CREATE A CONSORTIUM AND DEVELOP PREMIUM CARBON PRODUCTS FROM COAL

TECHNICAL PROGRESS REPORT

For the period ending May 31, 2002

FRANK RUSINKO, JR.

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Technical Progress Report Budget Period 4

Abstract

The Consortium for Premium Carbon Products from Coal, with funding from the U.S. Department of Energy's National Energy Technology Laboratory and matching funds from industry and academic institutions endeavored to develop innovative technologies to use coal as coal-derived feedstocks to produce value-added carbon/graphite products.

During Budget Period 4, eight projects were supported and sub-contracts were awarded to three organizations. The CPCPC held three meetings at various locations during the year.

The first meeting was held at the Pure Carbon Lodge in St. Marys, PA on April 29-May 1, 2001 for project reviews funded in Budget Period 3 and to elect a Council Member to fill the unexpired term as a result of a resignation from the Council. In addition, the Council met on April 29 and the Advisory Committee met on April 30. There were 32 people in attendance.

The summer tutorial was held at the Radisson Hotel Pittsburgh on July 2001 having the theme of an introduction to the integrated steel industry and the coal tar pitch industry. Plant tours were taken to The Clairton Works and Koppers Industries. There were 24 people in attendance.

The fall meeting was held at the Lakeview Scanticon Conference Center in Morgantown, WV on October 29, 2001 to hear presentations of member project proposals for possible funding for Budget Period 5, to elect the Chair of the Advisory Committee and to elect 3 new Council Members. Dr. John D. Weete, Associate Provost for Research at WVU welcomed CPCPC members and indicated how much the Consortium has meant to non-fuel uses of coal and wished all the success in the world to find new uses for coal. Plaques were presented to the outgoing Council Members and Advisory Committee Chair. Dr. Thomas Falkie, Chairman of Berwind Corporation addressed the group on "The Coal Industry at the Turn of the Century", discussing the changing scene in production, productivity, consumption costs and selling prices for the last 10 or so year period. The Council met and discussed the proposals and then recommended those for funding.

Copies of the final project reports for Budget Period 4 are enclosed.

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Summary

As we move into Budget Period 5, we will continue to maintain our current membership and attempt to increase our membership by attracting new companies and academic institutions.

The spring meeting was held in St. Marys, PA, the summer tutorial was held in Pittsburgh, PA and the fall meeting was held in Morgantown, WV.

There are also 3 meetings scheduled during Budget Period 5 and again proposals will be solicited from the membership. The membership and Council has recommended that several of the projects vie for additional funding to be able to take the laboratory results and scale them up to pilot plant and/or semi-production.

The Development of an All Coal-Derived Anode

FINAL REPORT

Reporting Period
January 1, 2001 to February 28, 2002

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1.0 ABSTRACT

Arch Coal (PSOC 3001) was hydrogenated and then deashed by extraction in the organic solvent N-methyl pyrrolidone (NMP) to produce the two primary ingredients required for carbon anodes used in the electrochemical reduction of alumina to aluminum metal. Conventional aluminum industry carbon anodes are currently produced from calcined petroleum coke filler and byproduct coal tar pitch from steel industry metallurgical coke production. The current project sought to develop coal extracts such that an all coal-derived alternative to carbon anodes can be fabricated for testing and evaluation. Based on the results of earlier work, the coal-derived binder was made in batch autoclaves by hydrogenation at 450°C for one hour. Reactions were repeated until sufficient binder was produced. The coal-derived extract for conversion to filler was made similarly by blending the products from hydrogenations conducted at 400°C and 425°C in order to ensure that an adequate degree of anisotropy would be developed after carbonization. About one hundred pounds of this coke precursor were produced. The pitch blend was then converted to green coke in an atmospheric-still coker by carbonization to 600°C to produce about 50 pounds of coke material. The green coke was calcined in a laboratory calciner to about 1300°C to remove volatiles, increase density, and promote crystallinity. Both the coal-derived binder and calcined coke were mixed, formed, and baked into carbon test anodes in a prescribed manner. Standard methods of testing of the green and baked artifacts were followed. Comparisons of the coal-derived anode properties with a conventional petroleum, Type A, and coal tar binder were conducted. It was found that the coal-derived calcined coke was equivalent in virtually every way to the benchmark calcined petroleum coke. Moreover the coal-derived coke showed significantly lower levels of nickel and vanadium leading to an anode with greatly reduced air reactivity, i.e., a 3wt% loss for the coal-derived anode vs. 25wt% loss for the petroleum-based anode. The coal-derived coke also contained nearly an order of magnitude less sulfur than the standard petroleum coke. The coal-derived binder pitch was also quite comparable to the standard coal-tar binder pitch.

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4.0 EXECUTIVE SUMMARY

The primary focus of the present work was the fabrication of an acceptable carbon anode, as required for the smelting of aluminum, completely from bituminous coal. The procedure uses two techniques to tailor the resultant properties of the coal-derived anode precursors. The first is hydrogenation, which enables control over the salient properties of the pitch and coke. The second is solvent extraction, which is responsible for the virtual elimination of sulfur and metals from the product.

Currently anodes are composed of a petroleum-derived calcined coke mixed with about 15wt% of a coal-tar binder pitch. The former is a by-product of the refining of petroleum and is made via the use of the delayed coker. The latter is a by-product of the volatile fraction from metallurgical coke ovens. As crude oils are becoming more sour and laden with metals, aluminum smelters are faced with ever-decreasing quality of petroleum coke. Moreover, with the decline of the basic iron industry in the United States, the supply of quality coal-tar pitch is also dwindling. This is in spite of an increased demand for both coke and pitch by the aluminum industry. Thus it is important to explore alternate sources of these raw materials, and domestic coal is an obvious candidate.

The preparation of the coal-derived anode requires that both the coke and binder pitch be made from coal. Since the coke and pitch have different properties, their preparation is also different. For the pitch, raw coal was treated in 1-gallon autoclaves at 450°C for one hour under an hydrogen atmosphere. It was subsequently solvent extracted in the solvent N-methyl pyrrolidone (NMP) resulting in about 3kg (6.6lbs) of coal-derived binder. After some careful adjustment of the properties, the resultant binder had a softening point of 112.2°C, an ash content of 0.02wt%, and a sulfur concentration of 0.4wt%. These properties agree very favorably to those of standard coal-tar pitch binder currently in use.

In a similar manner, raw coal was converted to calcined coke. The coal was hydrogenated under two separate conditions: 400°C and 425°C for one hour under hydrogen. These products were then blended in solution by dissolving both in NMP to effect not only removal of mineral matter but also to accomplish intimate mixing of the two materials. This procedure resulted in a coke precursor with completely homogenous properties. Following a careful heating schedule, approximately 50lbs of the coke were produced. The coke was subsequently calcined at about 1300°C for one-half hour in a specially constructed laboratory scale calciner.

The coke and pitch were then sent to Alcoa where they were mixed, formed, and baked into test anodes of approximately two inch in diameter and six inches long. After measurement of the properties of these green anodes, they were baked at a temperature up to 1125°C for 10 hours. For comparison purposes, a variety of combinations of anodes with petroleum coke, coal-tar binder, petroleum binder, coal-tar/petroleum (Type A) binder, as well as the coal-derived coke and pitch were fabricated. Also anodes with varying degrees of binder levels were made.

The pitches were subjected to a battery of standard tests performed at Koppers. Among these were the pitch softening point, viscosity, sulfur concentration, toluene and quinoline insolubles, carbon residue (coking value), density, and ash content. For the baked anodes, the following properties were determined: apparent density, air permeability, electrical resistivity, compressive and flexural strength, coefficient of thermal expansion (CTE), thermal conductivity, and metals content. Details of all testing and a complete tabulation of all results are contained in the attached report.

It was found that the coal-derived binder pitch performed adequately as a binder. It also proved to be an acceptable substitute for petroleum pitch in the blended (Type A) binder pitch.

The coal-derived anode coke showed nearly an order of magnitude less sulfur and nickel and nearly two orders of magnitude less vanadium than the conventional petroleum coke. All other properties were well within the typical coke specifications as given by Alcoa. The bottom line is that the coal-derived anodes proved equivalent to conventional anodes in nearly all respects. The most remarkable feature of anodes containing the coal-derived coke was the extremely small value for the air reactivity (i.e., 98% residue compared to about 75% residue). This was attributed to the very low levels of vanadium and nickel, which catalyze the air oxidation. Moreover, the very low sulfur value for the coal-derived materials makes them environmentally attractive. Lower sulfur also limits the impact of corrosion of pot components, which indirectly can affect metal quality. Thus the coal-derived coke is a substitute for calcined petroleum coke and can be used as is. More importantly it can act as a premium-blending agent to be used with petroleum coke, which would allow careful control over the resultant properties of the coke blend.

5.0 INTRODUCTION

Anodes for the production of aluminum by molten salt electrolysis are normally manufactured from a blend of calcined petroleum coke and coal tar pitch [1]. Because anodes are oxidized in the electrolysis cell to carbon dioxide and hence consumed, large quantities of coke and pitch are needed yearly. Typical annual calcined coke usage in the United States for anodes is approximately 1.6 million metric tons whereas the annual demand for binder pitch is nearly 700,000 metric tons. If all this coke and pitch were made exclusively from bituminous coal in the process described herein, it would amount to the consumption of approximately 6 million metric tons of coal per year.

Conventional coal tar binder pitch comes from crude tars, which originate from the metallurgical byproduct recovery coke oven [2]. Binder pitch is the heavy bottoms which results from the distillation of crude coal tar. However, due to the diminishing need for metallurgical coke as well as the recent environmental constraints being placed on the byproduct coke oven, the coal tar industry in this country is faced with declining production. Nevertheless, aluminum manufacturers project an increasing need for quality binder pitch. Hence it is important that an alternate domestic source of acceptable binder pitch be developed.

The second component of anodes is petroleum coke, which is a byproduct from the petroleum refining process [3]. This coke originates from the residue products of several refinery operations used to produce gasoline and other commercial hydrocarbons. Usually these residue products are sent to a delayed coker where additional oil is produced from the volatile stream, leaving behind a solid coke mass. It is important to note that impurities in the crude oil become concentrated in the coke and can have deleterious effects in the aluminum production [4]. For example metals such as vanadium and nickel can significantly catalyze carbon oxidation in the electrolysis cell and hence lead to higher carbon consumption than required stoichiometrically for aluminum production. In addition, the introduction of sour crudes results in higher amounts of sulfur in the petroleum coke. It is anticipated that the concentrations of these

contaminates will only rise in the future as the reserves of lighter and sweeter crudes become depleted.

For the above reasons, an alternate supply of binder pitch and anode coke is desired to augment the conventional supply of these important carbon feedstocks. With huge domestic reserves, coal could represent a possible solution to this problem for the United States. The focus of this project explores the conversion of coal to anode coke and binder pitch and seeks to develop an all coal-derived anode free of petroleum coke and independent of the recovery coke oven. The project is especially timely since one of the principal concerns of the CPCPC membership is the critical need for a secure supply of domestic coke and binder pitch low in metals and sulfur.

In order to use coal as a carbon source for anode coke and binder pitch two problems must be overcome. First, a method must be devised to reduce the concentration of inorganic matter and sulfur in the raw coal. Second, control over such characteristics as the pitch softening point and degree of coke anisotropy must be exercised. Prior work at WVU has shown that solvent extraction is an effective mechanism whereby the inorganic constituents of coal can be removed leaving behind a 'reconstituted coal' with significantly reduced levels of inorganic impurities and sulfur. Moreover, previous work has shown that mild hydrogenation of raw coal prior to solvent extraction allows significant control over the properties of the resulting extract [5]. For example, with appropriate processing, a solvent extract with a softening point of approximately 120°C and a coking value upward of 55 wt% can be realized. This material has been shown to be a suitable additive to conventional coal tar binder pitch for use in carbon anodes. By altering the processing conditions, carbonaceous feedstocks can be produced which, when coked, possess a level of anisotropy nearly identical to that of petroleum-derived anode coke.

The objective of the current project is a culmination of previous work conducted at WVU, Alcoa, and Koppers to determine the feasibility of producing anode coke and binder pitch directly from coal by a combination of hydrogenation and solvent extraction

[6,7]. The coal-derived binder pitch and coke were used in the making of all coal-derived carbon anodes, which were subjected to thorough testing and characterization. Comparisons between the all coal-derived anodes and anodes made of conventional coal tar binder pitch and calcined petroleum coke are reported herein. Results of the comparison with binders comprised of blends of a petroleum derivative and conventional coal tar binder, and of the coal-derived pitch and conventional coal tar binder are also presented. In addition, coal-derived coke was blended with petroleum coke in the fabrication of test anodes and examined for compatibility.

6.0 EXPERIMENTAL

6.1 Coal-Extract Production for Binder Pitch Development

The Pennsylvania State University supplied the bituminous coal from Arch Coal, Incorporated. The coal is given the designation PSOC 3001. Some characteristics of the coal are shown in Table 1.

Table 1. Properties of Arch Coal (PSOC 3001).

Moisture, wt % as received 1.79		Ash, wt % dry 7.36		Volatile Matter, wt % dry 31.57
Carbon wt % dry 80.31	Hydrogen wt % dry 4.56	Nitrogen wt % dry 1.41	Sulfur wt % dry 0.71	Oxygen by difference 5.65
Vitrinite vol % mf 57.2	Liptinite vol % mf 8.3	Inertinite vol % mf 30.3	Mineral Matter vol % mf 4.2	

The coal was ground in a hammer mill to about 20 mesh (Tyler sieve) top size and then dried in a vacuum oven overnight at 100°C to remove excess moisture. The dried coal was then sealed in 4L glass bottles and stored in a refrigerator until ready for use.

Coal-derived binder pitch was produced in batches by placing 600g of coal along with 1.5L of tetralin into a 1gal bolted-closure autoclave. The reactor was purged of air with hydrogen gas and then pressurized to 400psig with molecular hydrogen at room temperature. The reactor contents were stirred while heating and brought to 450°C for 1 hour. Following reaction, the reactor was cooled to room temperature and vented. The

products were collected in a 10L flask. The tetralin was then removed by rotary evaporation. Three liters of NMP were added to the flask and agitated for 2 hours at 110°C. Afterward, the mixture was transferred to 750mL centrifuge bottles and centrifuged for 1 hour at 2000 times the force of gravity (2000G) to separate unconverted coal and other insoluble material. The supernatant liquid was decanted and placed in a rotary evaporator device to remove the NMP. Finally, the coal-derived pitch was vacuum dried at about 150°C. Additional reactions were conducted until about 3kg (6.6lbs) of coal-derived binder pitch was produced.

6.2 Coal-Extract Production for Carbon Anode Coke Filler

Studies have shown that the more severely coal is hydrogenated the more anisotropic the cokes become after carbonization of the extract product. To produce coke with sufficient degree of anisotropy for carbon anode application, other studies had indicated that hydrogenation of coal at 400°C to be an appropriate reaction condition. However, to ensure a greater probability of developing the required coke anisotropy after the coking operation, a blend of coal extracts was made by combining the products from 400°C and 425°C reactions in a 5:2 wt:wt proportion, based on the initial weight of dry coal. The hydrogenations conducted at 400°C were accomplished by placing 3kg of coal along with 7.5L of tetralin in a 5-gal batch autoclave, Figure 1. The reactor was purged of air with hydrogen gas and then pressurized to 200psig with molecular hydrogen at room temperature. The reactor contents were stirred while heating and brought to 400°C for 2 hours. Following reaction, the reactor was cooled to room temperature and vented. The products were recovered from the reactor and tetralin removed by rotary evaporation. N-methyl pyrrolidone (NMP) was then added to the hydrogenated coal products to form a low-viscosity slurry and agitated for 2 hours at 110°C. Afterward, the mixture was transferred to 750mL centrifuge bottles and centrifuged for 1 hour at 2000 times the force of gravity (2000G) to separate unconverted coal and other insoluble material. The supernatant liquid was decanted into a clean holding container for mixing with the coal products as described below.

Figure 1. Preparation of 5-gal reactor for hydrogenation of coal.

The hydrogenations conducted at 425°C were accomplished in a pair of 1gal autoclaves by placing 600g of coal along with 1.5L tetralin into each reactor. The reactors were purged of air with hydrogen gas and then pressurized to 400psig with molecular hydrogen at room temperature. The contents of each reactor was stirred while heating and brought to 425°C for 1 hour after which the reactors were allowed to cool to room temperature. The products from the two reactors were combined. Tetralin removal and solvent extraction were similar to that described above. Since both of the products made at 400°C and 425°C were still dissolved in NMP, they could be thoroughly mixed together at room temperature in the holding container, Figure 2. Finally, the NMP was removed from the blend by rotary evaporation, Figure 3, and the blend dried in a vacuum oven at about 170°C for about 24 hours. These hydrogenation reactions and blend preparations were repeated until about 50kg (110lbs) coal extract was produced for green coke making.

Figure 2. Storage of blended coal extracts in preparation of NMP removal.

Figure 3. Rotary evaporation of NMP from coal extracts.

6.3 Carbonization of Coal-Derived Extract Blend to Green Coke

An atmospheric-still coker was made from schedule 80 steel pipe about 10 inches inside diameter and 21 inches in length. A steel blind flange was welded to the bottom of the pipe and functioned as a support stand. A collar was welded to the top of the pipe so that a steel cover could be bolted to it ensuring a leak-proof fit. The cover also had two openings machined into it. One opening was to allow for the admission of a nitrogen purge while the other opening was for the conveyance of condensable volatiles out of the reactor to a collection vessel.

Between 3-5kg of the coal extract blend were placed into the coker vessel. The cover was bolted securely to the body and the vessel placed into a temperature-programmable kiln. Several heating cycles were investigated. Based on the physical appearance and yield of green coke, the following was determined to be the “standard” heating procedure. A nitrogen purge of about 1L/min was started and the kiln programmed to heat at 3°C/min to 450°C and held at this temperature for 2 hours. After this soak period, the kiln was then programmed to heat at 3°C/min to 600°C and held at this temperature for 5 hours, whereupon the heating was stopped and the contents allowed to cool to room temperature.

After cooling to ambient temperature, the coker was opened and the carbonized extract removed for weighing. The condensable volatiles generated during carbonization were also collected and weighed. A photograph of the coker being placed into the kiln is shown in Figure 4. Figure 5 is a photograph of the kiln in operation with the coker vessel inside it. Usually the green coke could be removed from the atmospheric-still coker as a single solid mass.

Figure 4. Atmospheric-still coker being placed in the kiln.

Figure 5. Carbonization of coal extracts in the atmospheric-still coker.

6.4 Laboratory Calcining of Green Cokes

Samples of green and commercially calcined petroleum coke were received from an industrial coke supplier. The calcined petroleum coke was delivered in screened fractions, which consisted of medium, fine and super-fine (dust collector) material. These particle sizes are customarily used to produce commercial anodes. Commercial anodes would also normally contain coarse material from recycled anode or butt material. However, since butt material is typically very coarse, it was not included in the anode formulations to avoid having butts as a disproportionate mass in the small laboratory anodes.

The green petroleum coke and green coal-derived coke were calcined in a laboratory-scale calciner. A schematic of the calciner is shown in Figure 6. Laboratory calcination was performed as a static procedure at standardized conditions to allow comparison of differences among cokes. Standard conditions use an open graphite tray containing about 500 grams of crushed green coke, with a 30-minute total time in a graphite tube furnace set to about 1300°C (2375°F). Figures 7 and 8 show the calciner in operation.

Figure 6. Schematic of the laboratory calciner.

Figure 7. Insertion green coke into the hot zone of the laboratory calciner.

Figure 8. Flaring of coke volatiles during calcining operation.

Previous studies at Alcoa have indicated that this method generates laboratory calcined samples with properties in the range of commercial calcination practices that use tertiary air injection and process conditions geared towards high production rates with fairly rapid coke heat up. While laboratory calcination performed herein does not purport to reproduce precisely the actual conditions imposed by commercial rotary kiln calcination, it is the best procedure available to provide a meaningful method to compare properties of cokes calcined under standard conditions.

6.5 Preparation of Aggregate and Test Anode Formulations

After calcining, the coke was crushed and sieved into three different particle sizes as shown in Table 2.

Table 2. Calcined coke size fractions, Tyler mesh.

Fraction Type	Size
Medium	-1/4 inch, +12 mesh
Fines	-12 mesh, +60 mesh
Superfines	-60 mesh

An aggregate recipe was used equivalent to the standard industrial recipe proportioned without butts according to the following: medium 30.5 wt%; fines 35.4 wt%; superfines 30.5 wt%. After screening, additional superfines was required so some of the oversized material was ground using a BICO Pulverizer with ceramic disks. This coke was ground to 46 wt% -235 Tyler mesh, to match the particle distribution of the industry calcined material.

All of the coke fractions were dried and preheated overnight in an oven at 110°C. The appropriate amount of binder pitch, equivalent to a starting weight content of 14 or 15 wt%, was measured. Enough of the coke components was sized and weighed such that ten 400g anodes could be made with each aggregate formulation increasing in binder content by 0.5 wt%. All pastes were mixed at Alcoa in an R&D Carbon RDC-161 Bench Scale Unit, as shown in Figure 9.

Figure 9. R&D Carbon RDC-161 Bench Scale Anode Paste Unit showing mixer (right) and test anode press (left).

The mixer was pre-heated to between 170 and 180°C to which was added about 4455g of aggregate preheated to about 160°C. The appropriate amount of room-temperature pitch was added and blended with the aggregate for 30 minutes to a final temperature of 160°C. Four hundred grams of the material were removed from the mixer, placed into a mold, and pressed at 135°C for 25 seconds. Additional binder pitch was added to the mixer in a 0.5 wt% increment and mixing continued for 3 minutes. Another 400g of material were removed, pressed, and additional binder added to the mixer. This process was continued until all 10 test anodes were formed with varying amounts of binder pitch.

After the green anodes had cooled to room temperature, preparations were made to determine green apparent density (GAD). This was accomplished by first marking with a grease pencil a reference point on top of the sample. The diameter was measured beginning at the top of the anode, center, and bottom 180 degrees apart from the reference point. Beginning from the same reference point, the length of the green anode was measured at 4 points, 90 degrees apart in a clockwise direction. The volume of the

cylinder was calculated. Determination of GAD is a simple mathematical operation after weighing the test anode.

The green anode samples were packed without touching one another “bottom” down into a baking furnace. The samples were covered with packing coke and the lid placed on the furnace. The furnace was purged prior to and during baking with argon flowing at no less than 3 scf/h. Baking of the green anodes was accomplished at 10°C/h to 600°C, then 25°C/h to 1125°C, and held at 1125°C for 10 hours. After cooling, the baked anodes were removed from the furnace, and brushed of loose coke. The same procedure as described above for measurement of the green anode dimensions was conducted to determination of baked apparent density (BAD).

6.6 Characterization and Testing Methods

The test methods used to characterize the binder pitch materials are listed in Table 3. Alcoa and Koppers are known leaders in the development and establishment of carbon anode testing methods. The typical tests conducted by them are provided in Table 4. Wherever possible, testing methods followed statistical process control principles.

Table 3. Test methods for measuring pitch properties.

Characterization	Method
Softening Point, °C	ASTM D3104
Toluene Insolubles, wt%	ASTM D 4072
Quinoline Insolubles, wt%	ASTM D 4746
Carbon Residue, wt%	ASTM D2416
Density, g/cm ³ /Specific Gravity	ASTM D4892/ASTM D71
Ash Content, wt%	ASTM D2415
Viscosity, cP	Brookfield Viscometry
S , wt%	XRF

Table 4. Coke or carbon anode property tests.

Test	Unit
Apparent Density	g/cm ³
Air Permeability	NPm
Electrical Resistivity	μΩm
Compressive Strength	MPa
Coefficient of Thermal Expansion	10 ⁻⁶ /°C
Thermal Conductivity	W/m-K
Metals, XRF	wt% or ppm

Hardgrove grindability index values (HGI) indicate the relative hardness of coke and thus provide information on grindability and propensity for dust generation. Fifty grams of coke of -14/+28 Tyler mesh are tumbled in a proscribed manner and the amount, which passes through a 200-mesh sieve, is determined. Note that the lower the HGI the more resistant the coke is to making fines.

Compressive strength was determined from the breaking load of a sample 50 mm diameter by 50 mm high and flexural strength was determined by using three-point loading in a similarly sized sample on a universal tester by Tinnius Olsen or Applied Test System. Coefficient of Thermal Expansion (CTE) was measured from room temperature to 300°C on a sample 50 mm diameter by 130 mm long using the Anter Digital Displacement Transducer. Thermal Conductivity (TC) was measured on a sample 50 mm diameter by 20 mm high at 20 to 60°C using the Anter Unitherm 2022. Electrical resistivity was determined by measuring the voltage drop across the length of a 50 mm in diameter and 130 mm long using a KII apparatus. Air permeability is a measurement of time in which a certain air volume is passed through a sample 50 mm diameter by 20 mm high (AP-50 apparatus by R & D Carbon). Carbon dioxide reactivity was determined on a sample 50 mm diameter x 50 mm high by heating in nitrogen to 960 °C and then subjecting the specimen to carbon dioxide atmosphere for 7 hours. Koppers conducted air reactivity tests such that RDC 151 results were obtained.

7.0 RESULTS AND DISCUSSION

7.1 Characterization of Binder Pitches

Some properties for the coal-derived pitch are shown in Table 5. Note that the Mettler softening point temperature is somewhat higher than was judged desirable for use as a binder pitch.

Table 5. Characteristics of coal-derived binder pitch.

Mettler Softening Point, °C	Conradson Carbon, wt%	Ash Content, wt%
128.3	50.1	0.02

To lower the softening point temperature, a sample of the coal-derived binder pitch was extracted in toluene to isolate the toluene soluble portion. About 10wt% of the toluene solubles were then blended with the same unextracted binder. As shown in Table 6, the softening point temperature was lowered by about 16°C without affecting the coking value adversely.

The WVU binder pitch is lower in both sulfur and ash contents than the commercial counterparts, i.e., conventional coal-tar pitch and petroleum-derived pitch. Type A pitch is a blend of 85% coal-tar pitch and 15% petroleum-derived pitch. The metals content of the WVU pitch is generally comparable or lower than for the other binder materials. However, the concentration of chlorine is very high for the coal extract pitch. A sample of the same pitch was reanalyzed for chlorine with the second analysis being very similar to the first determination (416ppm vs. 420ppm). It is not clear at the time of the writing from where or in what form the chlorine appears. For comparison, typical desired properties of an acceptable binder pitch are listed in the column titled "General Pitch".

Table 6. Properties of binder pitches used in anode making.

	WVU Pitch	Coal Tar Pitch	Petroleum Pitch	Type A Pitch	General Pitch
Softening Pt, °C	112.2	115.3	120.9	108-115	108-115
Toluene Insol wt%	11.00	24.42	4.05	22 min	24 min
Quinoline Insol wt%	0	7.9	0.26	8-17	8-17
Coking Value, wt%	49.4	55.2	50.5	52 min	53 min
Ash Content, wt%	0.02	0.12	0.02	5 max	5 max
Specific Gravity	1.22	1.31	1.23	1.30 min	1.30 min
Sulfur, wt%	0.41	0.6	2.81	0.8 max	0.7 max

Table 6. (Continued)

	WVU Pitch	Coal Tar Pitch	Petroleum Pitch	Type A Pitch	General Pitch
Viscosity, cP					
140°C	9240	28700	27600	--	--
160°C	1290	2880	2520	3000 max	3000 max
180°C	305	560	467	--	--
200°C	103	167	135	--	--
220°C	45	86	53	--	--
Metals, PPM					
Calcium	12	17	3	100 max	100 max
Chlorine	420	22	18	--	--
Iron	65	147	15	250 max	250 max
Lead	--	42	--	150 max	150 max
Nickel	4	4	4	--	--
Phosphorous	1	--	0	--	--
Potassium	1	17	1	--	--
Silicon	46	274	118	600 max	600 max
Sodium	15	25	--	250 max	250 max
Vanadium	2	3	4	200 max	200 max
Zinc	50	70	--	100 max	100 max

The viscosity of the binders as a function of temperature is shown in Figure 10. The viscosity profiles for the commercial pitches examined are virtually the same, while the viscosity of the WVU material is much lower at temperatures below 160°C. Above 160°C all of the pitches demonstrate essentially similar viscosity.

Figure 10. Viscosity as a function of temperature of selected binder pitches.

7.2 Characterization of Green and Calcined Cokes

Typical yields of coal-derived green coke recovered from the atmospheric-still coker were between 45 and 55wt%. Figure 11 shows a cross section of piece of WVU green coke after harvesting from the coker vessel. Note the sponge-like appearance around the outside edges and the elongated or needle-like texture toward the center of the coke.

Table 7 provides the target specifications for smelting-grade petroleum coke. In Table 8 are the results of the analyses of the WVU green coke and of the petroleum green coke. Also included in the table are data for the same cokes after calcining. In most instances the WVU coke compares favorably with the petroleum analogs in terms of HGI index and ash value. The WVU coke is especially low in sulfur, vanadium, and nickel.

Table 7. Typical aluminum smelting-grade-calcined petroleum coke target values.

Item	Specification, wt%
Sulfur	3.0 max
Silicon	0.02 max
Iron	0.03 max
Nickel	0.04 max
Vanadium	0.045 max
Ash	0.5 max
Volatile Matter	0.5 max
Moisture	0.5 max
Bulk Density	0.80 g/cm ³ min
Real Density	2.03 g/cm ³ min

Figure 11. Cross section of coal-derived green coke from the atmospheric-still coker.**Table 8.** Comparison of green cokes and laboratory and plant calcined cokes.

Sample ID	HGI	Ash %	Vol %	XRF								
				S %	Fe ppm	Si ppm	V ppm	Ni ppm	Ca ppm	Ti ppm	Na ppm	Pb ppm
Pet Green Coke	98	0.30	11.5	--	--	--	--	--	--	--	--	--
WVU Green Coke	43	0.13	6.2	0.32	189	30	11	22	79	50	66	2
Typical Pet Coke	--	--	--	3.0 max	300 max	200 max	450 max	400 max	150 max	No Spec	150 max	Report
WVU Lab Calcined	38	--	--	0.31	195	52	7	19	47	26	32	7

A few trials were undertaken to establish the effects and performance characteristics of the laboratory calciner on the properties of resultant cokes. Prior to and during the procedure, the laboratory calciner was purged with a stream of nitrogen to prevent burning of the coke and oxidation of the graphite tube in the furnace. The temperature of the calciner was maintained at the desired level by controlling the amount of current flowing through the graphite tube, which functioned as a resistance heater.

Two different graphite sample trays were available, small and large. The former could contain about 500g of green coke and the latter nearly double this amount. A known weight of green coke was placed in the tared sample tray. The tray was then placed into a water-jacketed and nitrogen-purged loading platform (Cooler, in Figure 6) in preparation for insertion into the calciner. A sliding gate was opened and the tray containing the green coke then inserted with a long metal rod into the heated zone, Figure 7. The sliding gate was closed except for a fraction of an inch to allow coke volatiles to escape. These volatiles were combusted by igniting with a flame, Figure 8. After 30 minutes, the sliding gate was opened and the tray pulled out into the nitrogen-purged cooler until the sample reached ambient temperature for weighing to determine weight loss. Table 9 lists the results of the trial experiments.

Table 9. Results of trial calcining of green cokes.

Run #	Sample	Sample wt, g	Temp, °C	Tray Size	Wt Loss %	ER ohm-in	Real Density g/cc	App. Density g/cc	L _c Å
1	Pet Coke A	503	1315	Small	13.2	0.0434	2.045	1.775	26.7
2	Pet Coke A	750	1320	Large	11.4	0.0495	2.007	1.757	23.1
3	*Pet Coke B	501	1315	Small	11.8	0.0438	2.029	1.752	24.6
4	WVU Coke	567	1315	Large	5.9	0.0441	2.022	1.757	22.3
5	WVU Coke	503	1315	Small	5.9	0.0410	2.072	1.796	27.3

* Petroleum Coke B used in test anode making.

Comparing the results for the same petroleum coke from Run 1 and Run 2 indicates that using the larger sample tray and weight produced a coke that still contained appreciable volatiles, higher electrical resistivity, lower density, and less crystalline development than

the coke made with the smaller tray. Based on these observations, all of the other calcining operations were made in the small trays using about 500g of green coke. A compilation of the weight loss results from the calcining of the petroleum and WVU green cokes is presented in Appendix A.

7.3 Characterization of Test Anodes

Table 10 gives details on the various types of test anodes developed in this project. The objective of the various combinations of cokes and binders was to maximize the amount of information from the available materials. Table 10 should be referred to frequently when comparing Figures 12 through 19. In total 12 mixes were developed including repeats of formulations (mixes 1 and 11 and mixes 4 and 12) to establish reproducibility. Appendix F contains the plots of the duplicate experiments and shows that reproducibility of the test anode fabrication was good. Details on the weights and materials used in each mix recipe are provided in Appendix B. Appendices C through E tabulate all the data accumulated on the properties of the test anodes.

Figure 12 top shows the effects of different calcined cokes and the same coal-tar binder pitch on green apparent density (GAD) as a function of binder pitch content. There is a notable difference in GAD between the laboratory calcined and commercial calcined petroleum coke (Figure 12, top, mix 1 and mix 3). This observation underscores the difficulty in comparing the results of laboratory-scale work with that encountered on the industrial scale. Nevertheless, the GAD using the WVU calcined coke compares favorably with the laboratory calcined petroleum coke (Figure 12, top, mix 5 and mix 3). Not unexpected, the GAD of a blend of WVU coke and the commercial calcined petroleum coke, mix 10, is intermediate between mixes 1 and 5. However, the all-coal anode exhibits the greatest GAD, perhaps because the WVU coke has a slightly higher apparent and real density (Table 9).

Figure 12 middle compares the effects of commercial calcined petroleum coke with different binder pitches on GAD. Figure 12 bottom compares the effects of commercial

calcined petroleum cokes with Type A binders. All of the GAD for the commercial petroleum-based cokes are similar no matter what binder pitch was used.

Table 10. Test anode formulations and comments.

Mix	Anode Components	Comments
1	Commercial Pet Coke + Coal Tar Binder	Control Anodes
2	Commercial Pet Coke + Petroleum Pitch	Alternant Commercial QI-Free Petroleum Binder
3	Lab Calcined Pet Coke + Coal Tar Binder	Compares Commercial Pet Coke with Lab Calcined Pet Coke
4	Commercial Pet Coke + WVU Binder	Compares WVU Binder with Conventional Coal Tar Binder
5	WVU Coke + Coal Tar Binder	Compares WVU Coke with Commercial and Lab Calcined Pet Cokes
6	WVU Coke + WVU Binder	All Coal-Derived Anode
7	Commercial Pet Coke + Type A Binder	Compares Commercial Blended Binder
8	Commercial Pet Coke + WVU Type A	Compares WVU Blended Binder
9	WVU Coke + WVU Type A	Compares Lab Calcined WVU Coke and WVU Blended Binder
10	85% Commercial Pet Coke/15% WVU Coke + Coal Tar Pitch	Compares Effects of Blending Commercial Pet Coke with WVU Coke
11	Repeat of Mix 1	Test Reproducibility
12	Repeat of Mix 4	Test Reproducibility

Figure 12. Green apparent density vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

Similar trends were observed after baking of the green anodes, Figure 13. Baked apparent densities (BAD) are lower than GAD because of volatile loss. It can be noticed that the BAD for the all-coal anode decreases as the proportion of the coal-derived binder increases. This, in part, may be because the coal-derived binder has a lower coking value than the other binder pitches (Table 6).

In general, electrical resistivity decreases as the content of binder pitch increases, Figure 14, probably because of an increase in “linkages” or “bridges” amount the coke particles. In nearly all of the anode formulations studied, those involving the WVU coke and/or WVU coke and coal-derived binder exhibited the lowest resistivity. Only a few of the anode formulations were used for carbon dioxide reactivity studies because this test is destructive and would preclude the use of the anodes in other tests. Nevertheless, as shown in Figure 15, all of the test anodes appear to have similar reactivity to carbon dioxide in general, with a trend in reactivity increasing as the quantity of binder pitch increases.

Flexural and compressive strength versus binder pitch content are shown in Figure 16 and Figure 17, respectively. The flexural strength is greatest for the test anodes made with the laboratory calcined petroleum coke and the conventional coal-tar binder pitch (Figure 16, top, mix 3) while the anodes fashioned totally or blended with the commercial calcined petroleum coke and coal-tar binder were weaker (Figure 16, top, mix 1 and mix 10). Test anodes made with the WVU coke and coal-tar binder and the all coal anode were intermediate in flexural strength (Figure 16, top, mix 5 and all coal). The anodes consisting of the commercial calcined petroleum coke and the all-petroleum binder (Figure 16, middle, mix 2 compare with mix 1) were weaker somewhat than the same formulation using the coal-tar binder pitch. A comparison of the “Type A” binders (Figure 16, bottom) reveals a stronger anode with the WVU coke and WVU Type A binder. The results of the compressive strength tests were somewhat variable, but the compressive strength appeared to increase as the level of binder increased.

Figure 13. Baked apparent density vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

Figure 14. Electrical resistivity vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

Figure 15. Carbon dioxide reactivity vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

Figure 16. Flexural strength vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

Figure 17. Compressive strength vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

The coefficient of thermal expansion (CTE) is a measure of the dimensional changes an anode undergoes during heating. Very high CTE values indicate that the anodes could be susceptible to breakage during service. As shown in Figure 18, all of the test anodes consisting of components of WVU coke and WVU binder were dramatically lower than any of the other anodes.

Figure 18. Coefficient of thermal expansion vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

Perhaps the most dramatic effects of using coal-derived extract precursors were noted after examining the results of the air reactivity studies, Figure 19. The results are easily discernable visually in Figure 20. In all instances, anodes consisting of WVU cokes or its blend were remarkable resistant to oxidation by air. This is attributable to the much lower content of vanadium and nickel. As shown in Table 8, the combined vanadium and nickel contents of the WVU cokes are much lower than 30ppm, while these metals are much more concentrated in the petroleum cokes. In addition, the sulfur content of the WVU cokes is nearly an order of magnitude less (0.3% vs. 2%) than commercially available petroleum coke. This fact, coupled with the reduced air reactivity, makes the WVU coal-derived coke either an excellent replacement for petroleum coke or good coke which can be blended with petroleum coke to help control (i.e. lower) the levels of sulfur and metals in the blended aggregate. The latter may be an especially attractive application as levels of sulfur and metals continue increasing in the future.

Figure 19. Air reactivity vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

Figure 20. Photograph of test anodes after air reactivity test. Left: WVU coke-based anode + coal-tar pitch, 3%wt loss. Right: Industrial test anode containing butts, 33wt% loss.

8.0 CONCLUSIONS

The results of this work have shown that hydrogenation of coal and solvent extraction are effective means by which the two precursors to carbon anodes, binder pitch and calcined coke, can be produced successfully. Through control of hydrogenation and processing conditions, coal-derived extracts can be developed into an appropriate binder pitch that not only functioned well as a binder by itself but also is compatible with conventional coal-tar pitch for blending into coal-derived Type A binders.

It was also demonstrated the coal-derived extracts can be converted into green coke, calcined, and fashioned into laboratory-scale test anodes. The coal-derived anode coke showed nearly an order of magnitude less sulfur and nickel and nearly two orders of magnitude less vanadium than the conventional petroleum coke. All other properties were well within the typical coke specifications as given by Alcoa. Thus, the coal-

derived anodes proved equivalent to conventional anodes in nearly all respects. The most remarkable feature of anodes containing the coal-derived coke was the extremely small value for the air reactivity (i.e., 2wt% loss vs. 25wt% for the standard air reactivity test). This was attributed to the very low levels of vanadium and nickel, which catalyze the air oxidation. Moreover, the very low sulfur value for the coal-derived materials makes them environmentally attractive. Lower sulfur also limits the impact of corrosion of pot components, which indirectly can affect metal quality. Thus the coal-derived coke is a substitute for calcined petroleum coke and can be used as is. More importantly it can act as a premium-blending agent to be used with petroleum coke, which would allow careful control over the resultant properties of the coke blend.

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APPENDIX A
Results of Laboratory Calcining Petroleum and WVU Green Coke

Petroleum Green Coke Weight Loss

Run	Calcining Temp, C	Sample wt, g	Tray Size	Tray wt, g	Start	End	End Sample wt, g	Loss Sample wt, g	Coking Loss %	Coking Yield %
					Tray +	Tray +				
					Sample wt, g	Sample wt, g				
6	1310	502.68	Small	563.35	1066.03	1007.1	443.75	58.93	11.7%	88.3%
7	1305	519.11	Small	908.87	1427.98	1366.64	457.77	61.34	11.8%	88.2%
8	1315	504.92	Small	633.04	1137.96	1080.66	447.62	57.30	11.3%	88.7%
9	1325	514.00	Small	921.70	1435.7	1373.59	451.89	62.11	12.1%	87.9%
10	1315	500.62	Small	561.25	1061.87	1002.94	441.69	58.93	11.8%	88.2%
11	1315	512.00	Small	905.98	1417.98	1358.3	452.32	59.68	11.7%	88.3%
12	1325	506.22	Small	631.86	1138.08	1077.21	445.35	60.87	12.0%	88.0%
13	1319	503.59	Small	918.50	1422.09	1361.09	442.59	61.00	12.1%	87.9%
14	1321	504.73	Small	559.82	1064.55	1006.37	446.55	58.18	11.5%	88.5%
15	1315	504.75	Small	903.97	1408.72	1346.27	442.3	62.45	12.4%	87.6%
Average	1316.5	507.3					447.2	60.1	11.8%	88.2%
Total Wt, g							4,472			

APPENDIX A (Continued)
Results of Calcining Petroleum and WVU Green Coke

WVU Green Coke Weight Loss

Run	Calcining	Sample	Tray	Tray	Start	End	End	Loss	Coking	Coking
					Tray +	Tray +				
					Sample	Sample				
					Sample	Sample				
Temp, C	wt, g	Size	wt, g	wt, g	wt, g	wt, g	wt, g	%	%	
16	1326	475.88	Small	629.88	1105.76	1078.54	448.66	27.22	5.7%	94.3%
17	1322	501.43	Small	915.63	1417.06	1388.65	473.02	28.41	5.7%	94.3%
18	1323	500.79	Small	558.58	1059.37	1030.11	471.53	29.26	5.8%	94.2%
19	1310	503.90	Small	900.37	1404.27	1374.11	473.74	30.16	6.0%	94.0%
20	1305	503.68	Small	627.48	1131.16	1100.72	473.24	30.44	6.0%	94.0%
21	1320	506.24	Small	912.74	1418.98	1389.26	476.52	29.72	5.9%	94.1%
22	1315	506.11	Small	555.60	1061.71	1033.07	477.47	28.64	5.7%	94.3%
23	1316	505.85	Small	896.90	1402.75	1375.2	478.3	27.55	5.4%	94.6%
24	1325	507.62	Small	625.48	1133.1	1101.94	476.46	31.16	6.1%	93.9%
25	1307	513.85	Small	910.47	1424.32	1394.03	483.56	30.29	5.9%	94.1%
26	1312	504.96	Small	553.22	1058.18	1030.1	476.88	28.08	5.6%	94.4%
27	1310	508.29	Small	894.60	1402.89	1371.13	476.53	31.76	6.2%	93.8%
28	1315	506.67	Small	622.20	1128.87	1100.17	477.97	28.70	5.7%	94.3%
29	1315	509.11	Small	906.91	1416.02	1387.53	480.62	28.49	5.6%	94.4%
30	1320	508.36	Small	551.02	1059.38	1028.82	477.8	30.56	6.0%	94.0%
31	1315	500.49	Small	890.25	1390.74	1361.28	471.03	29.46	5.9%	94.1%
32	1320	500.30	Small	619.75	1120.05	1091.3	471.55	28.75	5.7%	94.3%
33	1319	503.79	Small	904.55	1408.34	1379.96	475.41	28.38	5.6%	94.4%
34	1320	501.15	Small	548.13	1049.28	1019.51	471.38	29.77	5.9%	94.1%
35	1317	500.81	Small	886.61	1387.42	1358.73	472.12	28.69	5.7%	94.3%
36	1317	500.46	Small	616.95	1117.41	1087.85	470.9	29.56	5.9%	94.1%
37	1319	500.85	Small	900.94	1401.79	1372.45	471.51	29.34	5.9%	94.1%
38	1310	501.36	Small	545.43	1046.79	1018.79	473.36	28.00	5.6%	94.4%
Average	1316.4	503.1					473.9	29.2	5.8%	94.2%
Total Wt. g							10,900			

Formulation of Cokes, Pitches, and Mixes

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APPENDIX C
Data Table for Mix 1 – Mix 4

Mix No	Anode No	Binder Level, wt%	Alcoa GAD, g/cc	Alcoa BAD, g/cc	Koppers BAD, g/cc	ER, micro ohms-m
Mix 1	M1-1	14	1.543	1.511		
Mix 1	M1-2	14.5	1.549	1.507		
Mix 1	M1-3	15	1.554	1.503		
Mix 1	M1-4	15.5	1.555	1.508	1.501	70.7
Mix 1	M1-5	16	1.564	1.512	1.506	67.7
Mix 1	M1-6	16.5	1.565	1.516	1.51	67.2
Mix 1	M1-7	17	1.561	1.512	1.511	67.8
Mix 1	M1-8	17.5	1.573	1.518	1.515	65.2
Mix 1	M1-9	18	1.577	1.513		
Mix 1	M1-10	18.5	1.579	1.518		
Mix 2	M2-1	15	1.569	1.499		
Mix 2	M2-2	15.5	1.564	1.492	1.487	81.9
Mix 2	M2-3	16	1.567	1.49	1.488	74.1
Mix 2	M2-4	16.5	1.572	1.496	1.49	72.1
Mix 2	M2-5	17	1.573	1.494	1.49	68.2
Mix 2	M2-6	17.5	1.581	1.493	1.493	63.8
Mix 2	M2-7	18	1.588	1.493		
Mix 2	M2-8	18.5	1.587	1.491		
Mix 2	M2-9	19	1.59			
Mix 2	M2-10	19.5	1.597			
Mix 3	M3-1	13.5	1.574	1.545		
Mix 3	M3-2	14	1.595	1.554		
Mix 3	M3-3	14.5	1.602	1.56		
Mix 3	M3-4	15	1.606	1.564	1.557	63.6
Mix 3	M3-5	15.5	1.614	1.567	1.565	60.8
Mix 3	M3-6	16	1.621	1.572	1.557	58.6
Mix 3	M3-7	16.5	1.623	1.569	1.565	57.4
Mix 3	M3-8	17	1.63	1.574	1.573	55.6
Mix 3	M3-9	17.5	1.634	1.557		
Mix 3	M3-10	18	1.634			
Mix 4	M4-1	14	1.542			
Mix 4	M4-2	14.5	1.548			
Mix 4	M4-3	15	1.551	1.503		
Mix 4	M4-4	15.5	1.556	1.49	1.488	77.1
Mix 4	M4-5	16	1.568	1.49	1.491	72.2
Mix 4	M4-6	16.5	1.572	1.492	1.49	70.4
Mix 4	M4-7	17	1.576	1.495	1.491	65.6
Mix 4	M4-8	17.5	1.583	1.493	1.489	64.7
Mix 4	M4-9	18	1.581	1.491		
Mix 4	M4-10	18.5	1.591	1.491		

APPENIX C (Continued)
Data Table for Mix 1 – Mix 4

Mix No	Anode No	CO2 React Air Perm nPm	CO2 React wt loss %	CO2 Residue, wt%	%Dust + % Attr	Air wt loss, wt%	Air Residue, wt%	Air % dust + % Attr
Mix 1	M1-1							
Mix 1	M1-2							
Mix 1	M1-3							
Mix 1	M1-4					25.67	66.99	7.28
Mix 1	M1-5					24.73	68.91	6.32
Mix 1	M1-6					24.68	68.44	6.83
Mix 1	M1-7		8.39	90.34	1.23			
Mix 1	M1-8	1.48	7.73	90.75	1.5			
Mix 1	M1-9							
Mix 1	M1-10							
Mix 2	M2-1							
Mix 2	M2-2					24.78	66.81	8.36
Mix 2	M2-3	2.09						
Mix 2	M2-4	1.93				23.69	67.72	8.55
Mix 2	M2-5	1.9						
Mix 2	M2-6	1.96	5.67	93.39	0.93			
Mix 2	M2-7							
Mix 2	M2-8							
Mix 2	M2-9							
Mix 2	M2-10							
Mix 3	M3-1							
Mix 3	M3-2							
Mix 3	M3-3							
Mix 3	M3-4					23.56	69.06	7.35
Mix 3	M3-5	0.89				22.5	69.62	7.83
Mix 3	M3-6		6.7	91.88	1.41			
Mix 3	M3-7		6.19	92.84	0.96			
Mix 3	M3-8					20.16	74.23	5.57
Mix 3	M3-9							
Mix 3	M3-10							
Mix 4	M4-1							
Mix 4	M4-2							
Mix 4	M4-3							
Mix 4	M4-4					26.25	85.72	7.98
Mix 4	M4-5					25.23	67.45	7.26
Mix 4	M4-6					29.92	61.37	8.66
Mix 4	M4-7		6.79	92.46	0.73	24.94	69.48	5.56
Mix 4	M4-8	2.52	6.49	92.89	0.61			
Mix 4	M4-9							
Mix 4	M4-10							

APPENIX C (Continued)
Data Table for Mix 1 – Mix 4

Mix No	Anode No	Flexural Strength, MPa	Compressive Strength, MPa	CTE, E-6/C @ 300C	Thermal Cond, W/mK
Mix 1	M1-1				
Mix 1	M1-2				
Mix 1	M1-3				
Mix 1	M1-4	4.39	26.4	4.709	
Mix 1	M1-5	5.11	28.32	5.035	
Mix 1	M1-6	6.19	31.89	5.026	
Mix 1	M1-7	4.51	29.57	5.141	
Mix 1	M1-8	5.9		4.947	3.118
Mix 1	M1-9				
Mix 1	M1-10				
Mix 2	M2-1				
Mix 2	M2-2	3.16	21.22	4.897	
Mix 2	M2-3	4.07	23.32	4.926	2.538
Mix 2	M2-4				2.784
Mix 2	M2-5	4.52	21.27	5.014	2.64
Mix 2	M2-6	5.2		4.817	2.252
Mix 2	M2-7				
Mix 2	M2-8				
Mix 2	M2-9				
Mix 2	M2-10				
Mix 3	M3-1				
Mix 3	M3-2				
Mix 3	M3-3				
Mix 3	M3-4	7.44	33.3	5.218	
Mix 3	M3-5	7.91		5.304	2.28
Mix 3	M3-6	9.19	24.09	5.242	
Mix 3	M3-7	9.37	30.92	5.182	
Mix 3	M3-8	10.08	41.65	4.591	
Mix 3	M3-9				
Mix 3	M3-10				
Mix 4	M4-1				
Mix 4	M4-2				
Mix 4	M4-3				
Mix 4	M4-4	3.75	23.19	4.636	
Mix 4	M4-5	5.32	23.41	4.947	
Mix 4	M4-6	4.32	24.66	4.939	
Mix 4	M4-7	5.78	21.77	4.983	
Mix 4	M4-8	6.13		4.95	2.969
Mix 4	M4-9				
Mix 4	M4-10				

APPENDIX D
Data Table for Mix 5 – Mix 8

Mix No	Anode No	Binder Level, wt%	Alcoa GAD, g/cc	Alcoa BAD, g/cc	Koppers BAD, g/cc	ER, micro ohms-m
Mix 5	M5-1	14	1.598			
Mix 5	M5-2	14.5	1.606	1.573	1.568	74.7
Mix 5	M5-3	15	1.609	1.57	1.568	74.9
Mix 5	M5-4	15.5	1.614	1.575	1.573	69.1
Mix 5	M5-5	16	1.625	1.581	1.579	64.2
Mix 5	M5-6	16.5	1.633	1.58	1.578	62.4
Mix 5	M5-7	17	1.639	1.578	1.574	59.3
Mix 5	M5-8	17.5	1.644	1.576	1.575	56
Mix 5	M5-9	18	1.648	1.578	1.575	55
Mix 5	M5-10	18.5	1.652	1.575		
Mix 6	M6-1	14	1.626	1.564	1.561	69.3
Mix 6	M6-2	14.5	1.625	1.562	1.558	69.3
Mix 6	M6-3	15	1.632	1.563	1.561	66.7
Mix 6	M6-4	15.5	1.636	1.566	1.558	65.8
Mix 6	M6-5	16	1.64	1.568	1.561	61.7
Mix 6	M6-6	16.5	1.645	1.562	1.558	58.7
Mix 6	M6-7	17	1.647	1.559	1.554	57.4
Mix 6	M6-8	17.5	1.648	1.554	1.544	55.9
Mix 6	M6-9	18	1.646			
Mix 6	M6-10	18.5	1.648			
Mix 7	M7-1	14.5	1.543			
Mix 7	M7-2	15	1.543			
Mix 7	M7-3	15.5	1.553	1.507		
Mix 7	M7-4	16	1.561	1.51		
Mix 7	M7-5	16.5	1.566	1.512		
Mix 7	M7-6	17	1.569	1.513	1.51	70.4
Mix 7	M7-7	17.5	1.573	1.515	1.512	69
Mix 7	M7-8	18	1.575	1.509	1.507	68.3
Mix 7	M7-9	18.5	1.583	1.512	1.517	60.4
Mix 7	M7-10	19	1.589	1.507	1.51	59.2
Mix 8	M8-1	14.5	1.541			
Mix 8	M8-2	15	1.548	1.505		
Mix 8	M8-3	15.5	1.557	1.508		
Mix 8	M8-4	16	1.558	1.513	1.511	74.6
Mix 8	M8-5	16.5	1.566	1.515	1.512	71.9
Mix 8	M8-6	17	1.571	1.513	1.511	69.5
Mix 8	M8-7	17.5	1.575	1.511	1.511	67
Mix 8	M8-8	18	1.579	1.51	1.512	63
Mix 8	M8-9	18.5	1.579	1.507		
Mix 8	M8-10	19	1.593	1.507		

APPENDIX D (Continued)
Data Table for Mix 5 – Mix 8

Mix No	Anode No	CO2 React Air Perm nPm	CO2 React wt loss %	CO2 Residue, wt%	%Dust + % Attr	Air wt loss, wt%	Air Residue, wt%	Air % dust + % Attr
Mix 5	M5-1							
Mix 5	M5-2		3.34	95.12	1.52			
Mix 5	M5-3					2.06	97.79	
Mix 5	M5-4					1.75	97.86	0.37
Mix 5	M5-5							
Mix 5	M5-6	1.76				1.73	98.24	0.03
Mix 5	M5-7		5.26	92.04	2.66			
Mix 5	M5-8	1.98	4.09	94.64	1.25			
Mix 5	M5-9		4.56	93.8	1.63			
Mix 5	M5-10							
Mix 6	M6-1		7.42	87.81	4.75	2.45	97.42	0.12
Mix 6	M6-2		6.12	90.17	3069			
Mix 6	M6-3	1.62	11.08	83.08	5.79			
Mix 6	M6-4	1.58						
Mix 6	M6-5					2.34	97.52	0.14
Mix 6	M6-6	1.53						
Mix 6	M6-7	2.27						
Mix 6	M6-8					2.29	97.43	0.28
Mix 6	M6-9							
Mix 6	M6-10							
Mix 7	M7-1							
Mix 7	M7-2							
Mix 7	M7-3							
Mix 7	M7-4							
Mix 7	M7-5							
Mix 7	M7-6					20.83	75.33	3.81
Mix 7	M7-7	2.63				23.79	70.6	5.57
Mix 7	M7-8		5.38	94.26	0.35			
Mix 7	M7-9		5.91	92.05	2			
Mix 7	M7-10		5.37	94.08	0.53			
Mix 8	M8-1							
Mix 8	M8-2							
Mix 8	M8-3							
Mix 8	M8-4					23.52	71.68	4.74
Mix 8	M8-5					24.47	70.93	4.57
Mix 8	M8-6	1.32				24.07	69.96	5.91
Mix 8	M8-7		6	93.53	0.44			
Mix 8	M8-8		5.81	93.78	0.41			
Mix 8	M8-9							
Mix 8	M8-10							

APPENDIX D (Continued)
Data Table for Mix 5 – Mix 8

Mix No	Anode No	Flexural Strength, MPa	Compressive Strength, MPa	CTE, E-6/C @ 300C	Thermal Cond, W/mK
Mix 5	M5-1				
Mix 5	M5-2				
Mix 5	M5-3				
Mix 5	M5-4	5.78	21.57	3.859	
Mix 5	M5-5	7.37	22.62	4.504	
Mix 5	M5-6	7.14		4.615	2.889
Mix 5	M5-7	7.89	26.02	3.613	
Mix 5	M5-8	8.99		3.604	3.046
Mix 5	M5-9				
Mix 5	M5-10				
Mix 6	M6-1				
Mix 6	M6-2				
Mix 6	M6-3	6.7		3.776	2.854
Mix 6	M6-4	6.71	20.74	4.083	2.46
Mix 6	M6-5	7.05	21.27	3.999	
Mix 6	M6-6	6.95	19.56	3.997	3.082
Mix 6	M6-7		23.64	3.933	3.063
Mix 6	M6-8				
Mix 6	M6-9				
Mix 6	M6-10				
Mix 7	M7-1				
Mix 7	M7-2				
Mix 7	M7-3				
Mix 7	M7-4				
Mix 7	M7-5				
Mix 7	M7-6	4.8	28.21	4.52	
Mix 7	M7-7	5.57		4.458	2.92
Mix 7	M7-8	6.05	23.49	5.302	
Mix 7	M7-9	7.51	28.78	5.549	
Mix 7	M7-10	8.99	31.71	4.602	
Mix 8	M8-1				
Mix 8	M8-2				
Mix 8	M8-3				
Mix 8	M8-4	4.08	26.78	4.54	
Mix 8	M8-5	5.09	30.52	4.495	
Mix 8	M8-6	5.45		4.561	3.118
Mix 8	M8-7	6.31	25.14	4.182	
Mix 8	M8-8	6.56	25.03	4.372	
Mix 8	M8-9				
Mix 8	M8-10				

APPENDIX E
Data Table for Mix 9 – Mix 12

Mix No	Anode No	Binder Level, wt%	Alcoa GAD, g/cc	Alcoa BAD, g/cc	Koppers BAD, g/cc	ER, micro ohms-m
Mix 9	M9-1	14	1.6			
Mix 9	M9-2	14.5	1.609			
Mix 9	M9-3	15	1.614			
Mix 9	M9-4	15.5	1.623		1.559	67.4
Mix 9	M9-5	16	1.627		1.566	63.6
Mix 9	M9-6	16.5	1.634		1.566	60.8
Mix 9	M9-7	17	1.638		1.571	58.1
Mix 9	M9-8	17.5	1.645		1.568	56
Mix 9	M9-9	18	1.646		1.559	56.2
Mix 9	M9-10	18.5	1.651			
Mix 10	M10-1	14.5	1.559			
Mix 10	M10-2	15	1.572			
Mix 10	M10-3	15.5	1.574			
Mix 10	M10-4	16	1.581		1.521	69.9
Mix 10	M10-5	16.5	1.588		1.521	67
Mix 10	M10-6	17	1.597		1.524	64
Mix 10	M10-7	17.5	1.605		1.528	61.2
Mix 10	M10-8	18	1.605		1.522	60.2
Mix 10	M10-9	18.5	1.61		1.515	58.3
Mix 10	M10-10	19	1.619			
Mix 11	M11-1	14	1.524			
Mix 11	M11-2	14.5	1.533			
Mix 11	M11-3	15	1.541			
Mix 11	M11-4	15.5	1.55		1.493	78.2
Mix 11	M11-5	16	1.547		1.484	80
Mix 11	M11-6	16.5	1.559		1.494	74.2
Mix 11	M11-7	17	1.565		1.494	73.9
Mix 11	M11-8	17.5	1.564		1.502	67.3
Mix 11	M11-9	18	1.577		1.508	65.3
Mix 11	M11-10	18.5	1.582			
Mix 12	M12-1	17.5	1.573			
Mix 12	M12-2	17.5	1.587		1.476	59.1
Mix 12	M12-3	17.5	1.589		1.479	60.9

APPENDIX E (Continued)
Data Table for Mix 9 – Mix 12

Mix No	Anode No	CO2 React Air Perm nPm	CO2 React wt loss %	CO2 Residue, wt%	%Dust + % Attr	Air wt loss, wt%	Air Residue, wt%	Air % dust + % Attr
Mix 9	M9-1							
Mix 9	M9-2							
Mix 9	M9-3							
Mix 9	M9-4					2.45	97.31	0.23
Mix 9	M9-5	1.71				2.07	97.7	0.22
Mix 9	M9-6		8.18	88.87	2.93			
Mix 9	M9-7	1.77	6.69	90.59	2.7			
Mix 9	M9-8	1.62						
Mix 9	M9-9	1.93						
Mix 9	M9-10							
Mix 10	M10-1							
Mix 10	M10-2							
Mix 10	M10-3							
Mix 10	M10-4	1.57						
Mix 10	M10-5					16.74	79.55	3.7
Mix 10	M10-6	1.23						
Mix 10	M10-7	1.42				17.43	78.53	4.04
Mix 10	M10-8	1.84	3.81	95.76	0.42			
Mix 10	M10-9		4.87	94.73	0.39			
Mix 10	M10-10							
Mix 11	M11-1							
Mix 11	M11-2							
Mix 11	M11-3							
Mix 11	M11-4		2.99	96.73	0.28			
Mix 11	M11-5							
Mix 11	M11-6					21.17	72.36	6.47
Mix 11	M11-7		4.74	94.87	0.38			
Mix 11	M11-8		6.98	92.37	0.64			
Mix 11	M11-9					23.32	70.62	6.06
Mix 11	M11-10							
Mix 12	M12-1							
Mix 12	M12-2							
Mix 12	M12-3		4.04	95.43	0.52			

APPENDIX E (Continued)
Data Table for Mix 9 – Mix 12

Mix No	Anode No	Flexural Strength, MPa	Compressive Strength, MPa	CTE, E-6/C @ 300C	Thermal Cond, W/mK
Mix 9	M9-1				
Mix 9	M9-2				
Mix 9	M9-3				
Mix 9	M9-4	6.12	25.73	3.365	
Mix 9	M9-5	7.8		3.498	2.818
Mix 9	M9-6	8.37	27	3.617	
Mix 9	M9-7	9.05		3.685	2.928
Mix 9	M9-8	9.16	26.14	3.258	2.994
Mix 9	M9-9	9.83	32.31	3.42	3.09
Mix 9	M9-10				
Mix 10	M10-1				
Mix 10	M10-2				
Mix 10	M10-3				
Mix 10	M10-4	5.16	29.95	4.427	2.729
Mix 10	M10-5	4.94	26.24	4.388	
Mix 10	M10-6	6.17	28.84	4.134	2.661
Mix 10	M10-7	6.92		4.356	2.947
Mix 10	M10-8	6.45		4.429	3.16
Mix 10	M10-9	8.69	33.88	4.386	
Mix 10	M10-10				
Mix 11	M11-1				
Mix 11	M11-2				
Mix 11	M11-3				
Mix 11	M11-4	2.43		4.395	2.47
Mix 11	M11-5	3.58		4.631	2.393
Mix 11	M11-6	3.78	20.33	4.792	
Mix 11	M11-7	3.79	19.35	4.753	
Mix 11	M11-8	4.34	27.93	4.362	
Mix 11	M11-9	4.91	30.92	4.502	
Mix 11	M11-10				
Mix 12	M12-1				
Mix 12	M12-2	7.34	24.49	4.257	
Mix 12	M12-3	7.01	25.45	4.364	

APPENDIX F Reproducibility of Mix 1 and Mix 11 And Mix 4 and Mix 12

APPENDIX F (Continued)
Reproducibility of Mix 1 and Mix 11
And
Mix 4 and Mix 12

APPENDIX F (Continued) Reproducibility of Mix 1 and Mix 11 And Mix 4 and Mix 12

APPENDIX F (Continued)
Reproducibility of Mix 1 and Mix 11
And
Mix 4 and Mix 12

Anthracite Fillers for Specialty Graphite – Feedstock Selection and Product Improvement

FINAL REPORT

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Abstract

This report presents the findings of a study on the possible use of Pennsylvania anthracite as a replacement for petroleum coke in the production of isostatically molded graphite. The study had two main components: an investigation of the mechanisms of graphitization of anthracites, and the production of isomolded graphite articles in industrial tests. In the first part of the study, it was discovered that some of the mineral constituents in anthracites can act as *in situ* graphitization catalysts. The mechanism of graphitization catalysis involves the transformation of minerals, such as quartz and rutile, to the corresponding carbides. At higher temperatures, these carbides decompose, presumably releasing highly reactive carbon atoms. The highly reactive forms of carbon can eliminate crosslinks between the graphene layers or improve structural order in existing graphene layers, or possibly both. X-ray diffraction evidence shows the formation and disappearance of these carbides as heat-treatment temperature is increased. The disappearance of the carbides appears to coincide with the onset of the so-called graphitization jump, marked by sharpening of the (002) peak and the appearance of the (*hkl*) peak (the indicator of true three-dimensional ordering) in the X-ray diffractograms. Differences in the graphitization behavior of the four anthracites studied can be attributed to differences in *in situ* graphitization catalysis. LCNN anthracite was selected for scale-up studies. This anthracite was used as the filler material for the production of test pieces of isomolded graphite, being carried through an industrial processing scheme. Petroleum sponge coke was used to produce control artifacts in the same production cycle. The various properties of the anthracite-derived graphite fall into the low end of the range of acceptable specifications for isomolded graphites. Additional testing in future years could likely lead to commercialization of this premium carbon material made from anthracitic coals.

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List of Graphical Materials

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Figure 44 Demineralized Summit plus rutile, heated to 2600°C

Figure 45 Demineralized Summit plus quartz, heated to 2600°C

Figure 46 Demineralized Summit plus iron oxide, heated to 2600°C

Figure 47 Thermal expansion in the c-direction

Figure 48 Thermal expansion in the a-direction

Figure 49 Resistivity in the a-direction

Figure 50 Resistivity in the c-direction

Figure 51 Flexural strength in the a-direction

Figure 52 Flexural strength in the c-direction

Figure 53 Median pore differences

Figure 54 Ash levels

Figure 55 Optical micrograph of p18, 100X magnification

Figure 56 Optical micrograph of p19, 100X magnification

Figure 57 Optical micrograph of p20, 100X magnification

Figure 58 Optical micrograph of p21, 100X magnification

Figure 59 Optical micrograph of p22, 100X magnification

Figure 60 Optical micrograph of p23, 100X magnification

Figure 61 Optical micrograph of p24, 100X magnification

Figure 62 Optical micrograph of p25, 100X magnification

Figure 63 Optical micrograph of p26, 100X magnification

Figure 64 Optical micrograph of p27, 100X magnification

Executive Summary

Anthracites are high-carbon-content coals that behave as both a graphitizing and non-graphitizing carbon, depending on the heat-treatment temperature (HTT) to which they are exposed. The reason for this dual behavior must lie in the nature of the physical, organic, or inorganic properties of these coals. Previous studies have focused on one of these traits, and have not looked at any interaction between them. Thus, the theories developed to this time concerning the mechanism of anthracite graphitization are incomplete. This present study focuses on the interaction between the organic and inorganic portions of anthracites to show that graphitization is influenced by both properties, and that differences in degree of graphitization—how close in structure to graphite anthracite can become—can be explained by carbide formation and decomposition.

Carbides are able to form because the minerals in anthracites contain elements capable of reacting with carbon to form carbides. These carbides form at 2200°C after heating for one hour, and decompose by 2600°C. The carbon reacting with the metallic elements from the minerals is, we hypothesize, the least stable carbon present, or those carbon atoms not contained within a polynuclear aromatic ring system. The removal of these less-stable or disordered carbons allows the already planar ring systems to condense into graphite crystallites. Also, when the carbides decompose they leave behind a reactive dicarbene atom that will attack any imperfections in the adolescent graphite crystallites.

A suite of anthracites was tested to determine the most graphitizable anthracite. This information was used to select one anthracite for industrial graphitization trials by Carbone of America. The anthracite selected was used as a filler in the production of an isostatically molded graphite. The anthracite-based molded graphite was then tested against a petroleum-coke-based graphite, produced as a control experiment, to determine whether property differences could be detected. In some properties, the petroleum-based graphite was superior, but in others the anthracite-based molded graphite was better. These preliminary data show that, at the least, anthracite can be used as a “low end” specialty molded graphite; work is in progress to produce a normal grade specialty graphite from anthracite.

Introduction

Graphite is formed in nature in large deposits around the world, including Mexico, the United States, Brazil, Canada, and Sri Lanka. Natural graphite is entirely aromatic carbon, lustrous, soft, and is often used as a solid lubricant because it easily shears and flakes apart. Graphite can also be produced by heating some carbon materials to temperatures in the range of 2000-3000°C, or by pressurizing the carbon as it is heated to a lower temperature. The vast majority of artificial graphite is produced from the combination of an aromatic petroleum by-product filler, i.e. petroleum coke, and binders that allow the graphite to be shaped or molded for a specific application. Natural graphite is not used as a filler for manufacture of molded graphites because it is more expensive than petroleum coke, and, because of its lubricity, it forms a viscous, non-shapeable paste, when mixed with a binder. Petroleum coke is an acceptable feedstock for graphite production for three reasons: (1) it undergoes structural changes at graphitization heat-treatment temperatures of $\approx 3000^{\circ}\text{C}$ that leave the final structure close to that of natural graphite; (2) when mixed with a binder, it produces a shapeable product that has properties that make it suitable for electrical-conducting or thermal applications; and (3) it is less expensive than other aromatic feedstocks, such as anthracene, naphthalene, or natural graphite.

Anthracite is primarily carbon, having 92-98% fixed carbon on a mineral-matter- and moisture-free basis. Anthracite could also be used as a filler for graphite production if it met the three criteria listed above for petroleum coke. Therefore, it was necessary to determine why some anthracites will do better than others at achieving a structure similar

to that of natural graphite after being exposed to identical graphitization heat treatment temperatures. The reason for the differences in extent of graphitization must lie in differences in physical, organic, or inorganic properties. After this understanding had been developed, a selected anthracite was tested to determine whether it will form a product comparable to petroleum-coke-based graphite when mixed with a binder. The third criterion, cost, has already been met in that anthracite is $\approx$ \$200-300 per ton cheaper than petroleum coke.

One component of this project was the determination of which anthracite, selected from a suite of Pennsylvania anthracites, best approaches the structure of graphite when exposed to graphitization heat treatment temperatures. The hypothesis tested in this component was that the amount and identity of the inorganics in the selected anthracites are the crucial factors for explaining differences in their extent of graphitization, or why some better approach the structure of graphite. The determination of how close in structure a heat-treated anthracite is to graphite was made by a comparison of X-ray diffraction data available on natural graphite, and the X-ray diffraction patterns of the heat-treated anthracite samples. Natural graphite produces characteristic peaks during X-ray diffraction at specific angles that can be used to determine the dimensions and interlayer spacing of the graphitic crystallites comprising its structure. Therefore, the level of similarity to natural graphite in the heat-treated anthracites, or graphitizability, can be measured by analysis of the X-ray diffraction peaks produced by the heat treated anthracites. To determine if differences in graphitizability of anthracites that have been exposed to the same graphitization temperatures is the result of inorganic differences,

four samples, which had different levels of mineral matter content and weight percentages of carbon, were obtained from active Pennsylvania mines .

The second component of this research was the production, using standard industrial procedures, of a synthetic graphite, with properties suitable for industrial applications, using anthracite as the filler instead of petroleum coke. The hypothesis tested in this component was that the anthracite that best approaches the structure of natural graphite as a result of laboratory-scale heat-treatment will produce a graphite most similar to a petroleum-based graphite. The production of the anthracite-based graphite was carried out by Carbone of America, a graphite manufacturer located in St. Marys Pennsylvania. Carbone produces petroleum-based graphites as a standard product line, and thus they have a wealth of information on the properties of their materials, which can be compared to the properties of the anthracite-based graphite.

Experimental Methods

Sampling

Anthracite samples for the study were selected from the field by sampling from four active anthracite mines selected on the bases of mine longevity (with mining of same seam planned for, at minimum, five years) and geological variations, such as amount of mineral matter present. The mines which met these criteria were Jeddo, UAE, Lehigh Coal and Navigation (LCNN), and Summit. Jeddo and LCNN mine the Mammoth vein of the Eastern Middle Seam in Pennsylvania while UAE mines the Lykens Valley #2 vein. Summit mines a conglomeration of veins, but for this research run-of-mine, or unprocessed, anthracite was recovered from the Tracey vein. The Jeddo and LCNN samples were separated in heavy media into pea size and UAE was processed using a Diester table. Three 55-gallon drums of each anthracite (twelve total barrels) were collected from the pea-sized pile of processed coal. This method could be referred to as a “grab” sample from the preparation plant, as opposed to a “channel” sample taken underground.

In order to ensure the homogeneity of the coal for analysis, a rigorous sampling procedure was followed. First, all three barrels of a particular anthracite were dumped onto a clean surface. The coal was shoveled on top of itself until the particles that were originally at the bottom of the pile had cycled from bottom to top and through the pile twice. After this, the pile was coned and quartered, by simply forcing a plus-sign-shaped system of boards through the pile, separating it into quarters. These quarters were each returned to a barrel, with the idea that each barrel would now have the same makeup as

far as particle size and chemical composition. One of these barrels was coned and quartered again, taking opposite quarters (or half the barrel) and crushed down to $-\frac{1}{4}$ inch using a hammer mill. This quantity of $-\frac{1}{4}$ inch coal was put through a riffler three times. Next, one half of the $-\frac{1}{4}$ inch was saved in bags of approximately 10 lbs. each. The other half of $-\frac{1}{4}$ inch was put through the hammer mill again, this time with a -20 mesh screen in place. The quantity of -20 mesh was riffled again and broken down into aliquots of approximately 4 lbs. each.

After the above work was completed on all four samples, one bag of -20 mesh was separated into eight aliquots using a rotary splitter. Seven of these aliquots, weighing 250g each, were sealed in foil laminate bags under an argon atmosphere; the remaining aliquot was further crushed to -60 mesh. This 250g quantity of -60 mesh was also separated with a rotary splitter into sections weighing 35g each. These -60 mesh aliquots were then sealed in foil laminate bags under argon. This sampling should ensure a good representation of the entire coal sample that was collected. The argon atmosphere will prevent any further oxidation so consistency of analytical results from one date of testing to another will not be a problem. Also, the small quantities sealed in each bag will further increase accuracy because they eliminate the problem of having to constantly open the bag, select the desired quantity of anthracite, and reseal the bag. This opening and closing will allow oxygen into the system, which can alter the coal structure by oxidation.

Characterization

This suite of anthracites was characterized by proximate and ultimate analysis. The instruments used were a CHN-600, SC-132 sulfur determinator, and MAC-400 proximate analyzer, all made by the Leco Corporation. For the CHN-600 between 0.03 and 0.07 grams of sample were weighed and placed in a tin crucible of cylindrical shape. The crucible was then crimped and folded over twice in order to promote smooth entry into the combustion chamber, where the sample is burned and its CO₂ and H₂O infrared spectrum is reduced to a weight percentage of elemental C and H. The nitrogen is calculated via a thermal conductivity cell against a standard. Oxygen was calculated by difference.

The sulfur analyzer worked much on the same principle, except that instead of the IR spectrum of CO₂ and H₂O, the IR spectrum of SO₂ is measured and related to a weight percentage. In this device approximately 0.5 grams of sample is weighed and placed in a ceramic boat, which is then placed in a hot zone where all of the sample is combusted.

Proximate analysis was determined using the MAC-400. This involved placing approximately 0.5 grams of anthracite in the crucibles provided and following the weight loss percentages as heat is increased to the crucibles. The MAC-400 follows ASTM heating guidelines, which are 105°C for one hour to determine moisture, 950°C (no oxygen present) for seven minutes to determine volatile matter, and 750°C for two hours to determine ash.

The ultimate and proximate analysis results were then converted to a dry, or moisture and ash free basis (maf), and the fixed carbon from proximate analysis was also reported on a mineral matter and moisture free basis (mmmf). The equations used for

these conversions are listed below. The mmmf conversion requires the use of the Parr formula for percentages of mineral matter

$$\text{MAF: } \%X_{\text{maf}} = 100 * \%X_{\text{ar}} / [100 - (\%M_{\text{ar}} - \%A_{\text{ar}})]$$

$$\text{Parr formula: } \text{MM} = 1.08A + 0.55S$$

$$\text{MMMF: } \%X_{(\text{mmmf})} = 100 * \%X_{\text{ar}} / [100 - (\%M_{\text{ar}} - \%MM)]$$

In these equation "X" represents the property of interest, "M" represents moisture, "A" represents ash, "MM" represents mineral matter, and "S" is sulfur.

Graphitization

Following initial characterization, the samples were graphitized in a Centorr Vacuum Industry Series 45 furnace which operates in either a vacuum or argon atmosphere. The samples were weighed to 10 g and placed in graphite crucibles with lids, provided by POCO Graphite. These crucibles were then placed in the hot zone of the furnace (6 in X 9 in) and the top graphite plug and steel plate secured. The environment of the hot zone was purged by pulling a vacuum, and then backfilling with ultra-high purity argon three times. Following this purge, the samples were heated to 2000, 2200 2500, and 2600°C with a heating rate of 20°C/min and hold at the maximum temperature for one hour (in vacuum). Following heat treatment, the anthracites were removed from the furnace for further characterization.

X-ray Diffraction

X-ray diffraction data were acquired using a SCINTAG PAD-V X-ray diffraction unit that uses Cu K α radiation. The slit widths of this unit are 2° for the primary beam, and 0.1° for the diffracted beam. The PAD-V was set for continuous scanning at a rate of 2.5°/min from 5° to 90° 2 θ .

The anthracites were prepared for analysis in several different manners in order to check the effect of sample preparation on the X-ray diffraction pattern. First, the anthracites were taken directly from the graphitization furnace and mounted on a single crystal quartz slide from the Gem Dugout. The particle size of the anthracites was -60 mesh in this case, and the samples were mounted to the slide with petroleum jelly. The jelly was spread thinly over the surface of the slide and the anthracite powder was sprinkled over the top of this jelly layer. The idea behind this mounting process is to produce a random orientation of particles along the surface of the slide, approximately the same width everywhere. This method of sample preparation was repeated for -60 mesh anthracite samples that were heat-treated and then ground to pass a -100 mesh screen. The petroleum jelly must be used because the X-ray diffraction unit used for this research holds the quartz slide in a vertical position.

A second method of mounting the samples was carried out by drilling a 4-mm circular recess into the quartz slide and packing the powder into this constant volume. Again, -60 mesh and -100 mesh anthracites that had been heated to 2600°C were analyzed by this method. The two different mounting techniques produced different intensities, but the values for d-spacing, L_c , and L_a are all within experimental error. The

finer grinding also increased the peak intensity, but slightly reduced L_c , in agreement with grinding experiments in the literature.

The raw data curves were corrected for $\text{Cu K}\alpha 2$ scattering and smoothed by both Pierson VII and Box Car fitting software built into the SCINTAG operating system. Next, the peaks were found by the peak finder program, also built into the SCINTAG software. The peak finder application uses a digital filter that contains two parameters the user must input. The two parameters are the ESD multiplier, and the ripple multiplier, which were set at seven and nine, respectively—the most stringent settings available for what curves will represent an identifiable peak. Once the peak finder application was performed the properties of the identified peaks were exported to a viewable file where d-spacing, relative intensities (as percents), absolute intensities, and full width at half maximum (FWHM) were listed. The d-spacing, an important indicator of graphitic development, was instantaneously calculated from the (002) peak by the Bragg equation derived using simple geometry applied to the crystal configuration shown below.

The Bragg equation is:

$$n \lambda = 2 d \sin \theta$$

where n =diffraction order, or 1 for the (002) peak

λ = wavelength of Cu K_{α} which is 1.54059 Å

d = interlayer spacing

θ = diffraction angle of (002)

The crystallite size, L_c , was also calculated from the (002) peak for all the samples using the Scherrer equation:

$$L_c = K \lambda / (\beta \cos \theta)$$

where L_c = crystalline height

K = Scherrer constant, taken as 0.9

β = FWHM in radians and:

$$\beta^2 = B^2 - b^2$$

and B = peak broadening of the (002) reflection of the sample

b = peak broadening of crystal standard, quartz was used for this

As seen in the Scherrer equation a standard is used to correct for instrumental broadening. The standard was a highly crystalline material that should have little broadening due to its structure, thus any broadening can be attributed to the instrument. Quartz was used as the standard for this research. In the case of graphitized anthracite, broadening of the (002) peak is due more to small crystallite size than instrumental effects. The reason why small crystallite size causes broadening deals with the absence of planes capable of producing diffracted X-rays that will cancel out other rays that are very close to the Bragg angle.

The crystal diameter, L_a , was calculated by the Biscoe and Warren method where

$$L_a = 1.84 \lambda / (\beta \cos \theta)$$

A 95% confidence interval was placed on the X-ray diffraction parameters of d-spacing, L_c , and L_a obtained for the 2600°C samples. The equation used for this confidence interval was:

$$\text{Crystallite parameter} \pm 2.015 * (\text{stdev} / \sqrt{\text{\# of samples}})$$

where “stdev” is standard deviation.

Transmission Electron Microscopy

The structures of the four raw anthracites were analyzed using transmission electron microscopy (TEM). The goals of this analysis were to view the arrangement of the aromatic sheets of carbon comprising the anthracite, and to view the shapes of the pores present in the raw samples. The sample preparation used to accomplish these goals involved the grinding of the samples to as fine a possible size as possible; all could pass a –325 US mesh screen. The fine powders were then immersed in an alcohol solution and the larger particles sank to the bottom, thus leaving the finest particles in a suspended state. A tweezer was then dipped into the anthracite and alcohol mixture so that the suspended particles were contained in the droplet that adhered to the end of the tweezer. The droplet was then allowed to drip onto a TEM mount. The alcohol then evaporated, leaving behind the finest particles.

The analysis was performed using a Hitachi HF-2000 transmission electron microscope operated at 200 kV, with a point-to-point resolution of approximately 0.24 nm. High-resolution images were taken at magnifications of 100K to 500K on a negative

film on the vicinity of the optimal defocus. The films were then scanned on a flatbed negative scanning device at 400% image enlargement and 300DPI.

Computer Controlled Scanning Electron Microscopy CCSEM

The samples were prepared for analysis by first placing the anthracite or heat treated anthracite in a furnace at 90°C for 24 hours. Two grams of sample were then mixed with three grams of melted caruba wax and poured in a rubber sample mold. An epoxy was then used to cover the surface of the sample and wax. The epoxy was then polished in six steps with each step a less severe grade of grit used in the polishing. Once the polishing was complete, the samples were inserted into the computer controlled scanning attachment and the analysis begun. The electron beam was rastered over the surface of the sample at three magnification 800, 250, and 50X magnification. The shape of the particle is recorded using the equation:

$$\text{Shape factor} = (\text{perimeter})^2 / \text{Area} * 4\pi$$

The weight of each element comprising an inorganic was determined by totaling the number of X-ray counts and then dividing an individual element's number of counts by this total to get the percentage of an element's X-ray counts. This percentage was then multiplied by the amount of ash determined from proximate analysis.

Results and Discussion

Part 1. Anthracite graphitization via carbide formation

Introduction:

Anthracite behaves as both a graphitizing (soft) and non-graphitizing (hard) carbon [1-6]. Franklin used a detailed X-ray diffraction study of raw and heat treated anthracites to explain this phenomenon [1]. She found that the anisotropy of the pores in char samples heated to 1000°C were responsible for this dual behavior [1]. The flattened pores were created by the edge-on alignment of the basic, pre-graphitic crystallites in these pore walls. The edge-on alignment allowed for the crystallites to condense into larger crystallites when exposed to temperatures in excess of 2000°C. Franklin states that whole graphene layer movement was responsible for anthracites ability to graphitize, as opposed to individual carbon atoms being added to the end of an aromatic layer [1]. The evidence for this theory was the recognition of a significant increase in degree of graphitization, or graphitization “jump,” above 2500°C. A single carbon addition would be a continuous process, she argued, and therefore would not produce a dramatic increase in degree of graphitization over a narrow temperature range.

Franklin’s work was the first and most substantial in explaining the difference in behaviors during heat treatment between graphitizing and non-graphitizing carbons, and only minor modifications to her theories have been made. Mering and Mare followed up Franklin’s work by basically agreeing with her findings, but point out that the graphene or aromatic layers of carbon are not perfectly planar in the raw carbon source, whether it be a graphitizing or non-graphitizing carbon [4]. In her illustration depicting the graphitization process, Franklin shows perfectly flat graphene layers contained within

small crystallites at temperatures at or below 1000°C. Mering and Mare argue that these small crystallites exist, but the layers comprising them are twisted and non-planar, and that interstitials or cross-links can bind these stacked layers together [4]. Therefore the graphitization process occurs in several stages. First, the layers must be healed or annealed in order to become planar. Next, the interstitials connecting the stacked layers must be removed, which allows ordering in the c-direction and is evidenced by a narrowing of the (002) peak. Lastly, the now-planar graphene layers contained within small crystallites that have no cross-links can combine with neighboring layers to form larger crystallites. This last step is achieved by whole-layer movement, as Franklin stated, and leads to growth in the a-direction.

The next breakthrough in understanding of the graphitization process with particular reference to anthracite was made by Oberlin, using high resolution transmission electron microscopy (HRTEM) [2,3]. Oberlin used HRTEM to visualize the microtexture of anthracites heat-treated to various temperatures in order to determine whether the flattened or anisotropic pores described by Franklin could be detected. Indeed Oberlin saw the development of flattened pores and anisotropic microtexture as heat treatment temperature (HTT) was increased. The study included twelve anthracites from various parts of the world [2]. This method, in essence, provided pictorial evidence for Franklin's assumptions that made decades earlier when such powerful techniques as HRTEM were not yet available.

The use of HRTEM to study anthracite graphitization was continued by Rouzaud and co-workers [7]. They published no TEM images, but claimed to be able to predict differences in degree of graphitization of various anthracites by viewing the pore shape in

the raw, or unheated, anthracite samples. Four classes were defined: microtexture 1A consists of spherical pores where the basic structural units (BSU) show no preferential alignment and essentially form a pore wall by being compacted together in no particular order. Microtexture 1B shows a random distribution of BSU and is indicative of immature, or low-rank coals. Microtexture 2A is described as pore flattening and considered the best orientation for enhanced graphitizability. The BSU are aligned end-to-end and therefore are more easily able to experience dehydrogenation and condensation reactions necessary for crystallite growth. Microtexture 2B, or flow anisotropy, also has the end-to-end alignment, but flattened pores are not witnessed. So the anthracites with flattened or anisotropic pores present in the raw sample were the most highly graphitizable.

However, several items contradict this theory that degree of graphitization can be predicted by pore shape of the raw samples. In the original paper by Oberlin describing the novel use of HRTEM for carbon study, she showed two types of microtexture in the same anthracite sample [2]. Oberlin studied an Abernant anthracite char (heated to 1000°C) and showed that both Type A and Type B microtextures, which she described as isotropic or anisotropic microtexture respectively, were present in one sample of the char. Because at least two microtextures can be found in a single anthracite, it would seem difficult to define four classes of pore microtexture and be able to predict degree of graphitization based on these classes, because one anthracite sample has been shown to contain more than one type of microtexture.

Because no actual HRTEM images of the four types of microtexture described by Rouzaud were published, the four anthracites used in this study were analyzed using HRTEM in order to determine if these four types of microtexture could be visualized.

High Resolution Transmission Electron Microscopy for Microtexture Evaluation:

For this evaluation the experimental techniques developed by Oberlin were followed as closely as possible [2]. However, the HF2000 TEM unit located at Penn State's Materials Research Institute was not capable of completely re-creating Oberlin's work, but the images produced are sufficient for microtexture visualization.

Oberlin "gently grinds" her anthracites and used lattice fringe imaging, bright field, and dark field techniques to study the anthracites' microtextures [2]. Oberlin first produced a selected area diffraction (SAD) pattern in order to view what (*hkl*) bands are visible. She then used a beam aperture small enough so that visualizations could be made at various points along the (*hkl*) lines. The investigations were done in dark field, so she is essentially taking a picture of the diffracted image, so carbon layers appear dark and pores bright.

The HF 2000 instrument used in our work did not have dark field availability, nor a beam aperture small enough to view the structure at various points along a given (*hkl*) band. Therefore the investigations were done in bright field, where all (*hkl*) bands are present because the image seen is transmitted, not diffracted as in dark field work. In the case of raw anthracites, though, the only (*hkl*) band of any intensity is the (*002*), so a transmission image (i.e. a bright field image) would essentially be a (*002*) band image

anyway. The results of this bright field investigation are presented on the next page and show that Oberlin's method of visualization was adequately reproduced.

In summary, Oberlin used HRTEM to visualize the microtexture of twelve different anthracites that had been to various temperatures [2]. She found that the microtextures changed with increasing HTT from isotropic to anisotropic, indicating the transition from a non-graphitic carbon to a graphitic carbon. In the 1000°C heat-treated samples she identifies two types of microtexture, Type A and B, representing isotropic versus anisotropic. Oberlin also identified both types of microtexture in one sample, or in different regions of the same anthracite. Her TEM approach to explaining anthracite graphitization was later continued by Rouzaud, who identified, via cartoons, four different pore shapes and microtextures found in anthracite that will lead to different degrees of graphitization.

The TEM studies reviewed here serve two purposes. The first is to present a generic mechanism for anthracite graphitization that is true for all anthracites from all parts of the world. The second is to point out microtextural differences in raw anthracites from various geological regions and show that these differences are responsible for varied degrees of graphitization. Both studies focus on the physical and organic portion of the anthracites, in terms of pore shape and basic structural unit alignment. However, there is evidence from Oberlin's work that elements contained within the minerals of an anthracite react with the carbon present to form carbides [2,3,8]. Oberlin noted the formation of hollow graphitic shells left behind after the metal from the carbide vaporized at highest HTT. She did not go into detail about how these carbides formed and then how they formed hollow graphitic shells, but only said that this carbide

formation is “a parasitic effect that masks the true anthracite graphitization mechanism” [2]. So even in work that was undertaken to show the importance of microtexture as a controlling factor in the anthracite graphitization mechanism, evidence of “catalytic graphitization” or modified graphitization was found [2]. Therefore, the amount and type of mineral matter present may be responsible for observed differences in extent of graphitization of various anthracites, and, in some instances, may be the crucial factor in the graphitization mechanism itself.

X-ray Diffraction Analysis of Raw and Heat Treated Anthracites:

Oberlin used HRTEM to visualize anthracite graphitization, and Rouzaud used the technique to predict differences in degree of graphitization of various anthracites [2,7]. In our research, X-ray diffraction was used to follow the structural changes incurred during heat treatment, and to show any differences in degree of graphitization. The methodology of this research was to select a suite of anthracites from Pennsylvania and expose them to the same HTTs for the same period of time and then determine if any differences in extent of graphitization could be observed. This information would then be used to select an anthracite for use as a filler in graphite production. The four anthracites, LCNN, Jeddo, UAE, and Summit were all heat treated to 2000, 2200, 2500, and 2600°C for one hour in a vacuum. The X-ray diffraction patterns of the raw and heat-treated anthracites are shown in Figures 1 to 20 beginning on the pages that follow.

Figure 1 X-ray diffractogram of raw UAE anthracite

Figure.2 X-ray diffractogram of UAE anthracite heated to 2000°C

Figure.3 X-ray diffractogram of UAE anthracite heated to 2200°C

Figure 4 X-ray diffractogram of UAE anthracite heated to 2500°C

Figure 5 X-ray diffractogram of UAE anthracite heated to 2600°C

Figure.6 X-ray diffractogram of raw Jeddo anthracite

Figure 7 X-ray diffractogram of Jeddo anthracite heated to 2000°C

Figure 8 X-ray diffractogram of Jeddo anthracite heated to 2200°C

Figure.9 X-ray diffractogram of Jeddo anthracite heated to 2500°C

Figure 10 X-ray diffractogram of Jeddite anthracite heated to 2600°C

Figure 11 X-ray diffractogram of raw LCN anthracite

Figure.12 X-ray diffractogram of LCN anthracite heated to 2000°C

Figure 13 X-ray diffractogram of LCN anthracite heated to 2200°C

Figure.14 X-ray diffractogram of LCNN anthracite heated to 2500°C

Figure.15 X-ray diffractogram of LCN anthracite heated to 2600°C

Figure 16 X-ray diffractogram of raw Summit anthracite

Figure 17 X-ray diffractogram of Summit anthracite heated to 2000°C

Figure 18 X-ray diffractogram of Summit anthracite heated to 2200°C

Figure 19 X-ray diffractogram of Summit anthracite heated to 2500°C

Figure.20 X-ray diffractogram of Summit anthracite heated to 2600°C

A determination of which sample becomes more like graphite is made by comparing the diffraction patterns, and in particular the location and properties of the peaks present, of these heat treated anthracites to the characteristic X-ray diffraction pattern of graphite. Therefore, the (hkl) reflections and their locations for a typical graphite are given in Table 1, to act as a reference for discussion of the X-ray diffraction patterns of the heat-treated anthracites.

Table 1 (hkl) peak location of characteristic graphite peaks

(hkl) peak	Location in 2θ
(002)	26.54°
(100)	42.39°
(101)	44.58°
(004)	54.66°
(103)	59.91°
(110)	77.54°
(112)	83.67°
(006)	87.06°

All the raw anthracites show weak and broad (002) and (100) peaks. These broad peaks are shown by the red brackets present in the X-ray diffraction patterns of the raw samples, Figure 1 for example. In some cases, the X-ray diffraction patterns of the raw anthracites show mineral, or inorganic, peaks. Again, an example of this is seen in Figure 1, where an intense, narrow, quartz peak is seen at 26.68° , to the right of the broad (002) peak. The presence of a distinct quartz peak can also be seen in Figure 16, the raw Summit anthracite. The fact that all the anthracites exhibit broad (002) and (100) peaks indicates that they have a turbostratic structure. Stacking is indicated by (001) peaks, such as (002) , and two-dimensionality is observed as $(hk0)$ peaks, like the (100) peak.

As temperature is increased, the broad (002) and (100) peaks become more intense and begin to sharpen, or narrow. The 2000°C heat treated samples clearly show an increase in intensity and decrease in full width at half maximum (FWHM) of these peaks. Also, there is a faint indication of the (004) and (110) reflections in all the 2000°C heat-treated samples that becomes more pronounced in the 2200°C samples. The appearance of the (004) peak represents the second order diffraction of the (002) peak, or where constructive interference is observed when the term “n” in the Bragg equation is equal to two. The (110) reflection is not related to the (100) peak in terms of being a whole integer multiple, as the (004) reflection is to the (002), but is another and separate (*hkl*) plane that indicates two dimensionality.

Analysis of the 2200°C heat-treated samples shows the continued narrowing and intensity increase of the (002) and (100), plus the definite appearance of the (004) and (110) peaks, as seen in Figures 3, 8, 13, and 18. However, the presence of reflections unrelated to those characteristic of graphite are also observed. These new peaks must be carbide peaks, because carbide formation is common between carbonaceous materials and metallic elements at these temperatures [10-16]. The specific carbides responsible for these peaks can be determined by recording their peak locations and comparing them with characteristic peaks from a database of carbides. However, this will provide only a partial list of the carbides present because of three reasons: (1) the detection limit of X-ray diffraction for a carbide mixed with graphite is 0.75 weight percent, so a carbide could be present, but in a quantity below the detection limit of the instrument; (2) a carbide could be present in a detectable quantity, but have peaks in the angle range of graphite, so they would be obscured, for example, by the broader (002) peak; (3) a

carbide could be amorphous, and not detected by X-ray diffraction at any concentration. Nonetheless, there unquestionably are carbide peaks present in the 2200°C heat treated anthracites that can be identified and assigned a 2θ position. Comparing these positions with characteristic carbide peaks will at least give a partial list of the carbides formed during thermal treatment.

A method for defining the position of carbide peak must now be established. SCINTAG software, the manufacturer of the X-ray diffraction unit used for this research, is available that will take input from the user and analyze the diffraction pattern in order to “find” peaks. The user can vary the stringency of the requirements used by the peak-finder software from SCINTAG to find literally hundreds of peaks, or just one. Because of this variation in the number of peaks found based on the input parameters, the method for “finding” carbide peaks in the 2200°C samples was decided to be a visual inspection of the diffraction pattern. This method does introduce a bias into the number of peaks recorded for each diffraction pattern, but there is also bias involved in the peak-finding software because the number of peaks found depends upon the parameters entered by the user. In order better to define a peak visually, the 2200°C samples are presented again in Figures 21 to 24 but on exactly the same scale in terms of CPS and 2θ range. In these figures, the carbide peaks are labeled, as well as those characteristic of graphite.

UAE 2200

Figure 21 2200°C heat treated UAE anthracite, partial 2θ range

Figure 22 2200°C heat treated Jeddo anthracite, partial 2θ range

Figure 23 2200°C heat treated LCNN anthracite, partial 2 θ range

Summit 2200

Figure 24 2200°C heat treated Summit anthracite, partial 2θ range

Table 2 Peak location of carbides in 2200°C heat treated anthracite samples

Heat treated anthracite	2 Θ Angle of Carbide Peaks
UAE	33.34, 35.64, 38.06, 60.52°
Jeddo	33.34, 35.72, 38.10, 60.06°
LCNN	33.44, 35.64, 38.04°
Summit	33.72, 34.86, 35.68, 38.20, 60.10, 71.80°

The process of identifying the location of non-graphite related peaks and then determining what material has characteristic peaks in that angle range is similar to identifying the peaks present after heat-treating anthracite to various temperatures. In the case of the carbides that will form when an anthracite is exposed to graphitization heat treatment temperatures, though, the question of which peaks to look for becomes more complicated because a number of different carbides could be present. To better predict which carbides could form, the type and amount of minerals in the raw anthracites must be known. This information was obtained by computer controlled scanning electron microscopy (CCSEM), performed by Microbeam Technologies, Inc. Figure 25 shows the weight of a given element in the raw anthracites. The values on the y-axis represent the weight of each element normalized to 100 grams of anthracite. For example, in every 100g of the Summit anthracite there is 8.22g of silicon. The weight of each element was obtained by translating the number of characteristic X-ray counts for a given element into a percentage based on the total number of X-ray counts for every element, then multiplying that percentage by the amount of ash found during proximate analysis.

Figure 25 Weight in grams of each element for the raw anthracites

Figure 25 helps in predicting which carbides will form and also be detected by the X-ray diffraction unit. The detection limit for a carbide in graphite is 0.75 weight percent, or 0.75 g in a 100 g sample, so an element must be present in at least this amount in the raw anthracite in order to be detected by the diffractometer. Again, this is not to say that only those elements present in quantities greater than 0.75 grams, or greater than the horizontal line drawn in Figure 25, will form carbides, but they are the only ones that will be “seen.” According to this requirement, only aluminum carbide, silicon carbide, and, in the case of Summit, calcium carbide can be detected. Now that these three carbides have been established as distinct possibilities, their characteristic X-ray diffraction patterns can be reviewed in order to see if any match the peak position listed in Table 2.

Figure 26 is the X-ray diffraction card for aluminum carbide that shows the (hkl) peak positions, and which are most intense, or would be most likely to be observed during X-ray diffraction. In the upper right corner of the Figure the data are designated as “Quality data.” Only quality or “normal” data are used for this research, as “Doubtful quality” is also available, but, logically enough, of doubtful quality. Also, a “Calculated pattern” is not used because it is based on tabulated data for all the (hkl) peaks when the crystal system is known, regardless of whether or not all the listed peaks are observed in an X-ray diffraction experiment. Figure 26 shows that the two most intense peaks, and two most likely to be found, for aluminum carbide are at 31.74° and 55.04° . However, comparing these values with Table 2 does not produce a match for any of the 2200°C heat-treated anthracites. The only possible matches for all the heat-treated samples are the (015) peak at 35.85° , and the (0014) peak at 60.9° . These peaks can be ruled out as

aluminum carbide peaks, because peaks of roughly half and one-fifth maximum intensity, respectively, would not appear before the two most intense peaks.

A better match is observed between the peak positions listed in Table 2 and the card for silicon carbide. Figure 27 shows that the most intense peak for silicon carbide is found at 35.45° . All the 2200°C heat-treated samples have a peak in the 35° range. Granted, none are exactly 35.45° , but some discrepancy must be expected because these are not pure carbide samples, so their peaks can be influenced by the thermally stressed anthracite present. Another common peak in all the four anthracites, other than the LCNN anthracite, is found at approximately 60° . Silicon carbide's second most intense peak is located at 60.03° , which is in good agreement with peaks from the heat treated anthracites. Basically, should silicon carbide be present in a detectable quantity, its two most prominent peaks would be located at 35.45° , and 60.03° . All the anthracites exhibit peaks in this 2θ range, so silicon carbide must be present in all the 2200°C heat-treated samples. Table 2 confirms that silicon carbide should be present in all the anthracites because silicon is present in all the raw anthracites in a quantity capable of forming a carbide detectable by X-ray diffraction.

Lastly, the card for calcium carbide is presented because the Summit anthracite contained enough calcium to form detectable calcium carbide. Reviewing Figure 28 shows, however, that calcium carbide's two most intense peaks are located at 32.65° , and 43.47° . The peak at 43.47° would be obscured by the broad (110) peak, but the peak at 32.65° should be visible, but it is not. The Summit anthracite, after heat-treatment to 2000°C , has an additional peak at 34.86° that none of the other heat-treated samples exhibit. The Summit anthracite is also the only anthracite with enough calcium present to

Figure 27 XRD card for silicon carbide

Figure 28 XRD card for calcium carbide

form a detectable calcium carbide, so it was assumed that this additional peak was the result of calcium carbide, but the X-ray diffraction card for calcium carbide does not support this hypothesis. Therefore, another material besides calcium carbide, that none of the other anthracites have, must be responsible for the peak at 34.86° .

Figure 25 shows that the raw Summit anthracite has more iron than any of the other anthracites, but it is still present in a quantity slightly lower than 0.75 grams, so it would be undetectable by X-ray diffraction. However, the mineral content of the raw anthracites was also determined by ashing the anthracites and analyzing the ash with plasma emission. Figure 29 shows the elemental (oxide basis) composition of the ashes of the four anthracites. The values obtained by plasma emission are in good agreement with those presented in Figure 25. A significant difference is that the amount of iron in the Summit anthracite is now slightly over 0.75%, meaning if it were to form iron carbide in the 2200°C sample, the carbide could be detected by X-ray diffraction. Unfortunately, no iron carbide X-ray diffraction cards of normal or quality data exist. Of the cards of doubtful quality, none lists a peak in the angle range of 34° . This means the peak at 34.86° in the 2200°C heat-treated Summit sample is most likely one of three things: (1) a calcium-based species that is not calcium carbide, (2) an iron-based species that is not iron carbide, or (3) the (012) reflection of silicon carbide located at 34.06° . The (012) peak at 34.06° is certainly not an exact match for 34.86° , but it is the only peak at 34° for any of the possible carbides, including iron and calcium carbide. The (012) peak is 70% intensity of the most intense peak for SiC, so it would be one of the first peaks to be witnessed, but none of the other heat treated anthracites show this peak even though they

Weight of Elements Comprising Inorganics in Raw Anthracites (DCP)

Figure 29. Weight of elemental oxides by plasma emission

definitely contain silicon carbide. The peak at 34.86° must be attributed to silicon carbide, but iron and calcium definitely have an impact on graphitization behavior.

In summary, all the anthracites show clear silicon carbide peaks after heat treatment to 2200°C . Therefore, all that can be said with certainty is: (1) all the heat-treated anthracites contain silicon carbide, (2) none of the heat-treated anthracites contain aluminum carbide, (3) all the heat-treated anthracites could contain more than just silicon carbide, but they are not present in enough mass to be “seen” by the diffraction unit. The role of these carbides in terms of their effect on degree of graphitization is discussed following analysis of the 2500° and 2600° diffraction patterns for the heat-treated anthracites.

The 2500°C heat-treated anthracites show no carbide peaks, which does not mean carbides are not present, only that there is not enough carbide for detection by X-ray diffraction. This does, however, mean that less carbides are present in the 2500°C heat-treated samples than in the 2200°C heat-treated samples. The importance of this is discussed later, in a follow-up discussion to carbide formation and its impact on graphitization. The 2500°C samples show a continued increase in intensity of the (002) , as well as a broad and weak appearance of the (110) reflection.

The final heat treatment temperature was 2600°C , as shown in Figures 5, 10, 15, and 20. Again, the intensity of the (002) peak increases and the (100) , (004) , and (110) become more defined. Also, the broad (100) peak begins to split into the (100) and (101) peak, as evidenced by the “two humped” peaks over the 2θ range of 40° to 45° . Lastly, the appearance of the (112) peak is observed, which indicates that all the anthracites can be considered graphitizing carbons, or that they achieved long-range three-dimensional

crystalline order. Figures 30 to 33 show close-ups of the (110) and (112) peaks for all four heat-treated anthracites. The (112) peak is a broad hump, but even a weak presence is indicative of three-dimensional ordering. The (112) of a needle coke is also shown in Figure 34 for comparison purposes—needle coke is a well known graphitizing carbon and a main feedstock of the graphite industry.

Although all the anthracites exhibit a broad (112) peak following heat treatment, some differences in the degree of graphitization are observed in comparing their crystallite parameters obtained from the (002) and (100) peaks. The information indicative of graphitic development, assuming an (hkl) peak is present, is d-spacing. d-Spacing is obtained from the Bragg equation applied to the (002) peak. Figure 35 summarizes how d-spacing changes with increased HTT. None of the heat-treated anthracites achieves a d-spacing of 3.354 Å, the horizontal black line in the figure, but there are definite differences in how closely each comes. The curves in Figure 35 are shown only for visualization purposes and their slope is not indicative of any kinetics. Judging by the final d-spacing, the Summit sample has the highest degree of

UAE (112)

Figure 30 (112) peak for heat-treated UAE anthracite

Jeddo (112)

Figure 31 (112) peak for heat-treated Jeddo anthracite

Figure 32 (112) peak for heat-treated LCNN anthracite

Summit (112)

Figure 33 (112) peak for heat treated Summit anthracite

Needle coke (112)

Figure 34 (112) peak for heat-treated needle coke

graphitization, the UAE and LCNN are about the same, and Jeddo is the least graphitizing. The error in the d-spacing is $\pm 0.001 \text{ \AA}$, which is the thickness of the points on the line plots, which is why LCNN and the UAE anthracite appear to be the same in terms of final d-spacing.

Other measurements used to show differences in the graphitic development of the four anthracites are crystallite height, L_c , and crystallite diameter, L_a . Figures 36 and 37 show how crystallite height and diameter increase with HTT, respectively. The Summit anthracite, as seen in Figure 36, has the largest graphitic crystallites when compared to the other heat-treated anthracites. In this measurement, the LCNN and UAE samples are not identical; the graphitized LCNN anthracite has a larger L_c than the UAE sample. Again, the graphitized Jeddo anthracite has the least graphitic nature, evidenced this time by the smallest average graphitic crystallites. In terms of crystallite diameter, all the graphitized anthracites are about the same, based on the curves shown in Figure 37.

In summary, all of the anthracites are graphitizing carbons, because after heat treatment to 2600°C they all exhibit a broad (112) peak. However, not all the anthracites reach the same level of degree of graphitization in terms of a d-spacing close to that of graphite, $3.354 \text{ \AA}$. There must be a reason why differences in extent of graphitization are observed. As stated in the introduction, Rouzaud believes that these differences are the result of differences in pore shape in the raw anthracites, where a flattened pore leads to a higher degree of graphitization, and a spherical pore is less highly graphitized. The X-ray diffraction patterns presented here show that carbides form during heat treatment to 2200°C , and then the carbides decompose, at least to some extent, before reaching 2500°C . We hypothesize that this decomposition leaves behind a reactive carbon atom

that will add to the edge of a graphene layer, or react with cross-links between neighboring graphene layers, or layers stacked perpendicular to one another. If carbide formation and subsequent decomposition indeed affects the graphitization behavior of an anthracite, the crystallite properties of an anthracite should be altered by the addition or removal of minerals that contain elements that form carbides. This idea was tested by adding minerals to the least graphitizing Jeddo anthracite, and by demineralizing the most highly graphitizing Summit anthracite.

Figure 35 d-spacing decreased with increased HTT

Figure 36 Crystallite height increases with increased HTT

Figure 37 Crystallite diameter increased with increased HTT

Demineralization and Graphitization with Added Minerals:

Figure 35 shows that Summit was the best graphitizing anthracite, while Jeddo was the least graphitizing. It is believed that the amount of carbide-forming mineral matter present is responsible for these observed differences. Therefore, if Jeddo contained more mineral matter, then it might exhibit a higher degree of graphitization due to more carbide formation and decomposition to leave behind reactive carbon atoms. This hypothesis was tested by adding quartz, calcite, rutile, and iron oxide to the Jeddo anthracite in a 3:1 ratio. Quartz (SiO_2) was added because it is the primary contributor of silicon, calcite (CaCO_3) because it contributes calcium, rutile (TiO_2) because it contributes titanium, and iron oxide (Fe_2O_3) because it contributes iron. Rutile and iron oxide were added even though they are present in non-detectable quantities (i.e., by X-ray diffraction) because they have been shown in the literature to readily form carbides, and also because iron oxide and titanium oxide are commonly used in the graphite industry as graphitization “catalysts.” As stated before, titanium carbide, for example, could form at 2200°C , but be invisible to the X-ray diffraction unit. Addition of rutile and iron oxide provides enough quantity for a carbide formed from them to be seen. Figures 38 to 41 show the X-ray diffraction patterns of the Jeddo anthracite with added mineral and heated to 2600°C .

Before discussing the crystallite parameter changes incurred by adding these minerals, the X-ray diffraction patterns of the Jeddo anthracite plus calcite and iron oxide are analyzed in terms of the number of peaks present. It was discussed earlier in this report that the Summit anthracite heated to 2200°C showed an additional diffraction peak that none of the other heat-treated anthracites produced. It was thought possible this peak

Figure 38 X-ray diffractogram of Jeddo plus rutile heated to 2600°C

Figure 39 X-ray diffractogram of Jeddite plus iron oxide heated to 2600°C

Figure 40 X-ray diffractogram of Jeddo plus quartz heated to 2600°C

Figure 41 X-ray diffractogram of Jeddo plus calcite heated to 2600°C

could be an iron or calcium species that is not a carbide. However, analysis of Figures 39 and 41, that show the addition of iron and calcium, respectively, illustrates that no carbide peaks are present; only graphite-related peaks are seen. Enough iron and calcium had been added to the anthracite that if a carbide formed it would be detected by X-ray diffraction, but no carbide peaks were observed. This could be because no carbides actually formed, or they did form and were decomposed by the time 2600°C was achieved.

However, the addition of iron and calcium certainly have an effect on the properties of the graphite formed after heat treatment to 2600°C. Table 3 lists the d-spacings and crystallite heights for all the Jeddo plus inorganics.

Table 3 Crystallite parameters of Jeddo 2600°C after addition of “catalytic” minerals

Mineral added to Jeddo	d-spacing (Å) ±0.001	L _c (Å) ±2
Rutile	3.355	123
Quartz	3.358	135
Iron oxide	3.352	153
Calcite	3.354	248
None	3.371	123

All of the minerals had an effect on the d-spacing, and they are all roughly the same, with quartz aiding the least, but still reducing the d-spacing by 13 Å; calcite had the most dramatic affect on crystallite height.

Summit demineralized

Figure 42 Demineralized Summit heated to 2600C

Figure 43 (112) of Demineralized Summit

Figure 44 Demineralized Summit plus rutile, heated to 2600C

Figure 45 Demineralized Summit plus quartz, heated to 2600C

Figure 46 Demineralized Summit plus iron oxide, heated to 2600C

Figures 38 and 40 show that TiC and SiC form, respectively. The 2200°C X-ray diffraction patterns clearly show the formation of silicon carbide, so it is not surprising to see them present here. Titanium carbide, which was not seen before, is now present, suggesting that it must form at 2200°C, but be undetectable to the diffraction unit. It is also apparent that the formation of titanium carbide has an affect on the graphitization behavior of the Jeddo anthracite.

Table 3 shows that the addition of graphitization modifying minerals definitely enhances the graphitization of the least graphitizing Jeddo anthracite. This leads to the question of whether the removal of minerals will decrease the graphitizability of the Summit anthracite. To determine the answer, the Summit anthracite was demineralized, and then rutile, quartz, and iron oxide were added to the demineralized anthracite in a 3:1 ratio of anthracite:inorganic.

Figures 42 shows the X-ray diffraction pattern of the demineralized Summit anthracite heat treated to 2600°C. Upon further inspection of this pattern, it becomes apparent that the (112) peak is not present, and the (110) peak is not as well defined as in the raw heat-treated anthracites. Figure 43 is a close-up of the angle range where the (112) reflection should be located. This occurrence by itself shows that removal of mineral matter affects graphitization; in fact the Summit anthracite can no longer be considered a graphitizing carbon after demineralization.

Figures 44 to 46 show the diffraction patterns of the demineralized Summit anthracite plus rutile, quartz, and iron oxide. The (112) is visible in all the patterns, and it is obvious that the sharpness and intensity of the (002) peak is better than in any of the

other 2600°C heat-treated sample. Table 4 confirms that the crystallite parameters are much better than ever seen before.

Table 4 Crystallite parameters of demineralized Summit plus minerals

Inorganic Added	d-spacing (Å)	L _c (Å)
Rutile	3.352	544
Quartz	3.354	453
Iron oxide	3.349	480

Figures 44 to 46 show that the (112) returns to the demineralized Summit anthracite when the three inorganics listed in Table 4 are added to it. These figures and table clearly show that, at least in the case of the anthracites tested here, graphitization cannot occur without the presence of certain minerals. It also shows that minerals are not only responsible for differences in extent of graphitization, but are involved in the mechanism of graphitization itself.

In terms of a graphitization mechanism involving carbide formation and decomposition, the following is a general example of how a mineral could enhance graphitization.

Mineral melts→ Mobile liquid→ Reaction with defects, interstitials, cross-links→
 Carbide forms→ Graphene layers now free to diffuse to neighboring layers→ Carbide
 decomposes to leave a reactive carbon that adds to growing layers

A reaction sequence specific to, for example quartz, could proceed like this:

The $\cdot\text{C}\cdot$ above represents a dicarbene with unfilled valences, so it would be extremely reactive to any other carbons, which would mean it would preferentially react with defects and/or cross-links.

Conclusions:

All the anthracites analyzed in this project are graphitizing carbons because they all exhibit a (112) peak after heat treatment to 2600°C. The Summit anthracite was the most graphitizable of the anthracite because it had the d-spacing closest to that of graphite, 3.354 Å, and the largest crystallites. Carbides formed from all the anthracites when heated to 2200°C, as evidenced by non-graphite related peaks in these samples. It was found that SiC was present in all the anthracites, and that Summit showed an additional peak that was most likely related to silicon carbide as well. These carbide peaks vanished at 2500 and 2600°C, meaning that the amount of carbides decreased, or that some type of decomposition of the carbides occurred. This decomposition would leave behind a reactive carbon capable of adding to a layer edge or removing a defect. This idea of a reactive carbon healing defects and thus aiding graphitization was supported by the reduction in d-spacing of the least graphitizing Jeddo anthracite when carbide forming elements from the inorganics rutile, quartz, iron oxide, and calcite were added. Further evidence of carbide formation and decomposition being a valuable part of the graphitization mechanism is seen in the fact that no (112) peak is observed if the

Summit anthracite is demineralized before being heated to 2600°C. The (112) re-appears if the inorganics just listed are added to the demineralized sample, i.e. the Summit anthracite is not a graphitizing carbon if the minerals associated with it are removed.

Part 2. Results of industrial graphitization of LCNN anthracite as a filler for molded graphite.

The purpose of the industrial graphitization experiment was, in essence, the completion of the scope of work endeavored in this project—to determine whether a prediction could be made as to the acceptability of an anthracite as a filler based on laboratory-scale graphitization experiments. In this research, four anthracites were selected and exposed to the same reaction conditions to determine whether differences in graphitizability would be evident. Indeed, as shown in detail in Part 1, the anthracites chosen for this research did show varied levels of graphitic development. The next step was to establish which parameters were responsible for these observed differences in graphitizability; i.e., whether they were attributable to physical, organic, or inorganic properties. Part 1 of this report showed that inorganic differences are responsible for differences in graphitizability. The next step was then to determine whether or not observations made in a laboratory could be related to industrial-scale graphitization. That is, the best graphitizing anthracite in the laboratory would be the best filler for molded graphite production provided that the acceptability of its use as a filler was dependent only on its extent of graphitization. This is not the case, because acceptability of a filler is dependent on both its extent of graphitization and propensity to form a dense, mechanically sound graphite when mixed with a binder. Although the Summit sample showed the highest degree of graphitization, it was not selected for industrial graphitization because past experience has shown high levels of ash, in this case 17.6%, leads to inadequate graphite properties and a weak filler-plus-binder compound. Because of this knowledge, the LCNN anthracite was selected for industrial research because it

was the second best in terms of graphitizability—the UAE and LCNN were the same in terms of d-spacing, but the LCNN sample produces a larger crystallite. In principle, the Summit anthracite could be an acceptable industrial filler, but only after treatment to remove its mineral impurities. Added processing of the filler, through cleaning or extended heat treatment, is undesirable in terms of the suitability of an anthracite for replacement of petroleum coke as a filler.

Carbone of America carried out the manufacture and graphitization of the anthracite and coal tar pitch molded graphite as the industrial member of this CPCPC project. Also, Carbone has created a set of standards based on physical properties of the graphites they produce that determines the grade and possible applications. This set of standards is proprietary to Carbone and are not reported here.

The LCNN anthracite was selected for industrial graphitization, to be performed at the St. Marys plant of Carbone, because it was highly graphitizable and had the lowest ash levels of any of the four anthracites. A 55-gallon drum of pea-sized anthracite was shipped first to CCE Technologies for jet milling to an average particle of 15 micron. Following the particle size reduction, the LCNN anthracite was sent to Carbone to be used as a filler in their industrial molded graphite production scheme, which uses petroleum sponge coke and coal tar pitch binders. No extrusion is performed at this facility; rather, the graphites are formed from compression or isostatic molding. It was decided to use isostatic molding through discussions with our colleagues from Carbone. A good wetting of the filler by the pitch, and subsequent absence of voids in the contact area between the coke and pitch, is essential to the mechanical stability of the graphite that will be formed following graphitization heat treatment. Anthracite has a high

microporosity, which may inhibit its wetting by coal tar pitch because the pitch would have a difficult time entering pores smaller than 20 Å. Isostatic molding applies pressure from all directions and could possibly provide the needed energy to force pitch into the micropores.

Following the decision to use isostatic molding, the ratios of pitch to anthracite were determined. It was decided to begin with 44 weight percent coal tar pitch and decrease this value in intervals of two percentage units to 38 weight percent. Forty-four was the lowest value used in the previous work of Atria, and this ratio of coal tar pitch to anthracite seemed to produce the best graphite. Tables 5 to 7 list some of the properties recorded at Carbone for the green, baked, and graphitized carbons.

Table 5. Properties of green anthracite and coal tar pitch sample

Grade	raw material	coal tar pitch	green density	length	width	height	dry wt.	Wet wt.	Diff.
GREEN		(pph)	g/cm ³	inches	inches	inches	grams	grams	grams
P18	sponge coke	54.7	1.576	10.6	4.9	4.9	6400	2340	4060
P19	calcined coal	38	1.507	9.6	4.9	4.9	5710	1920	3790
P20	calcined coal	40	1.503	10.3	4.8	4.9	6100	2040	4060
P21	calcined coal	42	1.504	10.1	4.9	4.9	6180	2070	4110
P22	calcined coal	44	1.505	10.4	4.8	4.9	6200	2080	4120
P23	sponge coke	54.7	1.573	10.1	4.9	4.9	6260	2280	3980
P24	green coal	38	1.46	9.5	5	5	5660	1770	3890
P25	green coal	40	1.45	9.8	4.9	4.9	6000	1870	4130
P26	green coal	42	1.46	10.1	4.9	4.9	6120	1920	4200
P27	green coal	44	1.46	9.9	4.9	4.9	5900	1850	4050

Table 6. Properties of baked anthracite and coal tar pitch sample

Grade	raw material	coal tar pitch	baked density	length	width	height	dry wt	wet wt.	Diff.
BAKED		(pph)	g/cm ³	inches	inches	inches	grams	grams	grams
P18	sponge coke	54.7	1.66	9.9375	4.625	4.625	5780	2340	3440
P19	calcined coal	38	1.53	9.25	4.75	4.75	5220	1840	3380
P20	calcined coal	40	1.59	9.75	4.6875	4.6875	5580	2000	3580
P21	calcined coal	42	1.66	9.5625	4.625	4.6875	5640	2050	3590
P22	calcined coal	44	1.61	9.875	4.625	4.6875	5660	2080	3580
P23	sponge coke	54.7	1.7	9.5	4.625	4.625	5660	2260	3400
P24	green coal	38	1.56	9	4.75	4.6875	5120	1820	3300
P25	green coal	40	1.66	9.125	4.6875	4.6875	5440	1940	3500
P26	green coal	42	1.63	9.5	4.6875	4.625	5500	2020	3480
P27	green coal	44	1.62	9.25	4.6875	4.625	5320	1970	3350

Table 7. Properties of graphitized anthracite and coal tar pitch sample

Grade	raw material	coal tar pitch	baked density	length	width	height	dry wt	wet wt.	Diff.
GRAPHITE		(pph)	g/cm ³	inches	inches	inches	grams	grams	grams
P18	sponge coke	54.7	2.15	9.75	4.0625	4.0625	5680	2400	3280
P19	calcined coal	38	1.6	8.875	4.5625	4.625	4910	1880	3030
P20	calcined coal	40	1.67	9.437	4.5	4.5	5240	2040	3200
P21	calcined coal	42	1.73	9.187	4.5	4.5	5280	2080	3200
P22	calcined coal	44	1.71	9.5	4.4375	4.5	5320	2120	3200
P23	sponge coke	54.7	1.75	9.312	4.5625	4.5625	5560	2330	3230
P24	green coal	38	1.6	8.687	4.625	4.5625	4800	1790	3010
P25	green coal	40	1.71	8.812	4.5	4.5	5080	1920	3160
P26	green coal	42	1.69	9.187	4.5	4.5	5160	2000	3160
P27	green coal	44	1.67	9.000	4.5	4.5	4980	1940	3040

Tables 5 to 7 give some basic dimensions and how they changed during the heat treatment regime. Following the production of the anthracite-based graphites, P19-P22 and P24-P27, the products were tested against the standard petroleum coke graphites, P18 and P23. Figures 47-54 compare the standard properties recorded by Carbone; the c- and a- directions are also differentiated for all but median pore and ash percentage.

Figure 47 Thermal expansion in the c-direction

Figure 48 Thermal expansion in the a-direction

Figure 49 Resistivity in the a-direction

Figure 50 Resistivity in the c-direction

Figure 51 Flexural strength in the a-direction

Figure 52 Flexural strength in the c-direction

Figure 53 Median pore differences

Figure 54 Ash levels

Based on the figures shown above, the anthracite-based graphites were described as "low-end" specialty graphite. The exact definition of low-end specialty graphite was not revealed. It also appears that there is very little difference in properties between the specimens made from calcined or non-calcined anthracites, which would provide another cost savings in addition to the price differential between coke and anthracite if anthracite were to be used as a filler.

Because the bulk of the research presented in this report dealt with describing the extent of graphitization of anthracite by X-ray diffraction, the anthracite-based graphites were also analyzed by X-ray diffraction. This is not a technique used by Carbone to characterize their commercial graphites, but it will help illustrate the differences between the coke- and anthracite-based graphites, and also show how an anthracite compares to a coke in terms of extent of graphitization when mixed with a binder. The d-spacing and L_c of all the samples is provided in Table 8. Table 8 shows definitively that the LCNN anthracite undergoes the same degree of graphitization as sponge coke. Thus all the criteria have been met in order to demonstrate that anthracite could replace petroleum coke as a filler for certain applications. The anthracite achieves exactly the same d-spacing and L_c of an accepted petroleum coke standard, and Figures 47 to 54 indicate it forms a sound product and has properties comparable to the coke standard. Basically, this industrial graphitization project is the culmination, or proof of concept, of this research. An anthracite that was found to be highly graphitizable in the laboratory was shown to be an adequate filler for the production of synthetic graphite.

Table A8 Crystallite parameters of "P" samples

Sample	d-spacing (Å)	L _c (Å)
P18	3.349	302
P19	3.350	177
P20	3.352	170
P21	3.349	194
P22	3.354	291
P23	3.354	291
P24	3.349	181
P25	3.359	170
P26	3.357	170
P27	3.352	167

The results of this research are so promising that scaling up to multi-ton quantities with the end goal a commercially available graphite made from anthracite would certainly be warranted.

A final confirmation of the equality of anthracite to petroleum coke as a filler for specialty graphite production is the similarity between the optical textures of the anthracite-based and coke- based graphites shown in Figure 55 to 63.

Figure 55. Optical micrograph of p18, 100X magnification

Figure 56. Optical micrograph of p19, 100X magnification

Figure 57. Optical micrograph of p20, 100X magnification

Figure 58. Optical micrograph of p21, 100X magnification

Figure 59. Optical micrograph of p22, 100X magnification

Figure 60. Optical micrograph of p23, 100X magnification

Figure 61. Optical micrograph of p24, 100X magnification

Figure 62. Optical micrograph of p25, 100X magnification

Figure 63. Optical micrograph of p26, 100X magnification

Figure 64. Optical micrograph of p27, 100X magnification

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List of Acronyms and Abbreviations

BSU	Basic structural units
CCE	(name of company)
CCSEM	Computer controlled scanning electron microscopy
CPCPC	Consortium for Premium Carbon Products from Coal
FWHM	Full width at half maximum
<i>(hkl)</i>	Miller crystallographic indices
HRTEM	High-resolution transmission electron microscopy
HTT	Heat-treatment temperature
LCNN	Lehigh Coal and Navigation (anthracite)
SAD	Selected area diffraction
SCINTAG	(manufacturer of X-ray diffraction equipment)
TEM	Transmission electron microscopy
UAE	United Arab Emirates (anthracite)

High-Performance Coal-Derived Pitches for Advanced Applications

FINAL REPORT

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ABSTRACT

A CPCPC member bituminous coal (PSOC 3001) was hydrogenated and then solvent extracted in N-methyl pyrrolidone (NMP) to remove mineral matter and other solids. Following this purification procedure, the coal extract was thermally treated to raise its softening point temperature, re-dissolved in NMP, and pressure filtered through a 0.2 μ m filter to remove the finer particulate material. Enough coal extract was made to demonstrate that spinning multi-tow isotropic carbon fibers from a coal-derived pitch could be possible. Careful heat-treating of the same coal extract further resulted in a pitch consisting primarily of fluid mesophase. This mesophase-containing pitch was used to demonstrate the utility of employing coal-derived extracts as matrix binders and for fabrication into electrodes in lithium battery applications. The fibers and carbon-carbon composites produced showed acceptable properties and performance. Larger quantities of pitch are needed, however, for further detailed testing in applications such as electrodes for lithium-ion batteries.

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1.0 EXECUTIVE SUMMARY

The primary focus of the present work was the conversion of coal into pitch-like materials for spinning into carbon fibers and for utilization as a matrix binder in a carbon-carbon composite and a lithium-ion battery. The procedure entails hydrogenation of coal followed by solvent extraction in N-methyl pyrrolidone (NMP) to remove mineral matter and other solids. This raw-coal product had a Mettler softening point temperature of 138.8°C, which was increased to 205°C by thermal processing into a coal-derived isotropic pitch. The softening point temperature of the coal-derived isotropic pitch was within the range of isotropic pitches developed in prior CPCPC projects, but these previous isotropic pitches were all successfully spun using only a single-hole spinneret. It was discovered that the softening point temperature should be increased to above 225°C for proper spinning with a forty-hole spinneret. The softening point temperature could be increased by additional heat soaking in a closed reaction vessel with stirring under an inert atmosphere of nitrogen. Heat treatment at 400°C for 10 hours raised the softening point temperature to 224°C. Carbon fibers with this pitch were spun through the multi-hole spinneret at 240°C, which after stabilization and carbonization exhibited strengths between 280 and 1200MPa. Further heat treatment at 420°C for 24 hours increased the softening point temperature to 252°C. This pitch was then spun at 270°C to result in carbonized fibers with strengths between 312-2045MPa. All of the coal-derived fibers had fiber diameters between 15-17 μ m, which is slightly larger than petroleum-based pitches of similar softening points.

The coal-derived isotropic pitch was heat treated in a stirred 1L autoclave under vacuum until it contained approximately 50vol% mesophase. Optical microscopy of the annealed sample of the coal-derived mesophase indicates general fluidity. This anisotropic pitch was used as a binder in a PAN-based carbon-carbon composite. X-ray diffraction (XRD) patterns of intermediately heated samples showed graphite peaks beginning as low as 1800°C. Based on XRD patterns, the composite appeared to be fully graphitized at 2250°C. Composite flexural strength of 300 MPa was achieved in the one-step composite fabrication that is quite adequate for many commercial applications.

The WVU anisotropic pitch was also utilized to produce a carbon-carbon composite for a lithium battery with a petroleum-pitch-based graphite fiber (P30X). Heat treatments up to 2790°C were performed. At this temperature, the composite was completely graphitized, as evidenced by XRD. The density after only the one-step processing and heat treatment to 2790°C was 1.67g/cc, which is excellent for many commercial applications. The strength of the composite was 350 MPa, which also is excellent for many commercial applications. In the Li-ion battery, the capacity was 320 mAh/g with an irreversible capacity of slightly less than 10%, which remained constant in cyclability. This performance is at least equivalent to an expensive mesophase carbon microbeads (MCMB).

2.0 INTRODUCTION

Carbon fibers and carbonaceous binders in carbon-carbon composites are finding ever-increasing use in a variety of materials because of their unique combination of mechanical, electrical, and engineering properties [1]. Currently there are two main types of carbon fibers produced commercially in which one type is based on thermally treating polyacrylonitrile (PAN) yarn [2]. Although PAN fibers generally exhibit high strength, they are dependent on costly precursors and suffer from low yields. Moreover, PAN fibers do not develop the long-range molecular arrangement of graphitic structures that are possible with some or mesophase-based fibers [3,4]. Thus, PAN-based fibers do not achieve high thermal and electrical conductivity possible with pitch fibers.

The other main type of carbon fiber is derived from pitch. Pitch-based carbon fibers offer the potential advantage over PAN fibers in that they can be made from inexpensive precursors, can have a higher modulus, and can be either isotropic or anisotropic in properties. Depending on the application, isotropic pitch-based fibers are used for general purposes where high strength and stiffness are not required while anisotropic or mesophase pitch-based carbon fibers yield high-performance materials.

Starting materials for pitch-based fibers are composed of complex aromatic hydrocarbons from polymerized model compounds or are obtained from the byproducts of pyrolysis, distillation, or heat treatment of petroleum or coal tar feedstocks [4-5]. Byproducts including vacuum residua, catalytic cracker bottoms, decant oils, and coal-tar pitches are some of the candidates for pitch fiber precursors. Unfortunately, since these materials are

industrial byproducts, they are subject to vagaries in quality and consistency. Fluctuations in the nature of the feedstocks influence the quality and behavior of carbon fibers obtained from them.

Carbon fibers and pitches derived from coal extracts offer several advantages over conventional sources. Coal extracts are obtained in high yield and are produced as the primary product, not the byproduct. More importantly, coal extracts are tailorable in terms of reactivity, softening point, rheology, and degree of anisotropy. The ability to alter and target coal-derived pitches with particular properties offers the potential to develop carbon fibers with unique and desirable characteristics.

In prior CPCPC sponsored research projects, solvent extraction and thermal treatment were used to convert a bituminous coal into an isotropic pitch suitable for fabricating carbon-carbon composites [7,8]. Enough isotropic pitch was produced such that specimens of continuous filaments could be spun for testing of their mechanical properties and for incorporation into a carbon-carbon composite. The coal-derived pitch underwent spinning and stabilization without any unusual difficulty. Individual filaments carbonized at 1100°C typically had diameters of 10-15 μ m, exhibited tensile strengths up to 1.36GPa, and displayed resistivities near 4m Ω -cm. These characteristics exceed those made from other corresponding isotropic pitches. Later, a larger quantity of pitch was also successfully produced for a more extensive and systematic evaluation of the fiber spinning and stabilization parameters.

The current project builds on these previous successes by developing two coal-derived pitches with quite different attributes. Similar to earlier work, one pitch is isotropic in nature and produced using processes previously established. However, for the current work, the pitch was melt spun into fiber tows rather than single filaments to reflect more closely commercial practices. The fiber tows were stabilized, carbonized, and tested for mechanical properties.

The other pitch consists predominantly of coal-derived mesophase. It should be emphasized that we are not aware of any other reports or publications that purport the development of flowable or spinning mesophase pitch from coal extracts, as described herein. Thus, the work completed in the current project must be considered a milestone in the possible use of coal extracts in advanced technologies.

As was stated in this year's proposal, it was the intent of the current project to test the coal-derived mesophase pitch only in lithium battery applications. However, to demonstrate another potential application of the technology, a portion of the mesophase-containing pitch was investigated both as a binder for PAN-based fibers in a carbon-carbon composite and as binder for pitch-based graphite fibers for lithium-ion battery anodes.

3.0 EXPERIMENTAL

3.1 Development of coal extract

Arch Coal (PSOC 3001) was ground to less than 60 Tyler mesh, dried, and stored in sealed glass jars under refrigerated conditions until ready for use. Properties of the coal are provided in Table 1.

Table 1. Properties of Arch Coal (PSOC 3001)

Table 1. Properties of Airco Coal (FSC 5001)				
Moisture, wt % as received 1.79		Ash, wt % dry 7.36	Volatile Matter, wt % dry 31.57	
Carbon wt % dry 80.31	Hydrogen wt % dry 4.56	Nitrogen wt % dry 1.41	Sulfur wt % dry 0.71	Oxygen by difference 5.65
Vitrinite vol % mf 57.2	Liptinite vol % mf 8.3	Inertinite Vol % mf 30.3	Mineral Matter vol % mf 4.2	

Hydrogenation was accomplished by placing 600g of coal along with 1.5L of tetralin into a 1gal bolted-closure autoclave. The reactor was purged of air with hydrogen gas and then pressurized to 400psig with molecular hydrogen at room temperature. The reactor contents were stirred while heating and brought to 450°C for 1 hour. Following reaction, the reactor was cooled to room temperature and vented. The products were transferred to a 10L flask and the tetralin removed by rotary evaporation. Three liters of N-methyl pyrrolidone (NMP) were added to the flask and agitated for 2 hours at 110°C. Afterward, the mixture was transferred to 750mL centrifuge bottles and centrifuged for 1 hour at 2000 times the force of gravity (2000G) to separate unconverted coal and other insoluble material. The supernatant liquid was decanted and placed in a rotary evaporator device to remove the NMP. Finally, the coal-derived pitch was vacuum dried at about 150°C

overnight before weighing. Hydrogenations were repeated until 8kg of the coal extract product were made.

3.2 Conversion of coal extract into isotropic and anisotropic pitches

The softening point of the coal extract was raised using the method developed previously. The process entails careful thermal treatment and removal of low-boiling components to increase the average molecular weight of the pitch. Following this step, the pitch was dissolved in NMP and pressured filtered through a 0.2 μ m Teflon filter to remove finely dispersed solids. The NMP was removed by rotary evaporation and the isotropic pitch vacuum dried for about 24 hours at 180°C under a slow purge of nitrogen. About 1.8kg of isotropic pitch were prepared.

The isotropic pitch was transformed into an anisotropic pitch by placing about 300g of the isotropic pitch into a 1-L stirred autoclave reactor. The autoclave was attached to a vacuum source and provision was made for a concurrent slow purge of nitrogen gas. The reactor contents were brought to about 400°C and about 20-30wt% distillate material removed. The reactor was cooled slightly to prevent solidification of the pitch, opened, and the product removed. A sample of pitch was annealed before being mounted in epoxy for examination by polarized microscopy [9]. It was judged that the pitch consisted of at least 50vol%mesophase. Test methods used to characterize the coal extract, isotropic pitch, and anisotropic pitch are shown in Table 2.

Table 2. Methods for measuring pitch properties.

Characterization	Method
Softening Point, °C	ASTM D 3104
Conradson Carbon, wt%	ASTM D 2416
Density, g/cm ³	ASTM D 4892
Ash Content, wt%	ASTM D 2415
Viscosity, cP	ASTM D 5018
C, H, S, N Content, wt%	CE Elemental Analyzer
Mesophase Content	Optical Microscopy

4.0 RESULTS AND DISCUSSION

4.1 Characterization of coal-derived pitches

Some of the characteristics of the coal-derived extract prior to conversion into either the isotropic or anisotropic pitch are provided in Table 1.

Table 3. Characteristics of hydrogenated and NPM-extracted PSOC 3001.

Yield ¹ , wt%	Mettler Softening Point, °C	Density, g/cm ³	Ash Content, wt%
64	138.8	1.244	0.13

Yield = $\frac{(\text{wt dry coal} - \text{wt dry residue})}{\text{wt dry coal}} \times 100$

Figure 1 shows the viscosity of the extract material as a function of temperature as well as that for a petroleum pitch. The petroleum pitch (Ashland) has been used as a precursor by other researchers to spin isotropic carbon fibers. As expected, because the softening point of the coal extract is comparatively low, its viscosity is lower compared to the petroleum material.

Figure 1. Viscosity vs. temperature for coal extract and petroleum pitch.

Some properties of the isotropic pitch precursor are shown in Tables 4 and 5. The Mettler softening point temperature and the other properties are within the range of pitches produced in prior CPCPC projects. Note that the elemental analysis indicates the pitch is relatively aromatic, C/H atomic ratio equal to 1.34, and relatively low in sulfur content. However, the nitrogen content above 2wt% is not unusual for coal-derived pitches and liquids [10].

Table 4. Properties of coal-derived isotropic carbon fiber precursor pitch.

Mettler Softening Point, °C	Density, g/cm ³	Conradson Carbon, wt%	Ash Content, wt%
205	1.290	72	0.03

Table 5. Elemental analysis of coal-derived isotropic carbon fiber precursor pitch.

Carbon	Hydrogen	Nitrogen	Sulfur	C/H Atomic Ratio
91.06	5.67	2.69	<0.1	1.34

Figure 2 shows the viscosity vs. temperature of the coal-derived isotropic pitch compared to a petroleum pitch with similar softening point temperature. Although the Mettler softening point temperature of the coal-derived material is only 3°C less than the petroleum pitch, the viscosity of the coal-derived pitch is significantly less.

Figure 2. Viscosity vs. temperature of coal-derived and petroleum isotropic pitches.

Tables 6 and 7 provide some characteristics of the coal-derived anisotropic pitch. As expected, the anisotropic pitch is more aromatic (C/H atomic ratio of 1.60) than its isotropic precursor because of the additional heat treatment. Also, the nitrogen and sulfur containing organic molecules in the anisotropic pitch appear to be enriched.

Table 6. Properties of coal-derived anisotropic pitch.

Mettler Softening Point, °C	Density, g/cm ³	Conradson Carbon, wt%	Ash Content, wt%
Approximately 310	1.307	75.1	0.09

Table 7. Elemental composition of coal-derived anisotropic pitch, wt%.

Carbon	Hydrogen	Nitrogen	Sulfur	C/H Atomic Ratio
91.60	4.78	3.18	1.28	1.60

Figure 3 is a photomicrograph of a sample of the coal-derived anisotropic pitch as it came out of the reactor and before annealing. Note the spheres of mesophase, which indicate a highly deformable and plastic state. Though it is well known that coal liquids and coal extracts can undergo a mesophase transformation, usually this mesophase is viscous or reactive. Figure 4 is a photomicrograph of the same anisotropic pitch after annealing. It is apparent from the figure that annealing promoted extensive mesophase coalescence.

Figure 3. Coal-derived anisotropic pitch before annealing.

Figure 4. Coal-derived anisotropic pitch after annealing.

4.2 Evaluation of coal-derived pitches for fiber spinning and binders

4.2.1 Spinning of the coal-derived isotropic pitch into carbon fibers

The isotropic pitch was directly used for fiber spinning in a multi-head spinneret set-up. In this case, there were forty spinneret holes in the spinneret head. Because the softening point temperature was relatively low for this pitch, spinning was carried out at 220°C, which is lower than would be typical for spinning other pitch fibers. Spinning at higher temperatures would result in a viscosity too low to achieve continuous fibers without breakage. However, at 220°C it was possible to spin multi-fibers successfully without any major difficulty.

After spinning, the fibers were stabilized by oxidization in air to prevent fusion during subsequent carbonization. Typical stabilization temperatures for conventional pitch fibers are usually conducted at above 270°C for a few hours. However, because the softening point temperature of the coal-derived isotropic pitch is low, attaining temperatures above 200°C too rapidly would cause the coal-derived isotropic fibers to fuse. Thus, stabilization was carried out by heating at 0.5°C/min to 180°C and held there for 24 hours. After the 24-hour hold at 180°C, the temperature was again raised at 0.5°C/min until 270°C was reached with a 4-hour hold and then increased to 300°C. This stabilization sequence was successful and the coal-derived fibers were then carbonized to 1100°C under an inert atmosphere. These fibers had an average diameter of 15µm and the strength ranged from approximately 250 to 516 MPa. This strength is considered relatively low even for isotropic fibers.

To improve the mechanical properties of the fibers, the same pitch was heated in a closed system under nitrogen to 400°C with stirring for ten hours to effect polymerization and increase average molecular weight. This thermal treatment raised the softening point to approximately 224°C. Fibers were again spun with the multi-hole spinneret at 240°C. After stabilization and carbonization, the strength of these fibers ranged from a low of 280 to a high of 1200 MPa.

The pitch was next heat treated as before but at 420°C under nitrogen with stirring for 24 hours, which increased the softening point to 252°C. The pitch was spun at 270°C and after stabilization and carbonization to 1200°C the strength of the filaments ranged from a low of 312 to a high of 2045 MPa.

By comparison, fiber diameters from the multi-head spinning system were slightly larger at approximately 15 - 17µm than commercially available petroleum pitch fibers at 10 - 12µm. A smaller diameter fiber would likely increase strength to some extent. It is probably possible, with additional coal-derived isotropic pitch and a few iterations with the multi-head spinning system, to produce 10 – 12µm diameter fibers.

4.2.2 Coal-derived anisotropic pitch as a matrix binder

The anisotropic pitch produced was ground to minus 200 mesh, oxidized in air at 270°C for four hours, and placed in an isopropyl alcohol diluted phenolic solution to produce a slurry. The slurry was painted onto each side of a PAN (T300 five-harness satin (5HS)) weave fabric. The coated fabric pieces were air dried and stacked in a steel mold. In a

heated platen press, the die was heated to 400°C under 500psi. As the pitch melts, it is squeezed into the fabric and continued heating brings the pitch to a low-temperature-char state while still under pressure. After cooling, the composite was removed from the steel die and heated in an inert atmosphere up to 2250°C. X-ray diffraction (XRD) patterns of intermediately heated samples showed graphite peaks beginning as low as 1800°C. Based on XRD patterns, the composite appeared to be fully graphitized at 2250°C. While 2250°C produces a graphite matrix in the case of PAN-base fibers, heating to higher than 1800°C is known to reduce fiber strength. Nonetheless, composite flexure strength of 300 MPa was achieved in the one step composite fabrication that is quite adequate for many commercial applications. An additional impregnation step with the coal-derived anisotropic pitch using vacuum plus pressure would substantially increase strength and, in the case of PAN fiber reinforcement, thermal treatment under 1800°C should also maximize strength. The main motivation to heat to higher temperatures is to graphitize the matrix in order to enhance electrical or thermal conductivity.

4.2.3 Evaluation of the coal-derived anisotropic pitch in a lithium battery

Petroleum-pitch based graphite fiber (P30X) also utilized to produce a carbon-carbon composite for a lithium battery utilizing the WVU anisotropic pitch. The composite was prepared using the same technique as with the PAN fabric. The P30X fabric is a plain weave, 19x19 rods from a 2K tow. With pitch-base fibers, higher heat-treatment temperature is desirable, thus heat treatments up to 2790°C were performed. At this temperature, the composite was completely graphitized, as evidenced by XRD. The density after only the one-step processing and heat treatment to 2790°C was 1.67g/cc,

which is excellent for many commercial applications. The strength of the composite was 350 MPa, which also is excellent for many commercial applications. A re-impregnation under vacuum and pressure with the WVU anisotropic pitch could be expected to produce a composite density in the range of 1.9g/cc.

This composite was utilized as an electrode in a lithium-ion battery. Although the thickness of this composite was greater than desirable (less than approximately 100 μ m is ideal for a Li-ion battery electrode), nonetheless, its performance was considered excellent. The capacity was 320 mAh/g with an irreversible capacity of slightly less than 10%, which remained constant in cyclability. This performance is at least equivalent to an expensive mesophase carbon microbeads (MCMB), which cost \$35 - \$50/kg. In other Li-ion battery work, MER has demonstrated there is a significant safety factor in overcharge-discharge with the composite anode over the MCMB. Thus, the anisotropic pitch provides an excellent binder to produce Li-ion battery composite anodes that have at least equal performance to MCMB and provides significant additional safety. Additional development with the coal-derived anisotropic pitch is required to produce thinner C-C composite electrodes. This pitch could also probably be spun into fibers to provide electrodes completely from coal.

5.0 CONCLUSIONS

Bituminous coal was successfully hydrogenated and solvent extracted to produce a pitch-like material. Thermal processing converted the raw hydrogenated product into an isotropic pitch suitable for spinning carbon fibers. Although the softening point of the

isotropic pitch was within the range of the softening points of similar pitches produced in prior CPCPC projects, all of the earlier studies spun filaments through a single-hole spinneret. The work completed in the current project indicates that the softening point of the coal-derived pitch should be raised above 225°C to achieve acceptable spinning characteristics through a multi-hole spinneret and to increase the rate of stabilization temperatures.

The anisotropic pitch performed well as a binder pitch with a high-char yield that readily graphitizes. It could be readily used to produce C-C artifacts advantageously because of the excellent density and composite strength achieved in one step. If used as a binder with pitch-based fibers, its excellent graphitizability could be useful for virtually any high electrical or thermal conductivity application, such as Li-ion battery electrodes and thermal management composites. It offers significant potential to produce an all coal-based electrode (fiber and binder) for Li-ion batteries.

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**Coal-Based Activated Carbon for Removing
Perchlorate and other Anions from Water**

Final Report

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ABSTRACT

The focus of this recent research has been on tailoring the activated carbon in a manner that provides better perchlorate adsorption. We have focused on two approaches to tailoring the activated carbon. The first has been to thermally treat the activated carbon with a reducing gas. The second has been to preload the activated carbon with organic cations. Both of these protocols have offered considerable enhancement of perchlorate removal. We have achieved three to ten times the adsorption capacity for perchlorate, above that for commercial activated carbon.

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EXECUTIVE SUMMARY

By employing reducing gas thermal treatment, the authors were able to achieve three times the bed volumes for removing perchlorate before initial breakthrough, when compared to virgin non-tailored activated carbon. By preloading the activated carbon with an NSF approved organic cation, the authors achieved four times the bed volumes for removing perchlorate before initial breakthrough, when compared to virgin non-preloaded activated carbon. By preloading with an organic cation that is not yet NSF approved, the authors achieved more than ten times the bed volumes to breakthrough.

REDUCING GAS TREATMENTS

From previous work, we noticed that three types of carbon from Calgon Carbon Company had higher pH_{pzc}/higher positive charges than the SAI carbon and that this helped increase the adsorption capacity of perchlorate.

A. Experimental

During this research, we tailored the SAI carbon with a reducing gas at different temperatures with various durations of time to compare the effect of tailoring on carbon's adsorption capacity for perchlorate.

The tailoring of the SAI carbon consisted of placing a sample of carbon in a TGA (Thermogravimetric Analyzer) under flowing nitrogen. The furnace was heated to the desired temperature and then the gas was switched to the tailoring gas. The samples were held for a predetermined time and then cooled to room temperature. The samples are

denoted using the carbon type, the temperature, and time. For example, SAI500-60 is a SAI carbon treated at 500°C for 60min.

We then investigated the effects of tailoring on perchlorate removal during small column tests. We also appraised these tailored carbons relative to their pore size, surface area, and surface charge. This helped us to gain an understanding as to the effect of physical and chemical characteristics of carbon on perchlorate adsorption. Pore structure analyses were conducted via Micromeritics (Norcross, GA) ASAP 2010 unit while surface charge distribution was done by a DL53 automatic titrator.

B. Results and Discussion

1. Characterization of pore structure

Table 1 lists the surface area, micropore volume (pore width <20Å), and average pore width of all the samples. Figure 1 shows the pore volume distributions for these tailored carbons. At treatment temperature 500°C, there is a decrease in all three parameters that may be the result of this tailoring gas reacting with surface groups/active carbon atoms. The resultant nitrogen-containing surface functional groups may block the previously accessible pores. While for treatment at 700°C, there was an increase in all these parameters compared with 500°C. One possible cause is that this tailoring gas is acting as an activating agent at this temperature, and more micropores are created by this activating effect.

Table 1: Physical characteristics of tailored activated carbon

Sample	BET surface area (m ² /g)	Micropore volume (mL/g)	Average pore width (Å)
Virgin SAI	874.09	0.193	36.64
SAI500-30	854.25	0.182	35.83
SAI500-60	861.28	0.188	36.36
SAI500-150	864.42	0.202	36.51
SAI700-30	1084.01	0.231	36.18
SAI700-60	940.96	0.202	35.91
SAI700-150	965.13	0.197	36.51

2. Characterization of surface charge distribution and pH_{pzc}

Automatic titrations were carried out using a DL53 titrator (Mettler Toledo) to measure the surface charge distribution of activated carbon. About 0.15 g carbon was added to 200 mL of 0.01 M NaCl solutions respectively. The surface charge distribution of samples was shown in Figure 2. The Figure indicates that the positive surface charge of all samples were increased remarkably after tailoring. In addition, for treatment time of 30 and 60 min, the carbon products had more positive charges at 700°C treatment than the 500°C treatment. When the thermal gas treatment time was 150 minutes, the temperature no longer made as great a difference in the surface charge distribution.

According to the research on pH_{pzc} during the last progress report period, slurry pH (pH of supernatant after the 0.01M NaCl solution was equilibrated for 24h with 10% carbon mass) is a fairly close representative of the carbon pH_{pzc} value. So we use this slurry pH to represent the sample pH_{pzc} . Table 2 is the slurry pH of tailored samples.

Table 2: Slurry pH

Sample	Slurry pH	Sample	Slurry pH
SAI500-30	9.59	SAI700-30	9.67
SAI500-60	9.86	SAI700-60	10.17
SAI500-150	9.92	SAI700-150	9.94

Compared with the slurry pH of virgin SAI carbon (8.75), after the tailoring, the pH_{pzc} increased for all tailored products.

In comparison to this, the point of zero charge (pH_{pzc}) determined by a 10% by mass slurry for the virgin material used in Redlands was determined to be 8.3, while the spent GAC had a pH_{pzc} of 5.7. In comparison the SAI GAC used in the lab had a pH_{pzc} of 7.6 for the virgin and 7.2 for GAC treated with the same number of bed volumes that the Redlands GAC saw at full-scale. A GAC with a pH_{pzc} of 5.7 would be negatively charged when water with a pH of 7.5-8 (the pH of the groundwater at Redlands) is flowing through it, and the adsorption of the negatively charged perchlorate ion would be poor.

3. Rapid small column test

Two of the tailored carbon products, SAI500-60, SAI700-60 were tested for perchlorate removal in small column tests. RSSCT columns used in this experiment were approximately 8 inches in length and had an inner diameter of 0.56 cm. Each test employed about 1.67 grams of GAC held in place by glass wool. The carbon sample was crushed and sieved to the US mesh 200*400. The actual EBCT of these columns were about 0.75 min to simulate a full-scale EBCT of 20min. Figure 3 shows the breakthrough curve for the tailored carbons. It indicates that tailoring can effectively improve the adsorption capacity for perchlorate. The bed volumes operated till the initial breakthrough was at 3500 BV for the SAI 700-60 tailored carbon; and was more than three times the capacity before breakthrough (1000 BV) that was observed for the virgin SAI carbon.

ORGANIC CATION TAILORING

Progress has also been made in the area of tailoring the GAC with organic cations. In previous research, a test was developed to screen cations to provide a way of determining which materials could provide the greatest improvements in perchlorate adsorption.

A. Experimental

The protocol used in this experiment was somewhat arbitrary, but they allowed for useful comparison amongst organic cations. This protocol called for 1.67 grams of 200 x 400 SAI GAC, 100 mL of a 4 g/L solution of the organic cation being tested (on a

dry weight basis), and recirculating the organic cation solution through the column of GAC for one day. In some cases, as listed below, the recirculation period proceeded for more than one day.

Figure 4 shows one round of tests conducted. Organic cations designated as C54a, C54b, C54c, C54d, and C54e were obtained from a Pennsylvania company. These organic cations have been NSF approved for use in drinking water; and they are commonly used in the drinking water industry. After one day of recirculating a solution of each through a column of SAI GAC, Redlands water was then passed through the column.

B. Results and Discussion

C54a showed a breakthrough point similar to that of virgin GAC, but showed continued adsorption of perchlorate through about 2000 BV. C54b and C54e had perchlorate breakthrough at approximately 2000 BV. C54c was able to treat 2500 BV before breakthrough. C54d performed the best in this round of tests. It was able to process 3300 BV of Redlands water prior to perchlorate breakthrough. This represented 3.3 times more water processed before breakthrough than for that of the virgin GAC (in this column configuration, perchlorate breakthrough occurred at 1000 BV).

Based on this finding, C54d was run in another set of experiments. This time the same solution would be allowed to recirculate through the column for a period of 2 days and 5 days respectively. Past experiments had shown that the length of exposure to the cation could have a dramatic effect on the number of BV processed prior to perchlorate breakthrough. These results are shown in Figure 5. There was a slight improvement with longer treatments: 3800 BV for 2-day recirculation and 4000 BV for 5-day recirculation.

Another set of 1-day recirculation experiments was run with three organic cations designated as C60a, C60b, and C60c from another source and one column was run with C54d. The authors herein are not aware that the C60a, b, c organic cations have been NSF approved for drinking water use. The column run with C54d utilized HD4000, a lignite based GAC from NORIT, while the other columns employed the SAI GAC. These results are shown in Figure 6. As you can see, there is nothing to see! No perchlorate breakthrough whatsoever, up to 6300 BV for C60a, 3900 BV for C60b, 13750 BV for C60c, and 4200 BV for C54d with the HD4000. This lack of breakthrough is both a good and a bad thing. Good because the longer the columns can run before breakthrough, the more economically feasible these treatment methods become. Bad in the sense that we are completely out of water and are awaiting more water so these columns can continue. These columns are showing tremendous promise. If you recall, the GAC at Redlands treated approximately 18,000 BV for TCE removal, and the ultimate goal was to bring the perchlorate removal in line with the TCE removal. While we aren't sure that these columns will reach 18,000 BV, C60c has reached 13750 BV without breakthrough. The treatments in these columns may exceed 18,000 BV individually, or we may be able to achieve that "magic number" by coupling these methods with another organic cation or reducing gas treatment.

CONCLUSIONS

Both the thermal pretreatment with the reducing gas and the organic cation preloading enhanced perchlorate removal considerably.

Figure 1: Pore Volume Distribution of Tailored Carbons

Figure 2: Surface Charge vs. pH for GAC Treated with a Reducing Gas

Figure 3: Perchlorate Breakthrough for GAC Treated with a Reducing Gas

Figure 4: ClO_4^- Breakthrough with 200x400 SAI GAC Tailored with Organic Cations from e-Calgon. 1 Day Loading.

Figure 5: Adsorption of Perchlorate from Redlands Water onto 200x400 SAI GAC Pre-Treated with Organic Cation C54d with Different Pre-loading Times

Figure 6: No Perchlorate Breakthrough to Date with SAI GAC Tailored with C60a, C60b, and C60c as well as HD4000 Tailored with C54d

Low Cost Carbon Fibers from Coal-Based Precursors

Final Report

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ABSTRACT

The program objective is to demonstrate commercial viability of using coal tar pitch (CTP) as a precursor to produce low-cost carbon fibers. A commercial demonstration spinning system with a 100 hole spinneret was constructed that provided trouble free spinning of CTP. This included a take-up system that utilized a graphite cylinder, which permitted stabilizing as well as pyrolyzing the fiber on the graphite cylinder. The processing of commercial CTP to provide a suitable spinning pitch was scaled-up to 10 Kg capacity. An isotropic pitch from West Virginia University (WVU) and both isotropic and mesophase pitches prepared on this program were spun in the multi-hole spinneret system that demonstrated operability. The strengths of the produced fibers, isotropic and anisotropic was up to 2.2 GPa. This phase of the program demonstrated that quality fiber in small tows can be produced from CTP that provides initial demonstration of commercial viability.

Introduction

During the first year program, calendar 1999, it was demonstrated commercial source coal tar pitch could be purified by solvent extraction, control oxidized with air and/or oxide chemical additions, thermal treated and spun into isotropic fibers, which could be pyrolyzed without oxidation/stabilization and without fiber fusion. The fiber strengths were in the 1.3 GPa range.

In the second year, calendar 2000, all processing steps were further improved that resulted in producing carbon fibers with strengths up to 3.8 GPa when heat treated to 1200°C and up to 4.2 GPa when heat treated to 1800°C. These strengths are greater than carbon fibers derived from petroleum-based pitch and equivalent to commodity fibers produced from petroleum based polyacrylonitrile (PAN). The coal tar pitch was also 80% converted to mesophase and anisotropic fibers were demonstrated. Fiber spinning in a 25-hole spinneret bead was demonstrated as well as microwaves heating of the fibers.

A goal of this fiber program is to utilize a domestic source coal tar pitch (CTP) as a precursor to produce low cost carbon fibers for use in transportation and a plethora of other applications. The automotive industry has stated that a carbon fiber price of \$5.00/lb in continuous form and \$3.50/lb in discontinuous form is required for large-scale utilization. If carbon fiber is fully utilized throughout automobile, over 50% weight savings is possible, which translates to substantial fuel savings and pollution reduction. Carbon fibers from petroleum stock that produces the PAN fiber precursor is quite a mature process whose cost has bottomed at approximately \$10/lb. If CTP based processing can meet the transportation industry cost goal, a paradigm in carbon fiber production will have been established. The objective of this program is to demonstrate such a paradigm is indeed possible. The goal/objective of the third year was to demonstrate a 100-hole spinneret system could be built to establish the commercial potential of the CTP process, which could be operated to project the cost of fiber production.

Executive Summary

Carbon Fibers have become a commodity for wide and diverse applications but have not penetrated transportation to any major extent because of high cost. All carbon fibers are made from petroleum precursors of polyacrylonitrile (PAN) or petroleum pitch. The cost of these carbon fibers have bottomed at approximately \$10/lb. The transportation sector and a variety of other applications require continuous carbon fibers at less than \$5.00/lb and discontinuous at less than \$3.50/lb. This CPCPC program has demonstrated that coal tar pitch (CTP) or pitch extracted directly from coal provides a low cost precursor to produce carbon fibers with properties equivalent to those produced from the petroleum precursor. CTP purification and the development of additives have resulted in the ability to spin fiber that do not require stabilization/oxidation to prevent fusion prior to heat treatment. Processing has been scaled-up that demonstrates producing small tows and provides a basis for predicting that coal base carbon fibers can be produced for the transportation cost goal. This program has demonstrated it is commercially feasible to produce coal base carbon fiber at low cost and is in the process of continued and expanded commercial demonstration.

RESULTS OF WORK DURING YEAR 2001

In order to commercially demonstrate the bench scale demonstrated CTP fiber processing system, three major units must be scaled-up. These are the CTP purification and processing to produce the pitch precursor suitable for spinning, the 100-hole spinneret system and the fiber take up system. An adjunct to these three units is the heat treatment to produce the final carbon fiber.

The first unit of purifying and processing the as received CTP has been scaled from about 50 grams processing to 10 kg. During 2001 it is now possible to process up to 10 kg of as received pitch, which provides an adequate supply of pitch for spinning and demonstrates it is possible to scale-up and maintain the quality of fibers. This scale of processing 10 kg of pitch provides more pitch than necessary for fibers investigations which allows the CTP to be investigated for other applications including foam and as a binder for C-C composites for general applications, as well as anodes for lithium-ion batteries. Thus, the scale-up in this fiber program provides the opportunity to utilize the low cost domestic source CTP for other applications.

A well functioning fiber take-up system is required to demonstrate the purified pitch and spinneret system can function to produce low cost fiber. The take-up system was build around a milling machine table linked to a speedometer-regulated drive. The linear advancement is capable of 0.1 mm per revolution that permits winding fibers side by side or as a tow, also side by side. The take-up spool is a polished graphite cylinder mounted on a Teflon cylinder attached to the melting table. The smooth polished graphite cylinder prevents any surface damage to the green spun fiber. The graphite take-up cylinder permits stabilizing the fiber while wound on the graphite cylinder, as well as pyrolysis/heat treating of the fiber to its final temperature. This is somewhat common practice in fiber processing. The take-up system showing columns of spun tows is shown in Figure 1.

Critical to spinning good fibers with the desired diameter of approximately 10 μ , which is the industry standard, is temperature control in the pitch reservoir, proper filtering of the pitch and attenuation or stretching of the green fiber in the 2-3 mm distance of the spinneret hole before the spun fiber hardens. In the second year effort,

Figure 1: Fiber Take-Up System

temperature uniformity was a major problem, i.e. either too low, non-uniform or over heating and coking the pitch. The reservoir system was revamped to achieve uniform temperature control and assure trouble free spinning.

To define the proper spinneret hole size, hypodermic needle heads were initially used in various sizes and the length of the needle varied to aid in defining the attenuation of the fiber as it exited the spinneret hole before hardening. An example of these spinneret needle heads is shown in Figure 2. The needle id varied from 0.050 inches up to 0.090 inches and length of the needle varied from zero to 1 mm long. In fiber spinning trials, a spinneret hole size greater than approximately 0.075 would not produce the desired fiber size of approximately 10 μ . The length of the needle of 0.05 up to 1 mm produced desirable attenuation that achieved fiber diameter, as well as enhanced strength of the final heat treated fiber. These parameters define the 100 hole spinneret head, which consists of 0.05 inch hole sizes that are recessed in the steel head by at least 0.05 mm, but no more than 1 mm.

The reservoir heating system was revamped which included internal heaters, as well as external band heaters with a proportional controller to independently control each set of heaters. For the internal heater, the controlling thermal couple was attached to the surface of the heater to prevent overheating and coking the pitch immediately in contact with the heater surface. This heating system proved to work very well and maintain the bulk pitch in the reservoir within plus or minus 1°C. This degree of temperature control provides the capability of maintaining close control on the spinning parameters.

With a well performing spinning system, it is possible to define the properties in the CTP and spinning parameters to provide high strength fibers that demonstrate the commercial viability of the process.

Pitch supplied from West Virginia University was investigated to demonstrate spinning from the multi-hole spinneret head. The pitch was isotropic with a softening point of approximately 205°C. It was possible to spin the fiber at 220°C, but difficult to stabilize due to the low softening point. The fiber strength was relatively low in the range of 250 to 516 MPa. MER performed further processing of the pitch to increase its softening point, which yielded higher strength fibers in the range of 312 to 2045 MPa. Three batches were spun and the results reported in WVU Final Report DE-FC26-

Figure 2: Spinneret Trials to Define Spinneret Hole Size

98FT40350. The conclusion for this report is that the multi-head spinneret system functioned successfully and the isotropic pitch supplied by WVU could be successfully spun into a coal-based carbon fiber with reasonable properties.

The commercial source coal tar pitch (CTP) was processed in the 10 kg treatment system and used for spinning in the commercial demonstration spinning system described above. The strength of batch one's fiber ranged from 880 to 2.2 GPa, which is considered exceptional for isotropic fibers. The modulus of the isotropic carbon fiber was 29 GPa. If high modulus is desired in the fiber, a mesophase pitch precursor is required. MER converted the CTP to about 80% mesophase and demonstrated spinning fibers in the multi-hole spinneret system. The fibers produced from mesophase are anisotropic whose properties are very dependant on final heat treatment temperature. Heating to the same low temperature of 1200°C for the isotropic fibers, the mesophase pitch fibers had strengths in the 1.7 – 2.3 GPa range.

CONCLUSION

The conclusion of the 2001 year investigation is a fully integrated system which has been demonstrated that provides the capability to commercially demonstrate the CTP fiber processing and establish a basis to project cost of fiber production.

Low Cost Carbon Electrodes For Batteries and Fuel Cells

January 1, 2001 to April 15, 2002

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April 15, 2002

Final Report

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Abstract

The primary objective of this Phase I program was to demonstrate the development of a low cost, carbon fiber obtained from domestic pitch-based sources as anode material for rechargeable lithium-ion batteries. The demonstration includes development of several half-cells and evaluation of reversible specific capacity and irreversible capacity loss of the developed anode material. Several prismatic design prototype lithium-ion cells were also developed with the chopped carbon fiber anode material and evaluated these cells for cycle life and deliverable capacity at different discharge rates.

The specific objectives of Phase I work were to (1) prepare low cost carbon fiber anode, (2) analytically characterize the anode material, (3) develop half-cells with lithium metal counter electrodes and evaluate reversible capacity and irreversible capacity loss for lithium-ion intercalation and de-intercalation, (4) develop prototype lithium-ion cells with the developed carbon fiber anode and commercially available cathode materials, and (5) evaluate performance and assess technical feasibility.

All the tasks were successfully completed and the project goal was fully achieved. In this program, we studied low cost carbon fiber from a domestic source as an anode material in half-cell configuration and evaluated reversible capacity and irreversible capacity loss in carbonate-based 1M LiPF₆ electrolyte. A reversible capacity of as high as 340 mAh/g was observed for lithium-ion intercalation and de-intercalation with the developed carbon fiber. An irreversible capacity loss of 4% was observed. These values are superior to those obtained from the industry standard carbon material (MCMB carbon currently available only from Japan) presently used in commercial lithium-ion batteries.

We also tested the developed carbon fiber anode against commercially used cathode material in prototype lithium-ion pouch cells and evaluated the performance with respect to cycle life and deliverable capacity at different discharge rates. Excellent cycling behavior and rate capability was observed.

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I. INTRODUCTION

Since its introduction and commercialization in 1991, lithium-ion battery systems have received considerable interest not only to the battery community but also to the academia and electronic industries. This is mainly due to their several advantageous characteristics over the competing technologies (e. g., Pb-acid, Ni-Cd and Ni-MH) such as high specific energy (~160 Wh/kg), long cycle life (~500 cycles with 80% capacity retention), low self-discharge (~8% per month), and environmentally compatible. Lithium-ion batteries are now widely used for consumer electronic applications such as cellular phones, laptop computers, and camcorders. Currently, these batteries are mass-produced only in Asia (Japan, China, and Korea) and available in the U. S. through Asian manufacturers.

In lithium-ion batteries, carbon is used as an anode, a lithiated transition metal intercalation compound as a cathode and LiPF_6 as an electrolyte in carbonate-based organic solvents. The reactions at the electrodes and overall cell reaction are

where LiMO_2 represents the lithiated metal oxide intercalation compound.

The electrochemical process is the uptake of lithium ions at the anode during charge and their release during discharge, rather than lithium plating and

stripping as occurs in metallic lithium rechargeable battery systems. As metallic lithium is not present in the cell, lithium-ion cells have enhanced safety and a longer cycle life than the cells containing metallic lithium.

Fig. 1: Electrochemical Potential of Some Lithium Intercalation Compounds vs. Lithium metal. PPY = Polypyrrole; PVF = Polyvinyl furan.

Hard carbon (1) and graphite (2) are used as anodes in lithium-ion batteries. The carbon materials deliver a reversible capacity of ~370 mAh/g corresponding to the chemical formula LiC_6 . The electrochemical potential of lithiated carbon is almost the same as that of metallic lithium as shown in Figure 1 (3). Thus, an electrochemical cell made with a lithiated carbon material will have almost the same open-circuit voltage as one made with metallic lithium. In practice, lithium-ion cell is manufactured in a fully discharged state with carbon and lithiation of the carbon is carried out by subsequently charging the cell.

During the first electrochemical intercalation of lithium into the carbon, some lithium is irreversibly consumed and a significant amount of capacity can not be recovered in the following discharge. This irreversible capacity loss, which depends on the electrolyte solution and the type of carbon material, is explained on the basis of the reduction of the

electrolyte solution and the formation of a passivating film (SEI layer) at the Li_xC interface (4). Chemical combination of lithium to the active surface functional groups of carbon may also play an important role in this irreversible capacity loss (3).

The state-of-art lithium-ion cells use some special-type of carbon materials that are only produced in Japan. The Japanese carbon materials provide high reversible capacity ($\sim 330\text{-}340\text{ mAh/g}$) and low irreversible capacity loss ($\leq 10\%$) but are expensive ($\sim \$50/\text{kg}$). The identification of relatively low cost domestic source of carbon anode that can deliver comparable reversible capacity and irreversible capacity loss would be of critical importance. This program focuses on the development of such carbon anode material.

II. EXECUTIVE SUMMARY

The primary objective of this Phase I program was to demonstrate the development of a low cost, carbon fiber obtained from domestic pitch-based sources as anode material for rechargeable lithium-ion batteries. The demonstration includes development of several half-cells and evaluation of reversible specific capacity and irreversible capacity loss of the developed anode material. Several prismatic design prototype lithium-ion cells were also developed with the chopped carbon fiber anode material and evaluated these cells for cycle life and deliverable capacity at different discharge rates.

The specific objectives of Phase I work were to (1) prepare low cost carbon fiber anode, (2) analytically characterize the anode material, (3) develop half-cells with lithium metal counter electrodes and evaluate reversible capacity and irreversible capacity loss for

lithium-ion intercalation and de-intercalation, (4) develop prototype lithium-ion cells with the developed carbon fiber anode and commercially available cathode materials, and (5) evaluate performance and assess technical feasibility.

All the tasks were successfully completed and the project goal was fully achieved. In this program, we studied low cost carbon fiber from a domestic source as an anode material in half-cell configuration and evaluated reversible capacity and irreversible capacity loss in carbonate-based 1M LiPF₆ electrolyte. A reversible capacity of as high as 340 mAh/g was observed for lithium-ion intercalation and de-intercalation with the developed carbon fiber. An irreversible capacity loss of 4% was observed. These values are better than those obtained from the carbon material (MCMB carbon) presently used in commercial lithium-ion batteries.

The electrode thickness and heat-treatment temperature plays significant roles in obtaining higher reversible capacity and lower irreversible capacity loss. The thinner electrode and higher temperature treatment provides better lithium-ion intercalation/de-intercalation behavior.

We also tested the developed carbon fiber anode against commercially used cathode material in prototype lithium-ion pouch cells and evaluated the performance with respect to cycle life and deliverable capacity at different discharge rates. Excellent cycling behavior and rate capability was observed.

III. EXPERIMENTAL

A. *Chemicals and Materials*

A high purity grade propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) were obtained from Grant Chemicals. A different combination of these solvents was used as received to prepare 1M LiPF_6 electrolyte in a glove box. LiPF_6 salt was purchased from Hashimoto Chemicals. The electrolyte solution was used as received. Copper foil (0.02 mm thick) and aluminum foil (0.04 mm thick), purchased from A. J. Oster, were used as substrates for the negative (anode) and positive (cathode) electrodes, respectively. Lithium metal foil of 50 μm was obtained from Foote Mineral. LiCoO_2 (obtained from FMC) was used as positive electrode material for the development of prototype lithium-ion cells. The carbon electrode materials were chopped carbon fiber from Conoco and pitch-based carbon fiber tow from Amoco. Celgard 2400, purchased from Hoechst Celanese, and polyethylene Tonen separator from Exxon Mobile were used as separators. The binder material was polyvinylidene fluoride (PVDF, obtained from Elf Atochem). Dimethyl formamide (DMF, Aldrich) was used as a solvent to dissolve PVDF. Soft plastic “White Bag” from Shield-Pack, Inc. was used as a packaging material for pouch cells. The “White Bag” is made with 3-layers of foils: aluminum foil is laminated in between white plastic foil at the top and a colorless plastic foil at the bottom.

B. *Processing to Produce Carbon-Carbon (C-C) Electrodes*

It has been determined for the electrode/anode in a lithium-ion battery made of C-C to properly function, it's thickness must be less than 120 μm and preferably less than

100 μ m ($\approx$ 0.004 inches) thick. Heretofore, C-C in such thin cross sections had not been produced. It was, therefore, necessary to develop processing methodology to produce very thin C-C composites.

In order to achieve the required high electrical conductivity, pitch base fiber is required as the reinforcement. In this case, two fiber types were investigated that consisted of P30X from Amoco and the discontinuous _ to 3-inch staple lengths from Conoco. Both fibers are produced from petroleum pitch and have an approximate diameter of 10 μ m. The P30X is a continuous 2k tow and the Conoco is the discontinuous random staple material.

Also, to achieve a high electrical conductivity of C-C composite, a graphitizable matrix must be used which must be derived from a pitch. WVU coal extract pitch (CEP) was utilized, since it is known to be a good binder pitch, as well as graphitizable. For lithium-ion batteries, any impurities will dramatically and adversely affect efficiency and irreversible capacity of the battery. Thus, the CEP was purified as developed in the CPCPC Fiber Program, which consists of solvent extraction and filtering of the extract to remove the insoluble ash impurities. Some organic sulfur remains in the pitch but is volatilized in subsequent graphitization. The solvent extract pitch was separated from the solvent by vacuum distillation and the remaining pitch ground to approximately minus 100 mesh. The pitch particles are heated in air and subsequently slurred with a dilute phenolic-alcohol mixture.

The pitch fibers are spread to achieve a thin layer of approximately 100 - 150 μ m. The spread pitch fibers are placed in a steel die and the slurry poured over the fiber array. The die is closed with pressure up to a few thousand psi with heat applied, the phenolic cures and holds the fibers in place, followed by the pitch becoming a liquid to fully form the matrix. Heating of the die is continued until at least 400°C is achieved up to as high as 550°C, which cokes the pitch binder. This pressure molding produces the required thin composite that is flat and uniform thickness.

The molded thin plate is then placed between graphite block to maintain flatness and heated to graphitize the matrix, as well as assure the pitch base fibers are exposed to high temperatures that maximize electrical conductivity. Heat treating temperatures of approximately 2900°C have been performed.

Significant iterative development was required to make C-C composite anodes at 100 μ m or below in thickness that had complete integrity and remained flat for suitable use as a lithium-ion battery electrode. Among the attributes of the C-C composite anode are that it is reusable or recyclable, as well as safety which is of considerable significance. During this year commercial petroleum based pitch fibers were used as the reinforcement, with most effort directed to establishing the methodology for fabricating an acceptable less than 100 μ m thick electrode. It is intended in the coming year to utilize coal tar pitch based fiber from the CPCPC Fiber Program that will result in the best quality electrode fabricated completely from coal derived materials.

C. Characterization of Carbon Fiber Electrode Material

The carbon composite electrode materials were characterized by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) technique. The in-plane and cross-sectional views of the C-C composite are shown in Fig.2 (a) and (b), respectively. The

Fig. 2: SEM images of Composite Electrode (a) in-plane, (b) cross-section

composite is composed of disordered carbon fibers.

Figure 3 shows a comparison of the X-ray diffraction patterns of the C-C composite with

Fig. 3: X-ray Diffraction Patterns of C-C Composite and MCMB Carbon

MCMB carbon. The d_{002} spacing of the C-C composite and MCMB are 0.349 nm and 0.337 nm, respectively. The higher interlayer spacing of the composite electrode allows lower expansion during lithium-ion intercalation.

D. Electrodes Preparation

i. Lithium Electrode

Expanded nickel mesh of 3 μm thick (Delker Corporation) was cut to the size of lithium electrode (2.5 cm x 3.5 cm) with an attached tab (6.3 mm wide and 19 mm long). Both sides of the expanded mesh were cleaned with acetone. The substrates thus prepared were transferred to a glove box ($\text{H}_2\text{O} < 1$ ppm) where metallic lithium of 50 μm thick (Foote Mineral) was press fitted to the substrates. The developed lithium electrodes were used as counter electrodes for half-cells measurements.

ii. Carbon Fiber Electrode

As prepared composite plate was cut to a desired electrode dimensions (2.5 cm x 3.5 cm for half-cells and 5.0 cm x 6.25 cm to 13.0 cm x 19.0 cm for lithium-ion cells) and nickel foil was riveted to one edge of the plates. The resulting electrodes with nickel tabs were used as working electrodes for half-cells and anodes for lithium-ion cells studies.

iii. LiCoO_2 Electrode

A slurry of 85% LiCoO_2 (FMC Corporation), 7% carbon black (Chevron Chemical Corporation), and 8% Poly(vinylidene fluoride), PVDF (Aldrich) was prepared in 1-methyl 2-pyrrolidinone, NMP (Aldrich) and coated on aluminum substrate (40 μm thick). The coated substrate was dried over hot air. It was then cut to the size of the positive electrodes (5.0 cm x 6.25 cm to 13.0 x 19.0 cm) with attached tabs for lithium-ion cells.

The resulting positive electrodes were pressed, vacuum dried and stored in a desiccator prior to use.

E. Development of Cells

i. Half-cells

Several half-cells were made according to the following configuration:

Lithium electrode (Li)/Separator (S)/Carbon Fiber electrode (C)/Separator (S)/Lithium electrode (Li)

The carbon fiber electrode was bagged with Celgard 2400 separator. The bagged working electrode was then sandwiched in between two metallic lithium counter electrodes. The electrodes stack assembly was then wrapped around with a solvent-resistant adhesive tape so that the position of the electrodes remained in place. The two counter electrode tabs were spot-welded. The resistance between the counter electrode and the working electrode was measured to insure that the stack was not electronically shorted. The stack assembly was then placed in between three-layer white plastic packaging material (Shield Pack, Inc.) and sealed first three sides of the stack except the opposite end of electrode tabs. The sealed stack was then vacuumed and filled with a measured amount of 1M LiPF₆ electrolyte in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) obtained from Grant Chemicals. The other end of the cell was then sealed. All these operations were carried out in a glove box (H₂O <1 ppm). The seal of the plastic bag was checked several times prior to taken out from the glove box for electrochemical measurements.

ii. Lithium-ion Cells

Prismatic design lithium-ion pouch cells were made with LiCoO_2 cathode and carbon fiber anode in 1M LiPF_6 electrolyte in EC/DMC (1:1 v/v). Figure 4 shows the pouch cell design. The cell configuration was as follows:

One-sided cathode (C/2)/Separator (S)/Carbon Fiber anode (A)/Separator (S)/One-sided cathode (C/2)

The fabrication procedure of the lithium-ion pouch cells was the same as that of half-cells as described above. A prototype lithium-ion pouch cell of capacity 500 mAh is shown in Fig. 5.

F. Electrochemical Measurements

i. Half-cells

The electrochemical measurements of the half-cells were carried out using an Arbin 24-channel cycler. The half-cells were first discharged at a constant current of 0.5 mA cm^{-2} to 0.005 V and then at a constant voltage (0.005 V) until residual current dropped to 0.05 mA cm^{-2} . The cells were then charged at a constant current of 0.5 mA cm^{-2} to a cut-off voltage of 1.0 V. The half-cells were discharged and charged for several times until a fairly constant value of charge capacity was obtained. The difference between the first discharge capacity and charge capacity provides the information on irreversible capacity loss of the working electrode (carbon fiber electrode).

Fig. 4: Schematic Diagram of a Lithium-ion Pouch Cell.

ii. Lithium-ion Cell

The lithium-ion pouch cells were “formed” according to the following procedure:

The cells were first charged at a constant current of 0.5 mA cm^{-2} to 4.2 V and then at a

Fig. 5: A Prototype Lithium-ion Cell

Cell constant voltage (4.2 V) for a total period of 8 hours or until the current dropped to a value of 0.05 mA cm^{-2} . The cells were then discharged at a constant current of 0.5 mA cm^{-2} to a cut-off voltage of 2.5 V. The charge-discharge process was continued for several (usually 2-5) times until a fairly constant values of charge-discharge capacities were obtained. The “formed” cells were then used for performance evaluation. The difference between the first charge capacity and discharge capacity also provides the information on irreversible capacity loss of the lithium-ion cell.

MER's 24 Channel Battery Cycler

MER's 8 Channel GSM Battery Cycler

MER's Battery Testing Environmental Chamber

MER's Glove Box

IV RESULTS AND DISCUSSION

A. Half-cell Studies

i. Chopped Fiber-based Composite Electrode

The carbon-carbon (C-C) composite made from low cost chopped fiber and heat-treated to 3000°C was used to examine the behavior of lithium-ion insertion and removal during charge-discharge, respectively, in a half-cell measurement. The charge-discharge profile provides indication of reversibility and specific capacity of the composite for lithium-ion insertion/de-insertion.

Several half-cells were developed with the composite working electrode, lithium metal counter electrode, and 1M LiPF₆ electrolyte in a mixture (1:1 v/v) of ethylene carbonate (EC) and dimethyl carbonate (DMC) organic solvents. The composite of two different thickness (0.21 mm and 0.26 mm) was used for this investigation.

Figures 6 and 7 show the discharge-charge behavior of two representative half-cells made with the composite electrodes of 0.21 mm and 0.26 mm thick, respectively. The cells were first discharged at a current density of 0.6 mA/cm² to 0.0 V and then charged at the same rate to a cut-off voltage of 1.0 V. The cell with the thinner electrode delivered a specific capacity of 242 mAh/g whereas with the thicker electrode cell, a specific capacity of only 212 mAh/g was obtained. The lithium-ions transport to the composite electrode and diffusion of these ions to the electrode structure play significant role in delivering the specific capacity. The relatively thinner electrode is, therefore, critical in obtaining higher specific capacity. In commercial lithium-ion battery, a carbon electrode

Fig. 6: Lithium-ion Intercalation/De-intercalation Behavior of C-C Composite made from Chopped Fiber. Counter Electrode: Li. Electrolyte: 1M LiPF_6 in EC/DMC (1:1 v/v).

of 0.15 mm thick is usually used which delivers a specific capacity of 330-340 mAh/g. Our focus will, therefore, be to produce C-C composite of approximately 0.15 mm thick using low cost chopped fiber.

Fig. 7: Lithium-ion Interpolation (Discharge)/De-intercalation (Charge) Behavior of C-C Composite in 1M LiPF₆ Electrolyte (EC/DMC).

Fig. 8: Cycling Behavior of C-C Composite in 1M LiPF₆ (in EC/DMC 1:1 v/v) Electrolyte. Counter Electrode: Li.

The cyclability of C-C composite material has also been examined. Figures 8 and 9 represent the cycling behavior of two half-cells made with the C-C composite electrode of thickness 0.21 mm and 0.26 mm, respectively. Both the cells show excellent cycling behavior.

Fig. 9: Cycling Behavior of C-C Composite in 1M LiPF₆ Electrolyte (EC/DMC 1:1 v/v). Counter Electrode: Li.

We then focused on to processing to fabricate relatively thinner C-C composite (160 μm or less) using low cost chopped fiber, heat treat to $\sim 3000^\circ\text{C}$, and testing the composite electrode for the intercalation/de-intercalation of lithium-ion in it.

Carbon-carbon (C-C) composite of 110 μm thick was made from low cost chopped fiber using the procedure outlined above and heat-treated to 2600°C . Several half-cells were developed with the composite working electrode, lithium metal counter electrode, and

1M LiPF₆ electrolyte in a mixture (1:1 v/v) of ethylene carbonate (EC) and dimethyl carbonate (DMC) organic solvents. The half-cells were then tested using Arbin 24 channel cycler which is equipped with a computer to monitor and store data.

Figure 10 shows the first discharge-charge behavior of a representative half-cell made with the composite electrode. The cell was first discharged at a constant current density of 0.6 mA/cm² to 0.0 V and then charged at the same rate to a cut-off voltage of 1.0 V. The first discharge capacity was 306 mAh/g and the corresponding charge capacity was 284 mAh/g. The irreversible capacity loss was, therefore, only 7% which is better than the best known commercial carbon material (MCMB ~10%).

Fig. 10: First Discharge Charge Behavior of C-C Composite at 0.6 mA/cm² in 1M LiPF₆ Electrolyte.

The deliverable lithium-ion intercalation capacity is still significantly lower than that of commercial carbon. The primary reason for this is due to the relatively higher impedance of the C-C composite electrode as is evidenced from the sharp rise in voltage at open-

circuit voltage after charge. The iR drop due to this impedance has not been compensated during electrochemical measurements and thus results in lower deliverable capacity.

ii. Continuous Fiber-based Composite Electrode

We examined the charge discharge and cycling behavior of a thin ($\sim 50\mu\text{m}$) C-C composite material, produced from P30X pitch-based carbon fiber and heat-treated to 2700°C , as anode in half-cell configuration. Metallic lithium was used as the counter electrode for half-cell studies in 1M LiPF_6 electrolyte.

Two half-cells were made. The electrode dimension was 2.5 cm x 3.5 cm. The open-circuit voltage of the cells were 3.31 V and 3.29 V. Both the cells were first discharged at a constant current of 0.5 mA/cm^2 to 0.0 V and then at constant voltage (0.0 V) for three hours or until the residual current dropped to 0.05 mA/cm^2 . The cells were then charged at a constant current of 0.5 mA/cm^2 to a cut-off voltage of 1.0 V. Figure 11 shows the first charge discharge profile of a representative half-cell.

The cell delivered a first discharge capacity of 331 mAh/g and charge capacity of 305 mAh/g. The irreversible capacity loss is, therefore, 8%. The half-cells were discharged and charged for several times until a fairly constant value of charge capacity was obtained. Figure 12 represents the first four charge profiles of the cell. A fairly constant charge capacity of 343 mAh/g was observed which is considered to be the reversible capacity of the C-C composite anode.

Fig. 11: First Discharge Charge Behavior of C-C Composite at 0.5 mA/cm². Counter Electrode: Li; Electrolyte: 1M LiPF₆.

Fig. 12: Cycling Behavior of C-C Composite in 1M LiPF₆ Electrolyte. Counter Electrode: Li

Similar type of composite electrodes were made with P30X pitch-based carbon fiber but this time heat-treated to 2850°C. The material was examined for lithium-ion intercalation and de-intercalation in 1M LiPF₆ electrolyte. Figure 13 shows the first discharge charge profiles. The charge capacity was 321 mAh/g with a corresponding discharge capacity of 336 mAh/g. An irreversible capacity loss of only 4% was observed. The irreversible capacity loss of 4% is significantly lower than that observed with MCMB carbon. The lower irreversible capacity loss improves specific energy and energy density of lithium-ion cells.

Fig. 13: First Discharge (intercalation) Charge (de-intercalation) Behavior of C-C Composite in 1M LiPF₆ Electrolyte. Counter Electrode = Li

B. Lithium-ion Cell Studies

i. Chopped Fiber-based Composite Electrode

A number of prismatic design lithium-ion pouch cells were built with LiNiCoO_2 positive and C-C composite negative electrodes made from chopped carbon fiber and 1M LiPF_6 electrolyte in a mixture of ethylene carbonate and dimethyl carbonate.

The cells were first charged at a constant current of 60 mA to 4.2 V and then at a constant voltage (4.2 V) for a total period of 6 hours or until the current dropped to a value of 3 mA. The cells were then discharged at a constant current of 60 mA to a cut-off voltage of 2.5 V. The charge-discharge process was continued for several (usually 2-5) times until a fairly constant values of charge-discharge capacities were obtained.

Fig. 14: Charge Discharge Behavior of a Prototype Prismatic Design Lithium-ion Pouch Cell.

The delivered capacities of the developed cells were determined at C/3 rate. Figure 14 shows the second to fifth cycles charge discharge profiles of a representative cell. During constant voltage charge, the residual current dropped to 2 mA sharply indicating very low impedance and no shorting of the cell. The charge capacities of the cell for the second to fifth cycles were 190.9 mAh, 190.9 mAh, 190.6 mAh, and 191.5 mAh and the corresponding discharge capacities were 188.5 mAh, 189.9 mAh, 192.6 mAh, and 190.5 mAh, respectively at 60 mA (C/3) current drain. The Coulombic efficiencies for the second to fifth cycles were 0.987, 0.995, 1.010, and 0.995, respectively.

ii. Continuous Fiber-based Composite Electrode

A number of prismatic design lithium-ion pouch cells were built with LiNiCoO₂ positive and C-C composite negative electrodes and 1M LiPF₆ electrolyte in a mixture of ethylene carbonate and dimethyl carbonate.

The cells were first charged at a constant current of 2 mA to 4.2 V and then at a constant voltage (4.2 V) for a total period of 6 hours or until the current dropped to a value of 0.2 mA. The cells were then discharged at a constant current of 2 mA to a cut-off voltage of 2.5 V. The charge-discharge profiles of two representative lithium-ion cells are shown in Fig. 15. The sharp fall of residual current indicates very low ESR of the cells.

Fig. 15: Charge-Discharge Behavior of Li-Ion Cells made with C-C Composite Anode and LiNiCoO_2 Cathode in 1M LiPF_6 Electrolyte

Several prototype lithium-ion cells were cycled in the voltage regime of 2.5 V to 4.1 V. The cycling behavior of a representative cell is shown in Fig. 16 for 14 cycles. For clarity, the y-axis is shifted for charge and discharge cycles.

Fig. 16: Cycling Behavior of a Li-Ion Cell made C-C Composite Anode and LiNiCoO_2 Cathode in 1M LiPF_6 . Discharge Rate: C/5.

After 14 cycles, the cell lost only 5% capacity.

The rate capabilities of the developed C-C composite-based lithium-ion cells have also been examined. Figure 17 shows the deliverable capacity of a representative cell at different discharge rates. The cell delivered almost 80% capacity at 2C rate.

Fig. 17: Relative Capacity of a Li-ion Cell made C-C Composite and LiNiCoO_2 in 1M LiPF_6 Electrolyte

C. Preliminary Cost Analysis

These costs relate only to producing the carbon-carbon composite anode. Fabrication of lithium-ion batteries is well established no matter whatever the anode is.

The cost to produce C-C composites in general is also well established. For example, MER commercially produces C-C and depending on a variety of factors of part complexity, thickness of cross section, size, fiber type and heat treatment temperature, the sales prices is in the \$2.50 to \$7.00/in³ range. Since a C-C composite for an anode,

depending on battery size, would be approximately 4 x 4 x 0.004 inches at 0.064 inches cube or at little less than 50 cents at the higher cost of \$7.00/in³. However, that cost is based on PAN based fiber and for the lithium-ion battery anodes, pitch based fiber and matrix is required.

The anodes produced in this year's investigation were Conoco discontinuous petroleum based pitch fibers and Amoco P30X continuous fibers. The Conoco fibers are at \$10/lb and projected to go to under \$5.00/lb. Coal tar pitch is used as the binder and its cost has been defined in another CPCPC program to produce fibers. Based on commercial coal tar pitch at \$400/ton and the purification cost, the pitch binder cost is \$0.4/lb, for a total cost of \$0.6/lb.

The processing to produce the very thin anodes is a bit more complex than standard C-C processing, but in general follows the same processing steps as described above. The estimated processing cost per pound is \$1.00.

The estimated cost for anode fabrication based on a 4 x 4 x 0.004 inch anode which weighs approximately 0.0035 lb is as follows:

<u>Item</u>	<u>Cost/lb in \$</u>
Pitch	0.20
Fiber	5.00
Processing	1.60
Total Cost	\$6.80

This cost is within the projected precision of the \$7.00/in³ and produces commercial composites that suggest the anode cost per cell size of 4 x 4 inches is under 50 cents. It is clear the costs are projected at being quite low and substantially below the use of MCMB's, the standard available only from Japan.

The cost of using coal based pitch fiber in the future is estimated as about the same as the petroleum base pitch fiber from Conoco, that will result in a totally coal based anode with superior performance as an anode in lithium-ion batteries.

V. CONCLUSIONS

The primary objective of this Phase I program was to:

- Develop low cost, carbon fiber as anode materials for lithium-ion batteries, and
- Demonstrate their performance in half-cells and prototype lithium-ion cells configuration.

Our program objectives are successfully met or exceeded. We have developed half-cells with chopped and continuous carbon fibers-based electrodes and evaluated their reversible capacity and irreversible capacity loss for lithium-ion intercalation and de-intercalation. Both types of carbon fiber offer excellent reversible capacity for lithium-ion intercalation/de-intercalation. The continuous fiber, however, provides better irreversible capacity loss

We also developed prototype lithium-ion pouch cells with the developed composite anode materials and evaluated their performance such as cycleability and rate capability.

The superior performances demonstrated with the developed anode materials led to the foundation of continuation of Phase II program for the development of low cost long life lithium-ion cells for transportation and other commercial and military applications.

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VII. LIST OF ACRONYMS AND ABBREVIATIONS:

C-C	Carbon-Carbon
CTP	Coal Tar Pitch
DEC	Diethyl Carbonate
DMC	Dimethyl Carbonate
DMF	Dimethyl Formamide
EC	Ethylene Carbonate
ESR	Equivalent Series Resistance
mAh	Milli Ampere Hour
MCMB	Mesocarbon Microbeads
NMP	N-Methyl Pyrrolidinone
PC	Propylene Carbonate
ppm	Parts per million
PVDF	Poly(vinylidene Fluoride)
SEI	Solid Electrolyte Interface
SEM	Scanning Electron Microscopy
V	Volt
Wh	Watt hour
XRD	X-ray Diffraction

CLEANABILITY OF ENRICHED FLY ASH CARBONS FOR THEIR UTILIZATION AS FEEDSTOCKS FOR CARBON MATERIALS

ANNUAL TECHNICAL PROGRESS REPORT **

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*** This project has a no-cost extension till May 31, 2002. An addendum to the present report summarizing the work conducted during the remaining period will be submitted after the project ending date.*

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Abstract

The implementation of increasingly stringent Clean Air Act regulations by the coal utility industry has generally resulted in high carbon fly ashes, that are rendered unsuitable as additives for the cement industry, and consequently, they are disposed. It is estimated that in 1998 around 6 million tons of unburned carbon were disposed due to the present lack of efficient routes for its utilization. Accordingly, Phase 1 and 2 of this research program conducted extensive studies on the characterization of unburned carbon and established routes for its utilization for the production of activated carbons and carbon artifacts. However, the unburned carbon must meet certain ash purity requirement for its utilization as precursor for carbon materials. Therefore, the overall objective of Phase 3 of this research program is to evaluate the cleanability of fly ash carbons from coal-fired power plants towards their utilization as feedstocks for carbon materials.

Following the previous industrial test in Phase 2 at Shawville power station (Reliant Energy), which successfully complied with DEP environmental requirements and it was shown that the carbon can be successfully concentrated in selected hoppers, the fly ash carbons have been further beneficiated by various conventional commercial techniques in the present report. The one-step activation process to utilize unburned carbon from coal combustion by-products to generate activated carbons has also been further investigated and optimized. The pretreatment protocol has been proposed and demonstrated to promote the microporous structure of resultant activated carbon.

The work reported in this report has also demonstrated the feasibility of application of froth flotation for the separation of power plant fly ash into carbon and ash streams, while the chemical digestion applied resulted in a fly ash sample with an ash content ~37wt%, and a fly ash carbon stream with ash content ~1wt%. By pretreating the fly ash carbons with 1.5wt% KOH, the surface area of the resultant activated carbon increased 35.5%, while retaining relatively high solid yields. For the second pretreatment method investigated here, the surface area of resultant activated carbon increased ~11-60%. The optimum pretreatment conditions found during the current reporting period are 400°C and 2 hours, where the resultant activated carbon has a surface area of 854m²/g and a pore volume of 0.56ml/g, which are comparable to those values reported for commercial activated carbons.

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1. Introduction

1.1 Rationale

The coal industry provides nowadays the main energy source for electricity generation in the US, where in 1999 the combustion of over 930 million tons of coal (around 90% of the total coal production) was used in coal-fired units to generate over 55% of the total electricity[1]. However, this also generated over 60 million tons of fly ash and around 6 million tons of unburned carbon [2]. Nowadays, the fate of these byproducts is mainly disposal due to the lack of routes for their utilization. Furthermore, the implementation of increasingly stringent Clean Air Act Regulations by the coal utility industry has resulted in an increase in the concentration of unburned carbon in coal combustion fly ash. This has restricted the principal use of ash in the cement industry, since the unburned carbon tends to adsorb air-entrainment agents that are added to the cement to prevent crack formation and propagation [2]. Consequently, the coal utility industry is facing potential annual losses of \$400 millions from the ash revenue and \$200 million from increasing disposal costs. The alternatives for the utility industry are to begin offsetting coal combustion with natural gas, or require additional coal cleaning to remove the ash prior to combustion, or simply start utilizing the unburned carbon. The first two alternatives would clearly jeopardize the future of the coal industry in this country. Accordingly, during Phase I and II of this research program, the authors conducted extensive studies on the characterization of unburned carbon, also referred to as fly ash carbon, from different coal-fired power plants and assessed its potential for the generation of premium carbon products[2,3]. Two potential routes were identified: (i) the use of unburned carbon as precursor for the production of activated carbons[4]; and (ii) the utilization of unburned carbon as a substitute for calcined petroleum coke in the production of carbon bodies[5]. The work conducted demonstrated the ability of unburned carbon from coal-fired power plants to generate activated carbons by one simple step activation process, in contrast to conventional precursors that require a two-step process (devolatilization and activation). Furthermore, after only 60 minutes activation time, the unburned carbon samples generated activated carbons with

microporous structure and surface areas close to 500 m²/g [3]. For the case of the carbon bodies, the unburned carbon samples present similar thermal history to that of calcined petroleum coke and the density of the carbon pellets prepared with unburned carbon was comparable to that using only petroleum coke [3]. Therefore, Phases I and II of this research program indicated that the added value generated from the unburned carbon utilization would bring substantial additional revenues to the coal-fired plants, where a ton of activated carbon sells for around \$400-\$5,000 and calcined petroleum coke usually costs around \$200/ton. However, the unburned carbon must meet the ash purity requirement for its utilization as precursor for carbon materials. For instance, to serve as a precursor in the production of activated materials, fly ash carbons must compete against wood precursors, that present very low ash contents (<5%). The ash requirement becomes even more stringent for the case of carbon artifacts, where typical commercial cokes contain less than 0.5% ash. Clearly, this cleanability issue stands in the way for the coal utilities to start commercializing the unburned carbon as a feedstock for carbon materials.

1.2 Potential markets for unburned carbon

The utilization of unburned carbon can bring enormous economical and environmental benefits to both the coal and utility industry. Although several technologies have been successfully developed to separate the unburned carbon from the fly ash, only a few power plants have installed a beneficiation process on their sites. This is due to the low value of the resultant separated materials, since a ton of fly ash generally sold for as little as \$10-20, and the unburned carbon is simply disposed or rerouted to the combustor. However, the economics of this process can be greatly enhanced if both separated materials can be used as precursors for high-value products. In fact, this is the case for the unburned carbon, which can be used as an excellent precursor for the generation of premium carbon products, like activated carbons and carbon artifacts. Therefore, the added value generated from the unburned carbon utilization would clearly offset the cost of the separation process. For instance, the average price for a ton of activated carbon ranges from \$500 up to \$4000, which implies a potential 25-200 fold

increase compared to the price of the ash (<\$20/ton). For the case of carbon artifacts, the calcined petroleum coke used for their manufacture usually costs ~\$220-250/ton.

1.2.1. Activated carbons

The present global consumption of activated carbons is over 350,000 tons and it is estimated to rise around 7% annually. The main reason for this expanding market is the ubiquitous use of activated carbons as adsorbent materials in a broad range of increasing household, medical, industrial, military and scientific applications. These range from gas-phase adsorption in household air conditioning equipment and industrial emissions control, to liquid-phase adsorption for water treatment and even gold recovery. Due to the expanding market for activated carbons, especially in applications related to environmental protection, new precursors are being sought. However, for these new precursors to compete effectively with conventional raw materials, such as wood, they must be inexpensive, have a low mineral matter content and be easily converted into activated carbons. The unburned carbon in the fly ash furnishes satisfactorily all these conditions, since it can (1) be easily obtained from the utility industries as a by-product; (2) beneficiated from the fly ash by commercially available techniques; and (3) it has already gone through a devolatilization process while in the combustor and, therefore, only requires to be activated [6,7].

1.2.2 Carbon artifacts: petroleum coke substitute

Currently, 6 million tons of calcined petroleum coke, worth around \$1,200 million, are sold annually in US for the manufacture of carbon artifacts. Even though calcined petroleum coke is the dominant precursor for carbon artifacts, the unburned carbon from coal combustion is a potential competitor, as described here. The unburned carbon has been treated at temperatures well above 1200-1300°C, and can be regarded as calcined coke. For instance, the H/C atomic ratios of the unburned carbon are below 0.02 and they are comparable with commercial precursors for carbon artifact production, where the typical H/C atomic ratios are around 0.01 [8]. The challenging issue in this task will be to meet the purity requirement, since typical commercial cokes contain less than 1% ash, preferably in the 100-300 ppm range. Sink/float methods using a high-density

liquid media can effectively enrich the carbon content, by reducing the ash to around 10-20% [9]. Other methods, such as acid digestions, can further reduce this value. Previous work conducted on the removal of mineral matter from coal, has shown that ash levels as low as 100-200 ppm are readily achieved by acid digestion [10]. Therefore, the unburned carbon from coal combustion could be a strong competitor to petroleum coke for the production of carbon artifacts.

1.3. Program objectives and research design

The overall objective of this research program is to evaluate the cleanability of fly ash carbons from coal-fired power plants towards their utilization as feedstocks for activated carbons. Due to financial constraints, it was not possible to investigate further in great depth the utilization of fly ash carbons for carbon artifact production.

1.3.1. Task 1: Suite procurement and characterization

A suite of coal-fired power plant fly ash were procured and characterized at The Pennsylvania State University. The samples were selected from the different hoppers located in Units #1 in a coal-fired power plant operated by Reliant Energy and located at Shawville, PA. During Phase 1 of this project, a detailed study of a series of fly ash hoppers of Unit #4 of the same plant revealed the presence of fly ash carbons with an ash content <50% [2], and during Phase 2 of this project, an industrial test was conducted on Unit #4 to implement the Carbon Plus separation technology to precipitate selectively the unburned carbon [3]. Additionally, samples from The Pennsylvania State University research boiler was also included in the suite. The samples were characterized using a battery of tests, previously developed by the authors and that includes thermogravimetric profiles, proximate analyses and elemental analysis, as well as petrographic analyses. Furthermore, the properties of these high-carbon fly ash samples towards their use as precursors for carbon products were also investigated. This evaluation included the study of their inherent properties, such as porous structure.

1.3.2 Task 2: Cleanability of fly ash carbons

As previously described, the challenging issue in the utilization of carbon from fly ash is to meet the ash purity requirement of precursors for carbon materials. Accordingly, this task was divided into the following subtasks: (2a) froth flotation, (2b) float/sink, and (2c) chemical digestions.

1.3.2.1. Task 2a. Froth flotation Bench scale froth flotation tests were conducted in The Penn State University on the above samples.

1.3.2.1. Task 2b. Float/sink Bench scale float/sink tests are presently being conducted at The Penn State University on the above samples and the results will be reported later on the addendum to the current annual report.

1.3.2.3 Task 2c. Chemical cleaning Preliminary studies conducted during Phase 1 and Phase 2 of this project have shown that ash levels can be reduced to $<0.5\%$ by standard acid digestion methods, and this protocol was further explored and optimized during Phase 3 at The Pennsylvania State University [10]. The ultimate goal of this Task is to facilitate a process, that can reduce the inorganic content of fly ash carbon to levels acceptable for the manufacture of carbon products, while still being an economically sustainable beneficiation process.

1.3.3. Task 3: Production of premium carbon products

The high purity carbon samples obtained from the above enrichment process were used to produce premium carbon products at the Pennsylvania State University following the protocols successfully developed in Phase 1 and 2 of this project. The activation of the fly ash carbon was carried out in a vertical tube furnace [2]. During Phase 1 and 2, the authors demonstrated that a one-step process, that includes simultaneous carbonization and activation, can be employed successfully for these materials. This is due to the thermal history of the fly ash carbon, that has already gone through a devolatilization step while in the combustor, and therefore, only requires to be activated. The activation process was further optimized. Furthermore, during Phase 3 the pretreatment process was

proposed and investigated to promote the porosity of the activated carbon from fly ash carbon. The properties of the activated carbons were systematically characterized at The Pennsylvania State University, including a detailed description of the porous structure (micropores or $<2\text{nm}$ in width, mesopores or $2\text{-}50\text{nm}$ in width, and macropores or $>50\text{nm}$ in width [11]) using conventional adsorption techniques, like N_2 adsorption isotherms at 77K .

In addition, the characterization of fly ash carbon also allowed to compare its properties with those of commercial carbon precursors for carbon artifacts, according to their H/C atomic ratio, petrographic evaluation and porosity analysis [5].

2. EXECUTIVE SUMMARY

The implementation of increasingly stringent Clean Air Act regulations by the coal utility industry has generally resulted in high carbon fly ashes, that are rendered unsuitable as additive for the cement industry, and consequently, they are disposed. It is estimated that in 1998 around 6 million tons of unburned carbon were disposed due to the present lack of efficient routes for its utilization. Accordingly, Phase 1 and 2 of this research program conducted extensive studies on the characterization of unburned carbon and established routes for its utilization for the production of activated carbons and carbon artifacts. However, the unburned carbon must meet certain ash purity requirement for its utilization as precursor for carbon materials. Accordingly, the overall objective of Phase 3 of this research program is to evaluate the cleanability of fly ash carbons from coal-fired power plants towards their utilization as feedstocks for carbon materials.

This research program firstly included the selection and characterization of a suite of coal-fired power plant fly ashes. The sample procurement was carried out by Reliant Energy and The Pennsylvania State University. The characterization of this suite included thermogravimetric profiles, particle size distribution, and proximate analyses. An industrial test conducted during Phase 2 at Shawville power station, that uses 1,500 tons of coal per day and is operated by Reliant Energy, showed that the carbon can be successfully concentrated in selected hoppers, while successfully complying with DEP environmental requirements. Following the previous industrial test, the fly ash carbons have been further beneficiated during Phase 3 by various conventional commercial techniques, and the results are reported here. In addition, following the previous work in Phases 1 and 2 that demonstrated the ability of unburned carbon from coal combustion by-products to generate activated carbons by steam activation, the one-step activation process was further investigated and a pretreatment protocol was proposed and optimized to generate activated carbons with properties similar to conventional commercial activated carbons.

The work reported in this report has demonstrated the feasibility of the application of froth flotation for the separation of power plant fly ash into carbon and ash stream. From a fly ash sample collected from Shawville station with a carbon content or LOI (loss-on-ignition) of 17%, it was possible to obtain a carbon stream with LOI of 70% and ash stream with LOI of 2.5% by applying froth flotation. As expected, the recovery yields are significantly reduced as the purity of these two streams was optimized. Chemical digestion has also been applied to a fly ash sample with an ash content of ~37wt%, and the resultant fly ash carbon stream has an ash content of only ~1wt%.

Following the previous work that demonstrated the ability of unburned carbon from coal combustion by-products to generate activated carbons by steam activation, the work reported here has also further investigated and optimized two kinds of pretreatment process to promote the microporous structure of the resultant activated carbon. After 2 hours steam activation, activated carbons with surface area up to 540m²/g have been generated from the unburned carbon in combustion waste. Pretreatment of the unburned

carbon with 1.5wt% KOH, resulted in a 35.5% increase of the surface area of the resultant activated carbon, while retaining relatively high solid yields. For the second pretreatment method, all the different pretreatment conditions studied in the report promote the porosity of resultant activated carbons, where the surface area increases ~11-60%. With increasing pretreatment time, there is an increase in the porosity (surface area and pore volume) of the resulting activated carbons. However, for extended pretreatment periods (4 hours for 300°C and 3 hours for 400°C), there is no further increase of the surface area, but rather a widening of the existent micropores, and an increase of the total pore volumes. Furthermore, with increasing pretreatment temperature, both the surface area and pore volume increase for the resultant activated carbon. The optimum pretreatment conditions found during the current reporting period are 400°C and 2 hr, where the resultant activated carbon has a surface area of 854m²/g and a pore volume of 0.56ml/g, which are comparable to those values reported for commercial activated carbons.

In addition, the work reported here also included the characterization of fly ash carbons. The unburned carbon has been treated at temperatures well above 1200-1300°C in the combustor, and therefore its elemental analysis shows a very high carbon content (97.7%), and conversely, low hydrogen content (0.02%), that are comparable with values also reported for conventional calcined petroleum coke. Furthermore, the sulfur content of the unburned carbon is significantly lower than that of petroleum coke, 0.94% vs. 3.42%. In contrast, the density of unburned carbon is somewhat lower than for petroleum coke, probably due to its surface area, that is created by the rapid heat treatment experienced in the combustor by the unburned carbon. Furthermore, both the unburned carbon and the petroleum coke present isotropic and anisotropic textures, where a given ratio of anisotropic over isotropic coke is required for different applications.

Finally, the long-term benefits of this research program can be summarized as follows: (i) the coal industry will continue being the main provider to the utility industry, where currently around 1 billion tons of coal are sold annually; (ii) the carbon industries, such as those producing activated carbons, will have cost-effective and novel precursors; and (iii) this program prevents pollution at its source by simultaneously reducing NO_x emissions and byproduct waste streams, including unburned carbon and ash, and will therefore have a vast benign environmental impact.

3. EXPERIMENTAL

3.1 Procurement and characterization of fly ash carbon samples

Reliant Energy conducted the procurement of the fly ash samples in the Shawville station Unit #1 and #2 (Bradford Township, PA). This unit has been retrofitted with a low-NO_x burner, and uses primarily Lower, Middle and Upper Kittanning and Lower and Upper Freeport seam coal. The sampling procedure was conducted all along the electrostatic precipitator of each train. The procedure used was to put the systems on hand and “pull” on each hopper in turn until plant personnel was sure that the hoppers were empty. Once all the hoppers on that boiler were certified as empty, they then went back, shut down the ash transport system and then got a hand sample (5 gallons) from each hopper in turn, thus assuring that the ash in the sample was “fresh ash” [3].

Additionally, another sample was also procured from PSU research boiler, which has been also retrofitted with a low-NO_x burner and uses a high volatile bituminous coal from Middle Kittanning seam.

The loss-on-ignition (LOI) contents of the fly ashes assembled were determined according to the ASTM 311 procedure. These analyses were conducted in duplicates. For fly ashes commonly derived from Eastern U.S. coals, the LOI value essentially equates to carbon content. The elemental analysis was conducted using a Leco CHN-600 analyzer. The petrographic analyses were performed on epoxy-bound polished pellets under polarized reflected white-light at 625X magnification and oil-immersion using a Zeiss Universal Research microscope. The thermogravimetric analysis was conducted on a Perkin Elmer TGA7. The porosity of the samples was characterized by conducting N₂ adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT [5].

3.2. Beneficiation of fly ash carbons

In order to determine the feasibility of pursuing the use of froth flotation for separating fly ash into two utilizable products: low ash carbon and low carbon ash, a fly ash sample with a carbon content of 16.3% from the coal-fired power plant at Shawville, PA, which is operated by the CPCPC member Reliant Energy, was used for the froth flotation study. A conventional laboratory froth flotation cell and conventional coal froth flotation reagents were applied to the test. An initial flotation test was conducted to determine the approximate reagent level to obtain carbon recovery and a stable froth. Based on its results, the second test with circuit variation was conducted, including a scavenger stage to remove additional carbon from the ash product and various cleaning stages to reduce the ash content in the carbon product [12]. Other froth flotation separation test were conducted on the fly ash sample with a carbon content of 58.3% from the Penn State University research boiler.

An acid digestion step was also conducted by following conventional HCl/HF treatments [13] under both room temperature and also at 65°C to further reduce the ash concentrations [14]. The enriched fly ash carbon was then dried and subsequently characterized by conducting LOI measurements and 77K N₂ adsorption isotherms.

3.3. Production of activated carbon

The unburned carbon samples (A) was firstly pretreated at 400°C for 2 or 3 hours, and the unburned carbon sample (B) was impregnated with potassium hydroxide (KOH) and dried at 110°C for 6 hours (B-KOH). Then the activation of the samples was carried out in an activation furnace that consists of a stainless steel tube reactor inside a vertical tube furnace. The sample with or without pretreatment was held isothermally at 850°C for 1-3 hours in flowing steam [15]. The porosity of the samples was characterized by conducting N₂ adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The total pore volume, V_t was calculated from the amount of vapor adsorbed at the relative pressure of 0.95, and the total surface area S_t was calculated by standard BET equation.

4. RESULTS AND DISCUSSION

4.1. Procurement and characterization

A total of 14 fly ash samples containing unburned carbon were collected from Shawville station unit #1 (Bradford Township, PA), that is operated by Reliant Energy. This unit has been retrofitted with a low-NO_x burner, and uses primarily Lower, Middle and Upper Kittanning and Lower and Upper Freeport seam coals. Samples were collected from the Research-Cottrell Precipitator hoppers #1-8 and Buell precipitator hoppers #9-14. Following the gas flow direction, the hoppers #1-4 are located in the first row and the hot-side, while hoppers #5-8 are in the second row and hoppers #9-14 are in the third row. During Phase 1 and 2 of this project, samples from Unit #4 were collected and characterized. Figure 1 shows the LOI of all fly ash samples and the hopper configuration and gas flow direction are also indicated.

Figure 1. Variation in LOI of the fly ashes collected from Shawville Unit #1, where the gas flow direction is indicated.

The loss-on-ignition (LOI) of all the 14 fly ash samples was determined according to the ASTM C 311 procedure, as described during Phase 1, and all the analyses were conducted in duplicates. As shown in Phase 1, the fly ash samples collected from the hot-side hoppers (#1-4) present the lowest LOI contents of only 8.8-9.7% (Figure 1). The LOI values become higher for hoppers in cool-side, where the LOI for the second row of hoppers #5-8 are 10.6-13.6%, while the third row hoppers #9-14 have the highest LOI of 15.7-22.9%.

4.2. Cleanability of fly ash carbons

4.2.1. Froth flotation

An initial flotation test was conducted to determine the approximate reagent level to obtain carbon recovery and a stable froth. Based on its results, the second test with circuit variation was conducted, including a scavenger stage to remove additional carbon from the ash product and various cleaning stages to reduce the ash content in the carbon product. The separation results including the LOI and yield for each fraction is shown in Figures 2 and 3. The result from the circuit variation test indicates that it is feasible to produce a low carbon ash product (< 3% LOI) using froth flotation. According to this test work, a second stage of flotation to remove additional carbon from the ash is required. As expected, the recovery yields are significantly reduced as the purity of these two streams was optimized. Additional test work will evaluate the use of higher concentrations of reagents to achieve this in one stage of flotation. The yield of low carbon ash was 62% in this test work with this sample.

Figure 2. Test conducted to set approximated reagent requirements

Figure 3. Froth flotation circuit variation test used to produce low ash carbon and low carbon ash.

The results from the circuit variation test also indicate that it will be difficult to produce a low ash carbon product from this material. The highest LOI of the carbon products was 69%--or 31% ash. The yield of this carbon product was also quite low at about 14.4%. Some ash is obviously present in this product, though the flotation products appeared to be quite black. The ash is either locked with the carbon or is in the form of cenospheres that were noted to be present in the floated material. It is currently being conducted a petrographical evaluation to determine the nature of the ash present prior to conducting additional flotation test work.

In addition, froth flotation tests were also conducted on the fly ash sample (LOI 58%) collected from the Penn State University research boiler, using a 2.5-liter WEMCO laboratory froth flotation cell. These tests were run with staged reagent additions to determine the floatability of the sample.

One hundred grams of the fly ash sample were wetted and placed into the laboratory cell where water was added to fill the cell and the slurry was mixed through the action of the flotation cell impeller. The slurry was mixed for approximately 2 minutes to ensure that the sample was sufficiently dispersed. Collector (fuel oil) was then added at a dosage of 62 microliters, which gives a dosage of about 1 lb of reagent per ton of fly ash. The collector was allowed to mix for two minutes prior to frother addition. For the first test, a commercial frother from American Cyanamid (now Cytec) was used. The dosage was 15 microliters or about 0.25 lb/ton. This was allowed to mix for one minute. The air was turned on and a lack of froth formation was observed. The air was turned off and additional reagents were added to attempt to float the carbon in the fly ash sample. After each dosage of collector or frother, the air was turned on and a lack of froth formation was observed. A total of 6 lb/ ton of collector and 1.5 lb/ton of frother was added in the first test, and further froth did not form.

A second test was performed with a different frother, that is a commercial frother from Nalco. This was tested to make sure that the frother quality was not an issue for the fly ash carbon separation. A total of 10 lb/ton of collector and 1 lb/ton of frother was added in stages to attempt to float the carbon from the fly ash. A froth did not form even with this high dosage of collector. Further analysis are presently being conducted, including based high carbon content, small particle size and high oxygen content.

4.2.2. Chemical cleaning

Table 1 lists the LOIs and porosities of the fly ash carbons before and after chemical cleaning. It can be seen that when the chemical cleaning was conducted at room temperature, the ash content can be reduced from 36.3wt% (precursor fly ash A) to 18.7wt% (A-W1). If the sample is subsequently treated again by chemical leaching, the

ash content can be further reduced to 1.1wt% (A-W2). This two-step process suggests that chemical demineralization is an effective method to produce a high purity carbon stream from fly ash. The same raw fly ash carbon, A, was also used to conduct the chemical cleaning experiment at 65°C to get the product A-W3. Upon increasing the temperature of the chemical cleaning process, a one-step treatment can directly reduce the ash content to 4.1wt% for A-W3. Furthermore, the produced cleaned sample A-W3, has similar surface area and pore size to those previously reported for the raw fly ash carbon, where the surface area and average pore diameter are 115m²/g and 2.75nm, compared to 112m²/g and 2.72nm for the original sample A. This may be related to the reaction residence time, which has been reduced to only 4 hr for the cleaning at 65°C, compared to the 2 days that were required for the cleaning process at room temperature. Finally, the long reaction residence time (2 days) resulted in a decrease of the surface area to 98m²/g, and an increase of the pore size also to 2.94nm, probably due to the prolonged stirring that may have damaged the original pore structure due to attrition.

Table 1. Carbon content (LOI) and porosity of the parent fly ash carbon and their chemically cleaned counterparts.

Sample	Treat temp. °C	LOI wt%	SBET m ² /g	Vt ml/g	Average Diameter, nm	Pore
A	-	63.7	112	0.0801	2.72	
A-W1	Room	81.3	N/A	N/A	N/A	
A-W2	Room	98.9	98	0.0718	2.94	
A-W3	65	95.9	115	0.0789	2.75	

The chemical cleaning process at 65°C shows that the ash content can be reduced to ~5wt%, and therefore, the resultant samples meet the ash content requirements of most applications, especially for activated carbons. A two-step chemical cleaning at room temperature can reduce the ash content to <1wt%, therefore meeting the more stringent ash requirements for certain carbon material applications, such as for the use of fly ash carbon as a replacement for calcined petroleum coke in carbon artifacts and anodes.

4.3. Production of premium carbon products

The high-purity carbon samples obtained from the above enrichment process were used to produce premium carbon products following the routes successfully developed in Phase 1 and 2.

4.3.1. Production of activated carbons

The fly ash carbon from coal-fired power plants can be used as precursor for the production of activated carbons, as demonstrated previously by the authors. As reported earlier, the one-step steam activation process can effectively convert fly ash carbons into activated carbons with surface areas as high as $540\text{m}^2/\text{g}$ [3]. However, as the activation time increases, the developing rate of micropore volume decreases, where micropore volumes are highly desired in commercial activated carbons. Therefore, a pretreatment process was designed and applied to fly ash carbons to improve their reactivity, and to modify the micropore structure of the resultant activated carbon [13]. Furthermore, a systematic parametric study on the pretreatment conditions has also been conducted.

4.3.1.1. The effect of activation time on steam activated carbons

Figure 4 shows the N_2 -77K isotherms for the steam activated carbons produced from the unburned carbon B with different activation time. Figure 4 shows that with increasing activation time, the isotherms change from Type 1 for 60 minutes activation, B-60, into Type 4 for 180 minutes activation, B-180. For the isotherm of B-60, the adsorbed volume increases rapidly at low relative pressure, while at higher pressure, the adsorbed volume increases very slowly, which implies that most of the pores in the samples are micropores. In contrast, for the isotherm of B-180, the adsorbed volume keeps increasing progressively with the relative pressure, and there is a distinct hysteresis loop in the isotherm, which indicates that the sample is mainly mesoporous.

Figure 4. N_2 -77K isotherms of steam activated carbons produced from unburned carbon B and the parent sample.

The solid yields and surface areas are listed in Table 2 for the parent and steam activated samples. After 1 hour activation, the resultant activated carbon surface area was $332\text{m}^2/\text{g}$. As expected, when the activation time increased to 2 hours, the solid yield decreased, while the total surface area and pore volume increase to $540\text{m}^2/\text{g}$ and 0.500ml/g , respectively. When the activation time was increased to 3 hours, the surface area was similar to that for 2 hours, but the pore volume increased to 0.556ml/g , suggesting a widening of the porosity.

Table 2. Solid yields and surface areas for the parent and stem activated carbons produced from unburned carbon in fly ash.

Samples	Activation time hr	Solid yield wt%	SBET m^2/g	Vt ml/g
B	-	-	40	0.03
B-60	1	73.2	332	0.237
B-120	2	34.8	540	0.500
B-180	3	30.6	534	0.556

4.3.1.2. The effect of KOH pretreatment on unburned carbon activation

Chemical pretreatment with KOH was performed to increase the reactivity of the unburned carbon. A known amount of KOH was loaded on the unburned carbon followed by steam activation. The isotherms of resultant activated carbons are shown in Figure 5. With 1.5wt% KOH, the resultant activated carbon, B-KOH-1.5, has an isotherm with similar shape to that of B-60, although it has larger adsorbed volume, which suggests a similar high microporosity as B-60.

Figure 5. N₂-77K isotherms of activated carbons made from the unburned carbon B loaded with KOH.

Table 3 lists the solid yields and surface areas for the parent and activated carbons produced from unburned carbon in fly ash by KOH pretreatment. With only 1.5wt% KOH, compared to that without pretreatment B-60, the surface area of AC can increase 35.5% (450m²/g vs. 332m²/g). However, with further increase in the KOH load up to 6wt%, the surface area decreases. This may be due to the limited amount of active sites on the surface of unburned carbon, which can adsorb KOH. Hence, with higher burn-off, the gasification reaction still happens on the same active sites, resulting in a widening of the exist pores.

Table 3. Solid yields and surface area for the parent and activated carbons produced from unburned carbon in fly ash by KOH pretreatment.

Sample	KOH load wt%	Activation time	Solid yield wt%	S _{BET} m ² /g	V _t ml/g
B-KOH-1.5	1.5	1	61.7	450	0.316
B-KOH-6.0	6.0	1	42.3	427	0.359

4.3.1.3. The effect of gas pretreatment on unburned carbon activation

During this reporting period, the samples were pretreated for 2 to 4 hours at 300°C to 400°C prior to 1 hour steam activation at 850°C. The N₂ isotherms of the resultant activated carbon are shown in Figure 6. For the purpose of comparison, the sample with no pretreatment is also included in Figure 6. The activated carbons prepared after pretreatment at 300°C have similar isotherm shapes to that of the sample without pretreatment, but they have much larger adsorbed volume, suggesting a similar microporosity structure, but a higher surface area and total pore volume. However, when the pretreatment time is extended to more than 3 hours, the more open knee of the isotherm at lower relative pressures indicates a broader pore size distribution with larger micropores and some mesopores.

Figure 6. N₂-77K isotherms of activated carbons made from the fly ash carbon (FA1) pretreated at 300°C and the parent sample activated without pretreatment.

The surface areas and pore volumes for the activated carbons produced with or without pretreatment at 300°C and 400°C are listed in Table 4. Although all the activated carbons were made using the same activation conditions (activation temperature and time are 850°C and 1 hour, respectively), the pretreatment can increase the surface area of the resultant activated carbon up to ~60% (from 534m²/g without pretreatment to 854m²/g with 2 hour pretreatment at 400°C) compared to that of the sample without pretreatment. In addition, the pretreated samples can also keep similar average pore size (2.47nm vs. 2.44nm).

Table 4. Surface areas and pore volumes of activated carbons from fly ash carbon

Pretreatment		Activation		St	Vt	Average pore diameter
Temp. °C	Time hr	Temp. °C	Time hr	m ² /g	ml/g	nm
No		850	1	534	0.329	2.44
300	2	850	1	591	0.359	2.41
	3	850	1	724	0.447	2.45
	4	850	1	733	0.457	2.56
400	2	850	1	854	0.535	2.47
	3	850	1	841	0.556	2.60

For extended pretreatment periods (4 hours for 300°C and 3 hours for 400°C), there is no further increase of the surface area, but rather a widening of the existent micropores and an increase of the total pore volumes (Table 4). For the samples pretreated at 300°C, the surface area only increases from 724m²/g for 3 hours pretreatment to 733m²/g for 4 hour pretreatment, while the average pore diameter increases to 2.56nm from 2.45nm, and the total pore volumes are enlarged to 0.457ml/g from 0.447ml/g. Similarly, for the samples pretreated at 400°C, the extended pretreatment time also decreases the surface area, from 854m²/g for 2 hr pretreatment to 841m²/g for 3 hr pretreatment. Therefore, it can be concluded that for the lower pretreatment temperature, the optimum pretreatment time is longer than that of the higher temperature pretreatment (3 hour for 300°C pretreatment vs. 2 hours for 400°C pretreatment).

Figure 7 compares the surface areas and pore volumes for the activated fly ash carbon samples pretreated for 3 hours at different temperature (300, 350, and 400°C) prior to activation. It can be seen that with increasing pretreatment temperature, both the surface area and pore volume increase for the resultant activated carbon.

Figure 7. Pore volume and surface area of activated carbons made from FA1 with 3 hours pretreatment at different temperatures.

4.3.2. Characterization of fly ash carbon towards its potential use as precursor for carbon artifacts

Table 5 lists the elemental analysis of both unburned carbon and the petroleum coke investigated in this work.

Table 5. Elemental analysis for the unburned carbon and petroleum coke.

Sample	%C(daf)	%H(daf)	%N(daf)	%S(daf)	%O(daf)	H/C (*10 ⁻³)
Unburned carbon	97.7	0.02	1.40	0.94	<0.01	2.46
Petroleum coke	96.2	0.02	0.57	3.42	<0.01	2.49

The unburned carbon has been treated at temperatures well above 1200-1300°C in the combustor, and therefore its elemental analysis shows that its carbon content is as high as 97.7% and hydrogen content is as low as 0.02%, giving an H/C atomic ration well below 0.01. These values are comparable with conventional calcined petroleum coke, that are also shown in Table 5. Furthermore, the sulfur content of the unburned carbon is

significantly lower than that of petroleum coke, 0.94% vs. 3.42%. This is indeed a very attractive characteristic, since the undesired increasing sulfur concentrations in petroleum coke are known to mar the carbon products used in the aluminum and steel industries.

Table 6 lists the surface area and total pore volume determined from the N₂ isotherm at 77K, and the density for unburned carbon compared to that of the petroleum coke. The density of the unburned carbon is somewhat lower than the petroleum coke (1.59 vs. 1.89g/ml), probably due to its higher surface compared to that of the petroleum coke (14.15m²/g vs 2.01-4.85m²/g). From the SEM image (Figure 8), it can be seen that the unburned carbon is generally solid carbon with some macropores, probable formed during the rapid devolatilization process experienced in the combustor.

Table 6. N₂-77K BET surface areas (S_{BET}) and total pore volume (V_t) and densities of the unburned carbon and the petroleum coke.

Sample	S_{BET} , m ² /g	V_t , ml/g	Density, g/ml
Unburned carbon	14.15	0.013	1.59
Petroleum coke	4.85	0.008	1.89

During the heat treatment experienced in the combustor by the unburned carbon, some coal particles have gone through a softening stage and have formed ordered carbon forms (anisotropic coke), while others have formed random configurations (isotropic coke), as illustrated in the optical micrographs shown in Figures 9-11 (horizontal field width is 220μm). The ratio of anisotropic over isotropic coke for this particular sample is about 7/1. The rapid heat treatment experienced in the combustor creates some porosity in the unburned carbon, and therefore, its surface area is larger than that of petroleum coke (Table 6). Figure 9 shows a typical large anisotropic mosaic texture derived from the carbonization of the vitrinite fraction. Figure 10 shows a typical isotropic material derived from coal inertinite trapped in an anisotropic matrix derived from the carbonization of vitrinite. Finally, Figure 11 shows a large particle of inertinite (macrinite) trapped in the anisotropic matrix of the unburned carbon. The presence of

isotropic and anisotropic textures is also characteristic of petroleum coke, where a given ratio of anisotropic over isotropic coke is required for different applications [16].

Figure 8. SEM image of the unburned carbon.

Figure 9. A typical anisotropic mosaic texture in unburned carbon.

Figure 10. A typical isotropic material trapped in an anisotropic matrix in unburned carbon.

Figure 11. A large particle of inertinite (macrinite) trapped in the anisotropic matrix of unburned carbon

5. CONCLUSIONS

The present work has evaluated the cleanability of fly ash carbons from coal-fired power plants towards their utilization as feedstocks for activated carbons.

The work reported in this report has demonstrated the feasibility of the application of froth flotation for the separation of power plant fly ash into carbon and ash stream. From a fly ash sample collected from Shawville station with a carbon content or LOI (loss-on-ignition) of 17%, it was possible to obtain a carbon stream with LOI of 70% and ash stream with LOI of 2.5% by applying froth flotation. As expected, the recovery yields are significantly reduced as the purity of these two streams was optimized. Chemical digestion has also been applied to a fly ash sample with an ash content of ~37wt%, and the resultant fly ash carbon stream has an ash content of only ~1wt%. Furthermore, the chemical cleaning process was also conducted at 65°C, where the ash content can be reduced to ~5wt% after only 4 hours. The resultant cleaned fly ash carbons meet the ash content requirements of most carbon materials applications.

Following the previous work that demonstrated the ability of unburned carbon from coal combustion by-products to generate activated carbons by steam activation, the work reported here has also further investigated and optimized two kinds of pretreatment process to promote the microporous structure of the resultant activated carbon. After 2 hours steam activation, activated carbons with surface area up to 540m²/g have been generated from the unburned carbon in combustion waste. Pretreatment of the unburned carbon with 1.5wt% KOH, resulted in a 35.5% increase of the surface area of the resultant activated carbon, while retaining relatively high solid yields. For the second pretreatment method, all the different pretreatment conditions studied in the report promote the porosity of resultant activated carbons, where the surface area increases ~11-60%. With increasing pretreatment time, there is an increase in the porosity (surface area and pore volume) of the resulting activated carbons. However, for extended pretreatment periods (4 hours for 300°C and 3 hours for 400°C), there is no further increase of the surface area, but rather a widening of the existent micropores, and an increase of the total

pore volumes. Furthermore, with increasing pretreatment temperature, both the surface area and pore volume increase for the resultant activated carbon. The optimum pretreatment conditions found during the current reporting period are 400°C and 2 hr, where the resultant activated carbon has a surface area of 854m²/g and a pore volume of 0.56ml/g, which are comparable to those values reported for commercial activated carbons.

In addition, the work reported here also included the characterization of fly ash carbons. The unburned carbon has been treated at temperatures well above 1200-1300°C in the combustor, and therefore its elemental analysis shows a very high carbon content (97.7%), and conversely, low hydrogen content (0.02%), that are comparable with values also reported for conventional calcined petroleum coke. Furthermore, the sulfur content of the unburned carbon is significantly lower than that of petroleum coke, 0.94% vs. 3.42%. In contrast, the density of unburned carbon is somewhat lower than for petroleum coke, probably due to its surface area, that is created by the rapid heat treatment experienced in the combustor by the unburned carbon. Furthermore, both the unburned carbon and the petroleum coke present isotropic and anisotropic textures, where a given ratio of anisotropic over isotropic coke is required for different applications.

This project has a no-cost extension till May 31, 2002. An addendum to the present report summarizing the work conducted during the remaining period will be submitted after the project ending date.

6. PROJECT RELEVANCE TO THE COAL INDUSTRY

The rise in unburned carbon concentration in coal combustion fly ashes may lead to the demand for the coal utility industry to begin offsetting coal with natural gas, or require additional coal cleaning to remove the ash prior to combustion. Both alternatives would clearly compromise the coal industry. Hence, the implication of this research program is to turn unburned carbon containing fly ash from a liability into an asset for the coal industry.

The U.S. energy industry requires a green chemistry and engineering solution that can guarantee a long-term source of energy by simultaneously reducing emissions and byproduct waste streams. This can be achieved by installing low-NO_x burners, which have been proven to efficiently reduce NO_x emissions, coupled with strategies to manage the associated increase of byproduct streams. Accordingly, the recovery and recycling of energy byproducts can bring enormous economical and environmental benefits to the U.S. energy industry and to society at large. However, the implementation of Clean Air Act Regulations is potentially detrimental to the marketability of ash, in the sense that more unburned carbon is present in the ash, with the subsequent rise in waste streams to follow. Several technologies have been successfully developed to recover and separate the unburned carbon from the ash. These technologies can be divided into wet (froth flotation) and dry (triboelectrostatic) processes, and they can give inorganic ash concentrates with purities that meet the requirement for the cement industry, as well as carbon concentrates with purities of 85% and above. However, only a few power plants have installed a beneficiation process on their sites. One of the main reasons for this is the low value of the resultant separation products, since one ton of “clean” fly ash is generally sold for as little as \$10, and the unburned carbon concentrated stream is simply rerouted to the combustor. However, the economics of this process can be significantly enhanced if both separated materials can be used as precursors for high-value products. Accordingly, this research program has developed novel routes for the commercial use of unburned carbon present in fly ash as a precursor for premium carbon materials, like activated carbons.

To conclude, the benefits of this research program can be summarized as follows:

- (i) the coal industry will continue being the main provider to the utility industry, where currently over 900 million tons of coal are sold annually;
- (ii) the carbon industries, such as those producing activated carbons, will have cost-effective and novel precursors; and
- (iii) this program prevents pollution at its source by simultaneously reducing NO_x emissions and byproduct waste streams, including unburned carbon and ash, and will therefore have a vast benign environmental impact.

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Coal-based Products from the Co-coking Process

For use in Anodes for Aluminum Electrolysis

Final Report

Reporting Period 1/1/2001 – 3/31/2002

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Abstract

Co-coking involves the simultaneous co-carbonization of coal and petroleum residua in order to produce coal-based liquids and coke. Co-coking is based around the delayed coking process used in many refinery operations. Previous work has been directed with the intention of producing a coal-based liquid, which may be subsequently refined into an advanced thermally stable jet fuel. During the course of the research interest was developed into the coke product, and its potential use in anodes for aluminum electrolysis and other specialty carbon products. Exploratory, small-scale experiments were conducted at Penn State to evaluate feedstocks, feed composition and reaction conditions. The interactions between the coal and the petroleum resid during co-coking develop interesting phenomena in the composition and morphology of the coke. To date the quantity of products produced in the co-coking studies has only allowed us to perform detailed characterization. In the present study Penn State has scaled-up the co-coking process by constructing a small pilot-scale delayed coker unit. This unit produces sufficient quantities of products to allow further processing and utilization. This will include the hydrotreating of the liquid products in a fixed-bed reactor. The coke has been characterized to determine what affect the co-coking conditions have on morphology and composition. The coke that was produced was then calcined and made into test anodes. The test anodes were compared with conventional anodes made with petroleum coke.

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1.0 Executive Summary

The objective of this study was to produce a coke product from the co-coking of coal and petroleum resid that could be used in the production of anodes for aluminum electrolysis. To this end, blends of cleaned coal and decant oil were fed into a pilot-scale delayed coker under various operating conditions. The resulting cokes were fully characterized using a variety of analytical techniques. Finally, the cokes were made into test anodes and compared with conventional petroleum coke-based anodes.

After a series of set backs with the construction and operational understanding of the pilot-scale delayed coker, a series of tests and a parametric study were performed. This study aimed to establish links between the changes in processing conditions and the quality of the resulting cokes. Traditional and non-traditional image analysis techniques, petrographic analysis and x-ray tomography, respectively, were used to measure some of the compositional and physical attributes of the green cokes. Furthermore, information on product yields, proximate and ultimate analysis were collected.

The resulting cokes were produced in bulk and calcined at 1400 °C. The calcined cokes were sent to Alcoa Inc. to be made into test anodes. The test anodes were sent to Koppers Industries Inc. to be baked. The baked anodes underwent a series of tests to determine their quality relative to a standard test anode, and industry target values.

Results show that in some aspects including density, strength, resistivity, reactivity, the coal-based cokes produced in this study met or exceeded the standards set by the industry. However, due to the presence of residual mineral matter from coal in the coke, the ash values for the coal-based anodes are high.

2.0 Introduction

Petroleum coke is the major constituent of anodes used in the aluminum electrolysis process. It is derived from the thermal cracking of petroleum residua in coking operations. The aluminum industry consumes approximately 1.6 million metric tonnes of petroleum coke annually. The inclusion of heavier oils in the refinery processing stream leads to a decreasing quality (higher sulfur and heavy metals content) of petroleum products, which subsequently leads to a reduction in the quality of the coke products. This is because the sulfur and ash from heavy metals tend to concentrate in the petroleum residua, and subsequently are higher in the coke products after thermal processing. Sulfur in the coke products leads to the formation of SO₂ emissions from the electrolysis cell, which are strongly enforced by the EPA. Heavy metals, such as nickel (Ni) and vanadium (V) are known to catalyze the oxidation of the carbon electrodes in aluminum electrolysis, increasing excess carbon consumption and reducing the useful life of the anode. It is therefore very important to keep the sulfur, Ni, and V concentrations low to improve the quality of the anodes. We believe that this can be achieved by using the products from the co-coking process.

The process of co-coking¹⁻³ involves the simultaneous co-carbonization of coal and petroleum resid in a delayed coking environment. A slurry of high volatile bituminous coal and decant oil is fed into a delayed coker drum at between 460-500 °C, at pressures between 10 and 150 psig. Under these conditions the coal and decant oil become very fluid and coke to form a homogenous solid product.

In order to produce a product that is suitable for use in anodes for aluminum electrolysis certain criteria must be met regarding the ash and sulfur content of the

anodes. By utilizing coal and decant oil with low sulfur contents, it will be possible to keep the sulfur levels in the coke products to a minimum. In preliminary studies we have shown that compared with the processing of individual feeds, using a blend of coal and resid enhances sulfur removal. Additionally, the use of a cleaned coal product will minimize ash derived from the coal. Work already conducted for Penn State by Preptech Inc. has shown that using specific fractions from coal beneficiation processes high volatile bituminous coal can be cleaned successfully to approximately 2% ash. One advantage to the co-coking process is that it produces a solid coke product that has less petroleum-derived coke in it. This in turn leads to a lower concentration of Ni and V. The lowering of the Ni and V content of the carbon products reduces catalytic oxidation and hence enhances their working life.

Strength is another factor in the quality of the anodes. The strength characteristics of anodes may be tailored by using a coke product with the appropriate degree of porosity, blending it with the correct amount of coal-tar binder pitch, and processing them under the correct conditions. Additionally, because of the potential interactions between the coal-derived coke and the coal tar pitch binder we believe that we can enhance the strength of the carbon product using the coke derived from the co-coking of coal and petroleum. The coke and the pitch still maintain the physical and chemical characteristics of their parent coals. These characteristics may enhance the wetting properties of the binder pitch through physical attraction. They may also under further processing conditions (e.g. baking) form strong chemical bonds via radical recombination reactions of the aromatic centers within the coal-derived structural units of the coke and

binder. Improved wetting and strong chemical bonds may in turn lead to a stronger, more uniform and denser product, which in turn should have a longer lifetime.

Figure 1 shows examples of the type of coke produced under the co-coking conditions (465 °C for 2 hours under an ambient nitrogen atmosphere in batch micro-autoclaves). The first image is of the coal-derived coke processed alone. The second is of the coal-derived coke processed with decant oil. The third is the decant oil processed under co-coking conditions. Results show that during co-coking with coal and decant oil, that the coal has an optical texture with greater similarities to decant oil-derived coke than coal-derived coke. In actuality the co-coked product shows signs of homogeneity, which is very beneficial, in terms of strength, if it is to be used as a product in anode manufacturing.

Figure 1. Photomicrographs of coke samples

3.0 Experimental

Table 1 gives a summary of the proximate and ultimate analysis, fluidity, particle size distribution and ash mineral composition of the deep cleaned Powellton coal. Preptech Inc. prepared the coal for this project from froth flotation samples taken from a coal cleaning plant. This operation cleans the coal to remove the majority of the mineral matter, and then Preptech further cleaned the sample using a more thorough separation technique. The resulting coal has an ash content of 1.9%. The major mineral composition in the ash derived from the coal is also listed in Table 1.

Over 70 % of the mineral matter in the coal is derived from clays (e.g. silicates and aluminates). The iron is predominantly iron sulfides (pyrite and pyrrhotite). The coal has a very high maximum fluidity. This is one reason why Powellton coal is desired as a metallurgical coking coal. Additionally, we believe that having a high fluidity in the coker operating temperature range will increase contact time between the coal and decant oil, and so ultimately improve the quality of the coke produced.

Tables 2 and 3 show the ultimate analyses data for the as received decant oil and the coal/oils slurry used in the initial experiments. The values for carbon, hydrogen, nitrogen and sulfur are very similar for both samples. The decant oil has no measurable ash content, but the slurry has a small contribution from the coal that was added at a 10 wt% fraction. The addition of the coal also increases the Conradson carbon number slightly from 7.13 in the as received oil to 8.49 in the slurry.

Table 1. Proximate and ultimate analysis, fluidity, particle size distribution and ash mineral composition of the deep cleaned Powellton coal.

Proximate Analysis ^a	
Fixed Carbon %	68.7
Volatile Matter %	29.4
Ash %	1.9
Ultimate Analysis ^a	
Carbon %	86.3
Hydrogen %	5.2
Nitrogen %	1.5
Sulfur %	0.9
Oxygen % (by difference)	6.1
Fluidity Data ^b	
Fluid Temperature Range (°C)	105
Maximum Fluidity (ddpm)	23,619
Softening Temperature (°C)	385
Particle Size Distribution ^c	
D[v,0.9]	152 µm
D[v,0.5]	61 µm
D[v,0.1]	10 µm
Ash Mineral Composition ^d	
Silicon Dioxide	45.16%
Aluminum Oxide	25.43%
Ferric Oxide	12.68%
Titanium Oxide	5.58%
Phosphorus Pentoxide	0.10%
Calcium Oxide	3.56%
Magnesium Oxide	1.51%
Sodium Oxide	0.34%
Potassium Oxide	2.51%
Sulfur Trioxide	3.49%

^a. Values reported on a dry basis

^b. Determined using a Geisler plastometer

^c. The D (v, 0.9), D (v, 0.5) and D (v, 0.1) values are the particle sizes where, respectively, 90, 50 and 10% of the particles, by volume, are less than the indicated size.

^d. Determined using ASTM D2795 and D3682

Table 2. Ultimate analysis of the as received decant oil.

Ultimate Analysis ^a	
Carbon %	90.7
Hydrogen %	10.3
Nitrogen %	0.2
Sulfur %	0.8
Ash content (wt%) ^a	0.0
Conradson carbon residue	7.13

^a. Values reported on a dry basis

Table 3. Ultimate analysis of the slurry of 10% Powellton coal in decant oil.

Ultimate Analysis ^a	
Carbon %	89.9
Hydrogen %	9.8
Nitrogen %	0.4
Sulfur %	0.8
Ash content (wt%) ^a	0.2
Conradson carbon residue	8.49

^a. Values reported on a dry basis

The green cokes in this study were produced in a small pilot-scale delayed coker at The Energy Institute at The Pennsylvania State University. The coke drum has internal dimensions of 7.5cm ID by 102.5 cm high, giving a volume of 4.5 liters. The unit is capable of operating under most delayed coking process conditions. The system pressure, temperature and flow rates are monitored by a number of computer-controlled devices, and data from these devices is recorded throughout the run. In this study the unit was run with and without continuous steam injection, so that the affect of steam on coke texture, coke morphology and product yields could be measured. The following operating conditions were set for the test runs: coke drum inlet temperature 465 °C, coke

drum pressure 25 psig, resid feed rate 16.7 g/min, steam feed rate of 2vol% water to feed rate, and length of run 360 minutes. On the conclusion of the run the mass of the liquid condensate was measured. In addition, the height of the coke bed was measured prior to a core being drilled from the center of the bed. The remaining coke was removed and weighed.

Once testing of the system was complete attempts were made to assess the affect of processing conditions on the composition and characteristics of the co-coking products. Multiple runs have been made under the following conditions:

Wt% Coal	Wt% Oil	Inlet temp. (°C)	Coke drum pressure (psig)	Water feed rate*	Sample set
10	90	470	25	2%	A
10	90	470	50	2%	B
20	80	470	25	2%	C
10	90	470	25	1%	D

* The water feed rate is a percentage of the feedstock feed rate. For the purposes of this study the feedstock feed rate was set to 1 kg/hr. The water is used for steam injection.

The cores that were removed from the coke bed underwent extensive image analysis to determine the affect of the changes in run conditions of the texture, pore structure, pore volume and coke density. These measurements were obtained using optical microscopy and x-ray tomography techniques.

Figure 2. Schematic diagram of Penn State's delayed coker unit.

In general, cores of coke were taken off the centerline of the coke mass in the coker vessel and sometimes removed in 25 mm segments (if the coke was brittle) or as fairly large 40 - 70 mm lengths. Beginning from the bottom inlet and progressing upward in the direction of flow, cores were dense and compact, followed by a generally longer, less-dense middle section and topped by a competent but highly porous top section. Coke material was often found above the top of each core, but was too brittle for coring (no samples were provided).

It was important to include a complete bottom section for study, because it was found that coal-derived material was concentrated at the bottom of each core (at the inlet). Also, from earlier work it was determined that longitudinal sections were far more informative with regard to coke properties than cross-sectional areas. Therefore, when possible longitudinal sections of about 25 mm and oriented in the direction of flow were obtained. In general, subsections of cores were selected to include the bottom inlet area, a competent area from the center and top of each core for comparison. A handsaw was used to cut approximately 25 mm lengths of the core and each length was cut in half to expose a longitudinal surface. These segments were oriented so that the direction of flow would be known. Each core segment was glued into a plastic mold and impregnated with a cold setting epoxy resin by placing them under vacuum several times. Vacuum impregnation effectively forces epoxy to replace the connected air-filled voids in the coke, whereas those voids not connected to the exterior surface remain unfilled. After the epoxy hardened, the oriented surface of each specimen was ground and polished using a series of grit papers (400 and 600 grit) and alumina polishing slurries (0.3 and 0.05 micron).

Image analysis was performed using polarized-light microscopy (PM). All specimens were inspected using a Zeiss Universal research microscope using a 10X air (120 total magnification) or a 16X oil (250 total magnification) or 40X oil (625 total magnification) Antiflex objective with reflected, crossed-polarized white light. Photographs of selected areas of each segment were taken using 200 ASA Elite Chrome color 35 mm slide film. In addition, a point count analysis of the volume percentage distribution of carbon textures was performed on all core segments. This analysis was performed at 625X magnification in oil immersion by traversing the sample based upon a 0.2 x 0.2 mm grid parallel to the direction of flow and identifying the textural element under a crosshair held in a microscope eyepiece. In most cases, a total of 1000 counts were accumulated from each surface and the results (calculated to a volume percentage) are given in Table 9.

Nine different textural (or compositional) elements were used to characterize coke textures made from runs employing either 100% decant oil or blends of decant oil and Powellton coal. These textural elements, based on the size of isochromatic areas and/or shape, are sufficient to characterize the carbon derived from the individual components (decant oil and coal), but are unable to adequately identify the carbon material derived from their interaction. The different elements of this classification are described as follows.

Isotropic – a relatively low reflecting, dark gray carbon material derived from decant oil that displays little or no optical activity when the specimen is rotated under crossed-polarized light.

Mosaic – a higher reflecting carbon textural element derived from decant oil or decant oil/coal interaction that displays optical anisotropy and is characterized by isochromatic units $<10\text{ }\mu\text{m}$ or between about 4 - $10\text{ }\mu\text{m}$ when coal is present.

Small Domain – is an anisotropic carbon texture derived from decant oil, which exhibits isochromatic units between 10 – 60 μm in diameter.

Domain – is an anisotropic carbon derived from decant oil having much larger isochromatic units of greater than 60 μm diameter.

Flow Domain – is an anisotropic texture exhibiting elongated isochromatic areas of greater than 60 μm in length and <10 μm wide.

Inertinite-derived – angular or rectangular fragments of isotropic carbon derived from inertinite coal macerals with sharp outlines or possessing remnant plant cell structure.

Vitrinite-derived Mosaic – aggregate areas composed of many anisotropic units of less than about 4 μm , which typically contain fragments of inertinite or mineral matter.

Vitrinite-derived Isotropic – recognizable fragments of vitrinite that have not developed thermoplastic properties either because they were not exposed to a high enough temperature or were oxidized.

Mineral Matter – the remnants of coal minerals that can be recognized including pyrite, clays and carbonates.

Analysis was conducted on each segment of coke and the results are recorded with respect to distance from the bottom inlet. Another approach to view this data is the sum of components that can be directly contributed to coal or decant oil. Because textural components derived from decant oil constitutes the majority of the coke material those components are normalized to 100% to assess the influence of the presence of coal. To compare the overall influence of operating conditions on textural components derived from decant oil, the average concentration of each component for each core is calculated from the segments analyzed.

The whole cores were analyzed using an OMNI-X x-ray CT scanner. The OMNI-X is a high-resolution industrial scanner. The system is mounted on a rigid optical grade

structure that can move in any angle between 0-90. The positioning table can also move between tube and detector to change the magnification of the image on the image intensifier. The x-ray source can produce a cone-shaped beam that allows the collection of volumetric data. Currently, the system is capable of producing 1024x1024 pixels per image and enables a maximum resolution of 5-10 microns (with micro-focus x-ray tube) with energy levels of up to 225 kV. The system is also capable of collecting data in a varying number of views during scanning for the satisfactory image quality. For the present study coke samples were scanned with 90 kV and 375 micro A tube energy. The 2-D real resolution was 20 microns and slice thickness was 24 microns single slice scans. Approximately 40 scans were taken at intervals along the green coke core samples.

The remainder of the coke was removed from the coke drum and calcined in batches. The samples were heated from room temperature to 1400 °C at 10 °C/min and held at the maximum temperature for 30 minutes. The calcined coke was then sent to Alcoa Inc. for evaluation and to be made into test anodes. In order for the samples to meet their requirements Alcoa Inc. determined that the green mix for the anodes should be set at 16 wt% coal tar pitch. Once the green anodes were formed they were sent to Koppers Industries Inc. (KII) for baking and testing.

The anode cores were baked by KII using the following baking profile:

Baking: Anodes baked to ~1100°C under nitrogen purge.

0-600°C	10°C/hr.
600-1170°C	25°C/hr.
1170°C	14 hrs. hold

Each core was measured for baked apparent density, electrical resistivity, coefficient of thermal expansion, thermal conductivity, air permeability, crush strength, and flex strength. Alcoa Inc. had previously determined the green apparent density.

4.0 Results and Discussion

4.1 Production

Much of the early work centered around the redesign of the preheater set up, and the sample collection system. Initial results showed tests that 1/4" tubing was unsuitable, as the slurry formed blockages soon after start up. To that end, we began to use 3/8" tubing. However, this brought its own problems. The space velocity of the feed to the coker drum dropped considerably, and the residence times in the primary and secondary preheaters dropped from around 3 minutes with the 1/4" tubing to around 10 minutes in the 3/8" tubing. In some cases this had the affect of delaying the coking, and resulted in complete blockage of the tubing. To overcome the problem of coke build up we initiated the use of nitrogen blasts. These were very short bursts of 100 psig nitrogen into the tubing to aid in the removal of coke deposits. However, the nitrogen blasts also had the detrimental affect of blasting much of the feed out of the lines and up the walls of the coke drum. This in turn affected the yields. The removal of the primary preheater reduced the residence time of the sample prior to the coke drum inlet through the preheater zone to 3 minutes.

A secondary problem was centered on the injection of steam. It was discovered late on in the experiments that we were using too much steam. The water injection rate should have been set at 2 vol.% of the feed flow rate; however, it had been incorrectly set

to 10 %. The water that had condensed in the product collection system was found to separate out the heavy molecular portions of the product, rather than remaining immiscible. The heavy waxes derived from the water/oil mixtures tended to concentrate in the valves, back pressure regulator and the mass flow controller. These problems forced us to re-plumb the collection apparatus to minimize the buildup of waxes in key components, and to date the results show that the efforts seem to be working well.

The measurement of sulfur content in the cokes produced during the experiments is shown in Table 4. These values indicate that there is very little difference between the sulfur content in cokes produced from decant oil alone or from the coal/oil slurry. The differences that are shown are probably within experimental error (although we have not confirmed this). What is interesting to note, however, is that there is definitely no concentration of the sulfur in the coke. In fact, it seems that we may be lowering the sulfur content, when compared to the starting feeds. This is not normally the case with coking operations. Usually sulfur tends to get concentrated in the coke fraction. We attribute our values to the use of steam injection. The steam may be stripping the sulfur from the reactive species as H_2S before it gets a chance to participate in the cross-linking type reactions that would lock it into the coke.

As expected the ash contents for the coke derived from the decant oil alone were zero (see Table 4). However, the ash contents for the cokes produced from the slurry were considerably higher than that of the feed. This indicates that we have concentrated the coal-derived material in the coke. Calculating the proportion of the coke that is coal-derived and that which is petroleum-derived would be very difficult. However, we may assume two things from these results. First, that we are performing liquefaction-type

reactions with the coal. The coal liquids that are evolved from the reaction mixture are combined with the oil-derived volatiles in the products. Second, the coal may enhance the cracking of the oil through some surface, solid/liquid interactions. This increase the fraction of the oil-derived volatiles in the low boiling fractions and thus reduces the amount of sample in the higher boiling fractions that would normally undergo retrograde reactions to form coke. Further evidence for these assumptions is that the coke yield (as shown in Table 5) does not change significantly when slurry is used instead of decant oil.

Table 4. Examples of sulfur and volatile matter for cokes formed under various operating conditions from decant oil and a slurry of 10% Powellton coal in decant oil.

Sample	Coker inlet temperature (°C)	Primary preheater	Run time (minutes)	Sulfur (wt%) ^a	Ash content (wt%) ^a
Decant oil (as received)				0.8	0.0
Slurry (unreacted)				0.8	0.2
Decant oil	475	Yes	210	0.6	0.0
Decant oil	466	No	360	0.6	0.0
Decant oil	490	No	347	0.7	0.0
Slurry	475	Yes	148	0.5	0.8
Slurry	463	Yes	300	0.5	1.2
Slurry	465	No	360	0.6	1.1

^a. Values reported on a dry basis

In Table 5 the two low coke yields of 8.1% and 6.7% for decant oil and slurry, respectively, are due to differences in the operating conditions. For the decant oil run there was evidence of unreacted pitch being combined with the coke. This explains why the corresponding volatile content of the coke sample is high. The pitch would normally convert to coke, and this is why the coke yield is low. We are unsure why the pitch was

not converted. We had not seen this phenomenon before, and have not since either. For the slurry example the low yield was due to the short run time (147 minutes compared with the usual 300-360 minutes). We have noted that the rate of coke yield is dependant on time in the early stages of coke bed formation, and after 3-4 hours of operation a maximum coke yield is reached. This result is due to the coke bed enhancing further coke formation by promoting cracking reactions. The volatile content of the cokes are consistent, except for the experiment where we detected unreacted pitch.

In comparison with some industry standards for green sponge coke (see Table 6) the results from the analysis of the coke produced in this program are very favorable. As we do not use a water lance to remove the coke from our drum, the moisture content of the coke produced in our experiments is close to zero. Our coke has very comparable volatile matter content, and our sulfur content is much lower than that in the standard specifications. This is predominantly due to the fact that we start with low sulfur feeds, and we also see no concentration of sulfur in the coke products. The measured ash content of our coke is high, and thus our silicon and iron contents will be higher than those specified too. It was not our intention to perform an ash mineral analysis of the coke until after it was calcined. At which point some of the mineral matter will become volatilized.

After these initial testing runs the program was continued with parametric study focusing on the effect of operating conditions (temperature, flow rate, solids loading, steam injection, etc.) on the composition and morphology of the coke being formed. These tests were performed in at least triplicate in order to make a bulk sample for calcining. Table 5 includes some of the average data determined in each sample set.

Table 5. Examples of coke yield and volatile matter for cokes formed under various operating conditions from decant oil and a slurry of 10% Powellton coal in decant oil.

Sample	Coker inlet temperature (°C)	Primary preheater	Run time (minutes)	Coke yield (wt%)	Volatile matter (wt%) ^a
Decant oil	475	Yes		11.6	8.9
Decant oil	466	No	300	11.1	7.9
Decant oil	490	No	347	8.1	16.6*
Slurry	475	Yes	148	6.7	8.1
Slurry	463	Yes	300	10.7	8.2
Slurry	465	No	360	12.8	8.5

^a. Values reported on a dry basis

* Coke was known to have unreacted pitch-like residue mixed in with it.

Table 6. Typical green sponge coke specifications [4].

Property	
Moisture	6-14%
Volatile matter	8-14%
Sulfur	1.0-4.0%
Silicon	0.02%
Iron	0.01%
Ash	0.25%

Table 7. Average product yields for co-coking runs with varying operating conditions.

Sample set	Coke yield (wt%)	Liquid yield (wt%)
A	18.5	61.6
B	29.3	51.8
C	24.0	65.2
D	20.2	65.4

Taking sample set A as the baseline set of runs the following observations can be made, with respect to the product yields:

1. With an increase in coke drum pressure, there was an increase in coke yield and a corresponding decrease in liquid yield. This is wholly consistent with results previously reported in the literature (2,5).
2. With an increase in coal in the feedstock, there was an increase in coke yield. This result is as expected. The ability to accurately determine how much of the coke is coal-derived has not yet been determined. The goal is to derive this value through yield calculations, with back up, concurring results from optical microscopy and other instrumental methods.
3. With the increase in coal to the feedstock, there was an increase in the liquid yield. This result would indicate that the volatiles, from coal, evolved during the coking process were resistant to thermal cracking, and so did not decompose to gaseous compounds.
4. A 50% decrease in water feed rate, and thus steam to the coker, resulted in an increase in coke and an increase in liquid yield. The coke increased because the lower steam rate resulted in less medium volatile compounds being swept from the coke drum. And so these medium volatiles subsequently coked. As there was an increase in liquid yield too, then the coking of the medium volatiles must have decomposed partially to intermediate lower boiling liquids, and produce gaseous products to a lesser extent.

4.2 Image Analysis of Green Cokes

4.2.1 Petrographic analysis of Green Cokes

Table 8 lists the samples analyzed using petrographic analysis techniques, and the experimental conditions under which the samples were produced.

Table 8. Conditions of Operation and Yield from Coker Runs

Coker Run Date	Feed Components	Feed Rate, g/min	Steam Injection Rate, ml/min	Drum Pressure psig	% Coke Yield	% Volatile Matter, daf	% Ash, dry
04/27/01	10% Powellton	16.5	na	25.2	9.1	13.64	1.57
06/04/01	10% Powellton	18.3	2.90	24.2	10.7	8.34	1.19
06/12/01	10% Powellton	17.7	2.80	26.3	12.8	8.58	1.10
06/20/01	100% Decant Oil	18.6	1.50	24.8	12.8	7.91	0.04
09/04/01	10% Powellton	17.4	0.30	24.7	19.3	7.79	0.85
09/11/01	10% Powellton	17.4	0.14	21.4	20.2	11.77	0.97
09/18/01	10% Powellton	15.8	0.30	50.2	31.3	24.89	0.48
09/25/01	20% Powellton	16.7	0.30	24.1	25.1	8.52	1.40

Regardless of operating conditions, in all cases coal-derived textural components are concentrated near the bottom inlet and decrease with increasing distance from the bottom (Tables 9 and 10). In contrast, the larger domain textures (domain and flow domain) derived from the decant-oil increase in concentration with distance from the bottom inlet. With respect to the one run (6-20-01) employing 100% decant oil (Table 11), operating conditions appeared to have had an influence on textures compared to earlier runs (2-26-01 and 3-7-01, Table 11). Generally, the coke of the 6-20-01 run was dominated by slightly smaller textures, but has a higher concentration of flow domain carbon owing to a greater porosity (which controls elongation of domains).

Table 9. Petrographic Analysis of Carbon Textures in Longitudinal Sections, Vol. %

Distance from Bottom of Core, mm	Vitrinite-derived Mosaic	Interinite-derived	Vitrinite-derived Isotropic	Mineral Matter	Pet. Isotropic	Pet. Mosaic	Pet. Small Domain	Pet. Domain	Pet. Flow Domain
Core 4-27-01; 10% Powellton Coal; with Primary Preheater									
0 - 34	9.4	4.6	0.1	0.3	0.0	26.8	54.2	2.8	1.8
Core 6-12-01; 10% Powellton Coal; 2.8 ml/min Steam rate; w/o Primary Preheater									
0 - 21	4.7	6.4	0.0	0.5	0.0	33.0	53.6	1.4	0.4
26 - 44	4.2	6.6	0.3	0.2	0.3	24.5	60.0	2.1	1.8
Core 6-20-01; 100% Decant Oil; 1.5 ml/min Steam rate; w/o Primary Preheater									
0 - 9	0.0	0.0	0.0	0.0	0.0	2.5	67.8	28.2	1.5
75 - 95	0.0	0.0	0.0	0.0	0.0	7.0	57.0	13.2	22.8
95 - 120 C*	0.0	0.0	0.0	0.0	0.0	8.2	55.8	16.6	19.4
Core 9-4-01; 10% Powellton Coal; 0.3 ml/min steam rate; 24.7 psig drum pressure									
0 - 14.5	13.9	11.7	0.0	0.3	0.0	28.5	37.4	6.4	1.8
102 - 127	5.4	7.1	0.0	0.1	0.3	8.8	54.1	19.3	4.9
280 - 305	1.2	4.4	0.0	0.0	0.0	5.3	68.1	18.1	2.9
356 - 381	0.2	3.8	0.0	0.2	0.0	13.6	49.8	14.0	18.4
Core 9-11-01; 10% Powellton Coal; 0.14 ml/min steam rate; 24.1 psig drum pressure									
0 - 26	5.1	9.1	0.1	0.1	3.3	38.7	41	1.9	0.7
52 - 72	0.0	6.2	0.2	0.8	79.0	11.8	1.8	0.2	0.0
127 - 150	1.3	4.2	0.2	0.1	4.5	19.7	54.3	12.8	2.9
Core 9-18-01; 10% Powellton Coal; 0.3 ml/min steam rate; 50. 2 psig drum pressure									
0 - 34	1.7	3.5	0.0	0.2	27.3	19.9	39.9	6.7	0.8
45 - 70	1.3	2.5	0.2	0.1	12.4	17.0	53.5	8.4	4.6
115 - 140	1.0	4.1	0.1	0.2	16.3	16.4	56.6	3.5	1.8
Core 9-25-01; 20% Powellton Coal; 0.3 ml/min steam rate; 24.1 psig drum pressure									
0 - 20	8.1	9.3	0.0	0.3	0.1	55.3	22.6	3.2	1.1
70 - 95	1.7	1.8	0.0	0.0	0.3	18.3	63.1	9.0	5.8
356 - 381	0.1	0.0	0.0	0.0	0.0	7.9	80.2	7.1	4.7

- C = Cross-section

Table 10. The Proportions of textures Derived from Coal and Decant Oil Compared with the Normalized Concentration of Decant Oil Textures, Vol. %

Distance from Bottom of Core, mm	%Coal-derived	%Petrol.-derived	% Isotropic	% Mosaic	% Small Domain	% Domain	% Flow Domain
Core 4-27-01; 10% Powellton Coal; with Primary Preheater							
0 - 34	14.4	85.6	0.0	31.3	63.3	3.3	2.1
Core 6-12-01; 10% Powellton Coal; 2.8 ml/min Steam rate; w/o Primary Preheater							
0 - 21	11.6	88.4	0.0	37.3	60.6	1.6	0.5
26 - 44	11.3	88.7	0.3	27.6	67.7	2.4	2.0
Core 6-20-01; 100% Decant Oil; 1.5 ml/min Steam rate; w/o Primary Preheater							
0 - 9	0.0	100.0	0.0	2.5	67.8	28.2	1.5
75 - 95	0.0	100.0	0.0	7.0	57.0	13.2	22.8
95 - 120 C	0.0	100.0	0.0	8.2	55.8	16.6	19.4
Core 9-4-01; 10% Powellton Coal; 0.3 ml/min steam rate; 24.7 psig drum pressure							
0 - 14.5	25.9	74.1	0.0	38.5	50.5	8.6	2.4
102 - 127	12.6	87.4	0.3	10.1	61.9	22.1	5.6
280 - 305	5.6	94.4	0.0	5.6	72.1	19.2	3.1
356 - 381	4.2	95.8	0.0	14.2	52.0	14.6	19.2
Core 9-11-01; 10% Powellton Coal; 0.14 ml/min steam rate; 24.1 psig drum pressure							
0 - 26	14.4	85.6	3.9	45.2	47.9	2.2	0.8
52 - 72	7.2	92.8	85.1	12.7	2.0	0.2	0.0
127 - 150	5.8	94.2	4.8	20.9	57.6	13.6	3.1
Core 9-18-01; 10% Powellton Coal; 0.3 ml/min steam rate; 50. 2 psig drum pressure							
0 - 34	5.4	94.6	28.9	21.0	42.2	7.1	0.8
45 - 70	4.1	95.9	12.9	17.7	55.8	8.8	4.8
115 - 140	5.4	94.6	17.3	17.3	59.8	3.7	1.9
Core 9-25-01; 20% Powellton Coal; 0.3 ml/min steam rate; 24.1 psig drum pressure							
0 - 20	17.7	82.3	0.1	67.2	27.5	3.9	1.3
70 - 95	3.5	96.5	0.3	19.0	65.4	9.3	6.0
356 - 381	0.1	99.9	0.0	7.9	80.3	7.1	4.7

The similarity between cores derived from using 10% Powellton coal and obtained from 4-27-01 (with primary preheater) and 6-12-01 (without primary preheater) is striking. The competent portions of both cores were short (34 and 44 mm, respectively), there was almost no difference in the distribution of carbon textures (Table 9 and 10) and there was no significant difference in the distribution of carbon textures derived from decant oil (Table 11). This suggests that the removal of the primary preheater to improve operations has had no influence on coke properties.

Table 11. Comparison of Coke Textures Derived from Decant Oil from Coke Generated with and without Addition of Coal, Vol. %

Coker Run Date	Feed Components	Isotropic	Mosaic	Small Domain	Domain	Flow Domain
02/26/2001	100% Decant Oil	0.4	2.4	44.3	40.8	12.1
03/07/2001	100% Decant Oil	Trace	1.2	51.6	39.2	8.0
04/18/2001	10% Powellton	14.5	12.4	56.3	13.4	3.4
04/27/2001	10% Powellton	0.0	31.3	63.3	3.3	2.1
06/04/2001	10% Powellton	na	na	na	na	na
06/12/2001	10% Powellton	0.2	32.4	64.2	2.0	1.2
06/20/2001	100% Decant Oil	0.0	5.9	60.2	19.3	14.6
09/04/2001	10% Powellton	0.1	17.1	59.1	16.1	7.6
09/11/2001	10% Powellton	31.3	26.3	35.8	5.3	1.3
09/18/2001	10% Powellton	19.7	18.7	52.6	6.5	2.5
09/25/2001	20% Powellton	0.1	31.4	57.7	6.8	4.0

The influence of reducing steam injection rate is observed best by comparing coker runs from 6-12-01 and 9-4-01. Both runs involved 10% Powellton coal and both were terminated after 6 hours of operation, but the 9-4-01 run had a 90% reduction in steam rate. Both cokes have an average of 11-12 vol. % coal-derived components, but the distribution of decant oil-derived components was significantly different. As seen in

Table 11, an increase in the concentration of larger optical textures (domain and flow domain) at the expense of the smaller textures (mosaic and small domain) was observed. Another important distinction between these cokes that will not show up in the data, was the fact that the mosaic textures derived from coal were significantly enhanced in the 9-4-01 core. Also, coal textures were intimately mixed with those derived from the decant oil. This degree of enhancement and mixing was not observed in the 6-12-01 core, which may be a direct result of the higher steam injection rate when coal is present.

When the steam injection rate was further reduced (0.14 ml/min, 9-11-01 core) operation of the coker appeared to be stable as nearly 370 mm of coke was generated in 6 hours of operation. However, a significant difference in the properties of the coke was observed. A considerable amount of isotropic carbon (without incorporated mesophase) derived from the decant oil filled the center section of the core (Table 9 and 10), whereas much less was observed near the bottom inlet and toward the top of the core. This amount of isotropic carbon contributed to a higher volatile matter content as shown in Table 8. The reason for the isotropic carbon cannot be necessarily blamed on the low steam rate, because in an earlier investigation that compared cokes from 100% decant oil with and without steam, a similar influence on coke properties was not observed. This suggests that other factors may have had an influence on the incomplete conversion of decant oil to an anisotropic carbon. Factors that may be involved in this unusual observation include the use of coal in the run, an unexpected loss of thermal control of the preheater, or there may have been changes in the chemical properties of the decant oil. The fact that mesophase spheres were not observed in the isotropic phase may support that latter two of these alternative factors.

Returning to the stable conditions and steam injection rate (0.3 ml/min) employed during the 9-4-01 run, problems were experienced in operation on 9-18-01. The run was terminated after about 3 hours as a result of excessive drum pressure (50.2 psig), although about 216 mm of coke was deposited. This run also produced a coke containing a great deal of isotropic carbon, except that there was a considerable amount of mesophase spheres trapped within the phase and the isotropic carbon was observed to be uniformly distributed throughout the core. Some of the isotropic carbon may result from how the run was terminated and may account for the high volatile matter content (Table 8). The high drum pressure that developed during the run may have had some influence on the formation of mesophase spheres in the isotropic phase. Furthermore, nearly all of the coal-derived material was significantly enhanced and intimately mixed with the decant oil derived carbon throughout the entire core. This too may be a benefit of the higher pressure.

Doubling the amount of coal to 20 wt.% at the low steam injection rate (0.3 ml/min, 9-25-01) did not adversely effect operations of the coker, as 381 mm of coke was generated during 6 hours of operation. However, the coke properties were significantly influenced, particularly near the bottom inlet, which was composed mostly of enhanced coal mosaic texture. Progressing in the direction of flow, coal textures showed less influence from contact with the decant oil and toward the top of the core much less coal-derived carbon was observed. This suggests that although most of the coal was isolated near the bottom of the core, it did not negatively effect coker operations.

4.2.2 X-ray Tomography of Green Carbon Products.

Figure 3 shows tomographs from the two green coke samples. Green coke core A (top) is from delayed coking with steam injection and green coke core B (bottom) is without steam injection. Tomographs 1, 2 and 3 represent green coke structures from the bottom, middle and top of the core sample, respectively. The white line on the photograph at the top is the area in the core where the tomograph was taken. Green coke B has a similar representation in tomographs 4-6.

It was observed that the bottom of core A had a much more open pore structure than core B. Therefore the steam injection significantly influenced the pore structure and coke deposition mechanisms in this region. This could be due to the steam keeping the medium volatile components from moving through this zone, and so stopping them from undergoing retrograde reactions leading to the formation of coke. The steam may also increase the volume of gas traveling through the pores, and hence could inhibit pore closure. Additionally, the steam may be cooling the surfaces within the coke structure and so may reduce the rate of coke formation. The green coke structures observed in the middle of both cores (tomographs 2 and 5) were very similar to each other indicating coking environments that are alike. The top two tomographs (3 and 6), however, are very different. This once again was due to the influence of steam. The image shown in tomograph 6 is of solidified froth. Froth is the first stage of coke formation on the leading edge of the coke bed as it rises up the drum. When the experiment was shut down the froth simply solidified in place. We do not see this in the core with steam injection (tomograph 3). This was because the overall coke bed height was 74 cm (bed height without steam was 30 cm), as the coring device was only 30 cm long we could not

get all the core from the drum. However, the structure of the coke in the “frothy” zone of the core produced with steam injection was so friable that the coring bit would have destroyed it.

The data collected from the CT imaging was also used to estimate porosity (Figure 4) and density (Figure 5) with respect to coke bed height. The porosity measurements match the visual observations of the tomographs of each green coke core. That is, at the inlet to the coke drum the coke from steam injection has greater porosity than that of the sample with no steam injection. Both cores then produce a zone with near equal porosities. This was different from the PM analyses, which noted that the steam generated an overall higher porosity in the middle section. Finally, in the core with no steam injection there is a distinct rise in porosity in the zone of solidified froth.

Figure 5 shows a comparison of average densities and carbon matrix densities for the two green coke core samples. The average densities are shown as x-ray absorption intensities for each tomographic analysis taken along the core. Therefore this representation of density takes into account the pores in the green coke structure. The values for the carbon matrix densities are measured by ignoring the pores in the green coke structure. These results show that there is essentially no difference in the green coke density with respect to bed height for both green cokes. Hence the differences shown in the average density are due to the changes in the relative degree of porosity.

Volume scans can be used to develop 3-D images. By manipulating the image a map of the pores can be rendered, essentially ignoring the coke matrix. The image of the pores can then be used to measure the length and orientation of the pores. This data may be correlated with PM observations as to the overall size of areas with elongated domain,

which would give an indication on what the quality of the coke would be after calcination and graphitization.

Figure 3. Tomographs of the green coke structures taken at intervals along cores from experiments with (A) and without (B) steam.

Figure 4. Porosity of the green coke samples with respect to bed height.

Figure 5. Average density and carbon density of coke samples with respect to bed height.

4.3 Analysis of Calcined Coke and Baked Anodes

Alcoa Inc performed the analysis of the baked anodes. Table 12 lists the concentration of some of the inorganic constituents of the calcined coke samples from the parametric co-coking study. The maximum values were obtained from Alcoa Inc. It can be seen that all of the Penn State samples exceed the limits set by Alcoa Inc. This is because of the residue clay minerals (Si, Na) and finely divided pyrite (Fe) that could not be cleaned full from coal when Preptech Inc. processed it.

Much of the mineral matter is disseminated and independent of the organic constituents of the coal, and this mineral matter can be mostly clean using froth flotation and other cleaning techniques. However, there is some mineral matter that is inherently

bound within the coal structure. It is this mineral matter that is mainly contributing to the inorganic constituents in the Penn State samples.

On a more positive note, the sulfur concentrations in the Penn State samples are much lower than the maximum permissible level set by Alcoa Inc. Therefore, if samples from co-coking were ever to be used on an industrial-scale the SO₂ emissions would be lower than those from a conventional petroleum-based coke. In addition, the petroleum-derived minerals such as vanadium (V) were much lower than the maximum allowable limits. The vanadium was low due to the dilution factor brought about because of the coal-derived material in the coke. Vanadium can act as an oxidizing catalyst to the carbon during smelting, and therefore is detrimental to the product's use.

Table 12. Concentration of inorganic elements in calcined coke samples.

Sample No.	Ash (wt%)	Inorganic constituents				
		Si (ppm)	Fe (ppm)	Na (ppm)	V (ppm)	S (wt%)
Max. values	0.37	350	785	300	200	2.00
A	1.57	1900	1400	340	<50	0.66
B	1.46	1900	800	480	<50	0.63
C	1.82	3100	1600	260	<50	0.61
D	1.06	1200	600	190	<50	0.62

Table 13 lists some of the typical physical properties that are looked for in a test anode. The Penn State samples were compared with an Alcoa Inc. standard anode. The standard anode was made under the same conditions as the Penn State anodes, but was made with petroleum-derived coke.

There is little difference between the Alcoa Inc. standard anode and the Penn State anodes in the green and baked apparent density measurements, except for Sample B, which is the sample where 1% steam was used. The low steam rate must not have

driven off the volatile matter like the 2% steam rate. This in turn may have led to a lighter, fluffier, less dense coke. The electrical resistivity of the Penn State samples was consistently lower than that of the Alcoa Inc. standard. This means that the Penn State samples would have used less electricity during the operation of the smelter. The air permeability for the Penn State samples varies quite a bit from that of the Alcoa Inc. standard. However, all the results are lower than that of the target value. A lower air permeability value is good because this means that there is less air infiltration into the sample, and thus reduces the level of reactivity with air. The Penn State samples are consistently stronger than the Alcoa Inc. standard. However, none of the samples meet the target values. The thermal conductivity values for the Penn State samples are closer to the target value than the Alcoa Inc. test anode.

Table 13. Physical properties measurements of baked test anodes

Sample No.	Green Apparent Density (g/cc)	Baked Apparent Density (g/cc)	Elec. Resist. ($\mu\Omega\text{m}$)	Air Perm. (nPm)	Crush Strength (MPa)	Flexural Strength Stress (MPa)	CTE Avg. Alpha ($E^{-6}/^{\circ}\text{C}$ @300°C)	Thermal Conduct. (W/mK)
Standard	1.614	1.535	70.8	1.25	24.41	5.59	4.351	2.43
A	1.623	1.543	58.5	1.08	29.00	7.47	4.657	3.08
B	1.568	1.491	66.8	1.42	29.41	6.32	4.769	2.87
C	1.648	1.558	53.7	1.09	31.58	9.05	4.849	3.45
D	1.624	1.529	57.0	1.76	30.94	6.60	4.637	3.04
Target values *		1.540	55.5	2.00	40-55	11.00	4.500	4.00

* These are values set by Alcoa Inc. or taken from *Anodes for the Aluminum Industry*. 1st Ed., R+D Carbon Ltd., Switzerland.

Table 14 shows the data from reactivity measurements of the test anodes in air and CO₂. In reactivity measurements the goal is to attain as high a residue percentage as possible. The CO₂ reactivity residue percents for the Penn State anode fall short of the

standard anode. Other than Sample D, the air reactivity resid values do not vary from the standard by too much.

Table 14. Reactivity measurements of baked anodes.

Sample No.	ISO CO ₂ Reactivity				ISO Air Reactivity				Net carbon consumption kg/t Al
	% Wt. Loss	% Dust	% Attr.	% Resid.	% Wt. Loss	% Dust	% Attr.	% Resid.	
Standard	4.68	2.15	0.82	92.32	16.42	4.94	1.03	77.58	66.2
A	11.59	8.68	4.46	75.16	8.86	15.82	2.56	72.61	106.4
B	7.47	8.63	2.25	81.51	8.60	16.51	2.40	72.31	97.6
C					7.42	8.43	6.61	77.35	
D	5.91	3.45	2.41	88.17	9.20	22.43	3.75	64.49	102.5
Target values*	4-10	1-10		84-95	8-30	2-10		65-90	

** These are values taken from *Anodes for the Aluminum Industry. 1st Ed.*, R+D Carbon Ltd., Switzerland.

This data, along with the other physical property measurements, can be used to predict the net carbon consumption of the anodes. Equation 1 was developed by Fisher *et al* [6].

$$\text{Equation 1.} \quad \text{NC} = \text{C} + 334/\text{CE} + 1.2(\text{BT} - 960) - 1.7\text{CR} + 9.3\text{AP} + 8\text{TC} - 1.5\text{AR}$$

Where:

NC = net carbon consumption in kg/t Al

C = cell factor in kg/t Al (set to 305 kg/t Al for this example)

CE = current efficiency (typical operations aim for a value of around 97%)

BT = bath temperature in °C (typical operations aim for a values ranging from 940-960 °C. for this example 960 °C was chosen)

CR = CO₂ reactivity residue in %

AP = Air permeability in nPm

TC = Thermal conductivity in W/mK

AR = Air reactivity residue in %

The net carbon consumption values are based on some general assumptions, and only serve to estimate differences between the standard anode and the Penn State

samples. Net carbon consumption for the Penn State samples is higher than that of the standard anode. It is unclear whether the differences are significant at this stage.

5.0 Conclusions

In many aspects this study has been very successful. The majority of the goals set out for the study were attained. Moreover, it has been shown that a coal-based product can be produced from the co-coking of coal and petroleum resid that may ultimately have an application as a premium carbon product.

The objective of this study was to produce a coke product from the co-coking of coal and petroleum resid that could be used in the production of anodes for aluminum electrolysis. To this end, blends of cleaned coal and decant oil were fed into a pilot-scale delayed coker under various operating conditions. The resulting cokes were fully characterized using a variety of analytical techniques. Finally, the cokes were made into test anodes and compared with conventional petroleum coke-based anodes.

This study aimed to establish links between the changes in processing conditions and the quality of the resulting cokes. Traditional and non-traditional image analysis techniques, petrographic analysis and x-ray tomography, respectively, were used to measure some of the compositional and physical attributes of the green cokes. Furthermore, information on product yields, proximate and ultimate analysis were collected.

The resulting cokes were produced in bulk and calcined at 1400 °C. The calcined cokes were sent to Alcoa Inc. to be made into test anodes. The test anodes were sent to Koppers Industries Inc. to be baked. The baked anodes underwent a series of tests to determine their quality relative to a standard test anode, and industry target values.

Results show that in some aspects including density, strength, resistivity, reactivity, the coal-based cokes produced in this study met or exceeded the standards set

by the industry. However, due to the presence of residual mineral matter from coal in the coke, the ash values for the coal-based anodes are high.

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8.0 List of Acronyms and Abbreviations

Ni	nickel
V	vanadium
μm	micron
psig	pounds per square inch
g/min	grams per minute
vol%	volume percent
wt%	weight percent
kg/hr	kilograms per hour
CT	computed tomography
kV	kilo-volts
H ₂ S	hydrogen sulfide
ml/min	milliliters per minute
daf	dry ash free
Pet.	petroleum
PM	polarized-light microscopy
Si	silicon
Na	sodium
Fe	iron
SO ₂	sulfur dioxide
g/cc	grams per centimeter cubed
μΩm	micro ohms per meter
nPm	nano perms
MPa	mega Pascals
CTE	coefficient of thermal expansion
Elec.	electrical
Resist.	resistivity
Perm.	permeability
Conduct.	conductivity
W/mK	watts per milli-Kelvin
CO ₂	carbon dioxide
Attr.	attrition
Resid.	residue
kg/t Al	kilograms per tonne of Aluminum
NC	net carbon consumption
C	cell factor
CE	current efficiency
BT	bath temperature
CR	CO ₂ reactivity residue
AP	Air permeability
TC	Thermal conductivity
AR	Air reactivity residue