runs. Again there was a rapid decrease in ash content during the early stages of chlorination, followed by a much slower rate of ash removal. It is seen that 40 min chlorination at 2000°C reduced both the total ash and individual element contents sufficiently to meet aluminum specifications. Other elements measured after 40 min chlorination time include: magnesium, <0.001%; aluminum, 0.03%; and copper, <0.001%.

In Table 3 densities, electrical resistivities and flexural strengths of chlorinated bodies formulated from anthracite A-1 are given. For comparison, values are also given for the body baked at 850°C prior to chlorination. The density of the baked body is considerably below that usually found, that is 1.4 to 1.6 g/cm³. This low density was achieved deliberately, by using a low molding pressure and a narrow size consist of filler, to permit more rapid access of chlorine to the interior of the body during subsequent chlorination. Of particular significance in Table 3 are the relative results. First, chlorination of the baked bodies at temperatures between 2000 and 2250°C resulted in a significant further decrease in density. This is primarily a result of

TABLE 3. PROPERTIES OF BODIES FORMED FROM CALCINED ANTHRACITE A-1

Time (min)	Density (g/cm ³)	Electrical resistivity ($\Omega\text{cm} \times 10^8$)	Flexural strength (lb/in ²)
Baked at 850°C			
150	1.12	1.38	3690
Chlorinated at 2000°C			
20	1.00	1.26	800
60	0.96	1.26	750
100	0.94	1.44	640
Chlorinated at 2100°C			
20	0.98	1.38	1020
60	0.99	1.28	880
100	0.99	1.31	980
Chlorinated at 2250°C			
20	0.98	1.23	750
60	0.98	1.14	820
100	1.00	1.09	910

removal of the mineral matter with its higher density, ca. 2.7 g/cm³,⁽¹²⁾ and loss of some carbon as carbon monoxide upon further reduction of mineral matter. It was anticipated that the use of elevated chlorination temperatures would result in

a sufficient removal of pores from the anthracite, such that its densification thereby would more than offset the density decrease caused by mineral matter removal. This is the first indication that such was not the case.

Second, chlorination resulted in a negligible decrease in electrical resistivity of the baked bodies heated up to 2100°C. Only at 2250°C was the decrease in electrical resistivity significant. A change in electrical resistivity will be caused by a number of factors. In the present case, since chlorination decreased body density and resulted in the pick-up of some chlorine (ca. 1% by weight as a result of chlorination for 20 min at 2000°C), the electrical resistivity would be expected to increase. This increase would be offset by a decrease in resistivity as a result of increase in crystallite size of the filler and binder carbon and further removal of hydrogen from the body upon heating between 2000 and 2250°C.

Third, as a result primarily of decrease in density, the flexural strength of the bodies decreased sharply upon chlorination.

(b) *Chlorinated anthracite A-1 and calcined petroleum coke*

Prior to comparing the properties of baked bodies formulated from the chlorinated anthracite and P.C. as fillers, it is informative to consider some of the individual filler properties. Chlorination of the 100×150 mesh anthracite for 20 min at 2000°C reduced its ash content to 0.28%. Table 4 presents results obtained from studies of (002)

X-ray diffraction profiles. Based on the FRANKLIN correlation,⁽¹³⁾ the interlayer spacing results indicate that the calcined P.C. had a completely turbostratic structure; whereas the chlorinated anthracite had mostly a turbostratic structure, but also a small amount of structure with three-dimensional lattice ordering. The chlorinated anthracite had a significantly larger average crystallite height, \bar{L}_c , than did the P.C. Despite this, the intensity of the (002) diffraction peak for P.C., above background radiation, was significantly greater than that for the anthracite. As discussed previously, the relative intensity of the (002) diffraction peak can be used as a measure of the relative orientation of crystallites within particles.^(8,11,14) The I(002) results indicate, therefore, that the calcined P.C. had larger domains of mosaic structure than did the chlorinated anthracite. This is consistent with the fact that typical delayed petroleum cokes have better graphitizabilities than do Pennsylvania anthracites.⁽¹⁾ That is, good graphitizability is dependent upon good crystallite alignment.

Table 5 presents density and porosity results for the filler materials. X-ray densities were calculated from the interlayer spacing data and a value of 1.42Å for the carbon-carbon bond distance within the layer planes.⁽¹⁵⁾ It is seen that the total porosity, as calculated from the X-ray and particle densities, was much higher for the chlorinated anthracite than for the calcined P.C. Further, for both fillers most of the total porosity was located in closed pores, or pores inaccessible to helium at room temperature. The closed porosity would be located in or behind openings less than ca. 3.6Å, if the walls of the openings are assumed to be formed by basal planes of adjacent carbon crystallites.⁽¹⁶⁾ These density and porosity results definitely stamp the chlorinated anthracite as an inferior filler material to the calcined P.C. This conclusion will be borne out when we examine the properties of bodies made from these fillers.

TABLE 4. X-RAY DIFFRACTION RESULTS FOR CHLORINATED ANTHRACITE A-1 AND CALCINED PETROLEUM COKE FILLERS

Sample	Interlayer spacing (Å)	\bar{L}_c (Å)	Relative intensity, (002)
A-1	3.43	67	23
P.C.	3.44	41	48

TABLE 5. DENSITY AND POROSITY RESULTS FOR CHLORINATED ANTHRACITE A-1 AND CALCINED PETROLEUM COKE FILLERS

Samples	Densities (g/cm ³)			Porosity (%)		
	X-ray	Helium	Particle	Total	Closed	Open
A-1	2.22	1.83	1.71	22.7	16.5	6.2
P.C.	2.21	2.07	2.03	8.9	6.1	2.8

TABLE 6. BULK DENSITY AND ELECTRICAL RESISTIVITY RESULTS FOR CHLORINATED ANTHRACITE A-1 AND CALCINED PETROLEUM COKE FILLERS

Samples	Compacting pressure (lb/in ²)	Bulk density (g/cm ³)	Electrical resistivity ($\Omega\text{cm} \times 10^3$)
A-1	2000	1.15	2.49
	5000	1.25	1.72
	10000	1.30	1.26
	20000	1.56	1.03
P.C.	2000	1.30	2.21
	5000	1.48	1.69
	10000	1.64	1.24
	20000	1.88	1.03

Table 6 presents results for the bulk density and electrical resistivity of the fillers under various compacting pressures. As expected, the bulk density of the anthracite was lower than that of the P.C. at equal compacting pressures. At a compacting pressure of 2000 psi, the electrical resistivity of the anthracite was significantly higher than that of the P.C. At compacting pressures of 5000 psi and greater, the electrical resistivities of the two fillers were equal. The important point here is that chlorination of anthracite A-1 at 2000°C did not produce a filler of lower electrical resistivity than that produced by calcining P.C. at 1400°C.

(c) *Baked bodies formulated from chlorinated anthracite A-1 and calcined P.C.*

Table 7 presents the properties of the baked bodies. As expected from the filler results, the densities of bodies formulated from anthracite A-1 were lower than those from P.C. at equal molding pressures. To obtain a density of 1.28 g/cm³, a

molding pressure of 20,000 psi was required for the anthracite body; whereas a pressure of only ca. 3000 psi was required for the P.C. body. At comparable molding pressures, the electrical resistivity of the anthracite bodies was higher than that of the P.C. bodies. At equal body densities, for example 1.28 g/cm³, the electrical resistivities were essentially equal. The electrical resistivities were a factor of two to three higher than those generally reported for baked bodies,⁽¹⁷⁾ primarily because of the low density of these bodies. As discussed earlier, the low densities were a result, primarily, of the narrow particle size distribution of the filler used in body fabrication.

At comparable molding pressures, the crushing strength of the anthracite bodies was less than that of the P.C. bodies. At equal body densities, for example 1.28 g/cm³, the crushing strength of the anthracite body was still less than that of the P.C. body. The crushing strength of the P.C. body went through a maximum somewhere between a

TABLE 7. PROPERTIES OF BAKED BODIES FABRICATED FROM CHLORINATED ANTHRACITE A-1 AND CALCINED P.C.

Samples	Molding pressure (lb/in ²)	Body density (g/cm ³)	Electrical resistivity ($\Omega\text{cm} \times 10^3$)	Crushing strength (lb/in ²)	Reactivity in CO ₂ (% burn-off/hr)
A-1	6000	1.13	1.50	630	—
	10000	1.16	1.39	—	—
	20000	1.28	1.16	950	4.5
P.C.	1000	1.23	1.33	1100	—
	2000	1.25	1.24	1300	5.5
	4000	1.34	1.05	3000	5.2
	15000	1.41	0.92	1300	—

molding pressure of 4000 and 15,000 psi. This behavior has been found previously for molded bodies and has been attributed to the crushing of filler particles during compaction, if the molding pressure is too high.^(18,19)

At a body density of 1.28 g/cm³, the reactivity of the anthracite body to carbon dioxide appears to be somewhat less than the reactivity of the P.C. body. In part, this may be attributed to the presence of some chemisorbed chlorine on the anthracite body. Chlorine chemisorbed on carbon is known to retard the gasification of carbon by oxidizing gases.⁽²⁰⁾

Certainly these results are discouraging insofar as the possible use of anthracite, demineralized by chlorine treatment at ca. 2000°C, as a filler for carbon electrodes for aluminum production is concerned. The higher cost of preparing anthracite as a filler for electrodes, using this approach, is not offset by the introduction of superior properties to the bodies, such as lower electrical resistivity and higher strength.

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