

TITLE PAGE

Report title/Type: Technical Progress Report for project entitled "Create a Consortium and Develop Premium Carbon Products from Coal"

Reporting Period: Period Ending May 31, 2003

Principal Authors: Dr. John M. Andresen

Report Issue Date: Revised Report Submitted August 2003

DOE Award Number: DE-FC26-98FT40350

Submitting Organizations: The Pennsylvania State University
Office of Sponsored Programs
110 Technology Center
University Park, PA 16802

West Virginia University
Office of Sponsored Programs
886b Chestnut Ridge Road, Room 202
Morgantown, WV 26506-6845

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government or any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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 continued to excel in developing innovative technologies to use coal and coal-derived feedstocks to produce premium carbon product.

During Budget Period 5, eleven projects were supported and sub-contracted were awarded to seven organizations. The CPCPC held two meetings and one tutorial at various locations during the year.

Budget Period 5 was a time of growth for CPCPC in terms of number of proposals and funding requested from members, projects funded and participation during meetings. Although the membership was stable during the first part of Budget Period 5 an increase in new members was registered during the last months of the performance period.

TABLE OF CONTENTS

Cover Page	page 2
Disclaimer	page 3
Abstract	page 4
Table of Contents	page 5
Executive Summary	page 6
Experimental	page 7
Results and Discussion	page 8
Conclusions	page 9
References	page 9
Appendix 1	page 10
“Anthracite Filler and Coal-Extract Binder for the Development of Isostatically-Molded Graphite”, Principal Investigator Dr. Peter G. Stansberry, West Virginia University, Morgantown, WV	

EXECUTIVE SUMMARY

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 continued to excel in developing innovative technologies to use coal and coal-derived feedstocks to produce premium carbon product.

During Budget Period 5, eleven projects were supported and sub-contracted were awarded to seven organizations. The CPCPC held two meetings and one tutorial at various locations during the year.

The first meeting was held at Nemaocolin Woodlands Resort outside Pittsburgh on May 13-14, 2002. The meeting concentrated on considering new proposals for Budget Period 5 and reviewing projects funded in Budget Period 4. Both the Council and the Advisory Committee met during the meeting. Three new proposals received funding and a total of \$250,000 was awarded with performance periods from July 1, 2002 to June 30, 2003.

The Summer Tutorial was held at the Hampton Inn, Hazleton, PA on July 16, 2002. This year's Tutorial focused on the use of carbon in the water treatment industry. The Tutorial consisted of a series of technical presentations, and tours of a local anthracite mine and a filter media preparation facility.

The Fall 2002 meeting that was to be held at the Penn Stater Conference Center at State College on October 21-22, 2002 was postponed due to a change of directorship of the CPCPC. On November 15, 2002 Dr. John M. Andresen replaced Dr. Frank Rusinko Jr. as director.

The second Consortium meeting was held at the Penn Stater Conference Center on January 13-14, 2003. Fourteen new project proposals for possible funding for Budget Period 6 was presented and nine were selected for funding by the council. Both the Council and the Advisory Committee met during the meeting. Four new council members and a new advisory committee chair were elected during the meeting.

Copy of one final project report for budget Period 5 is enclosed. Six projects have received no-cost extension of the performance period, one project report is being withheld to include additional data, and three projects are still ongoing. Final reports for these ten projects will be enclosed in the Technical Progress Report for Budget Period 6.

EXPERIMENTAL

The Spring CPCPC meeting was held at Nemaquin Woodlands Resort outside Pittsburgh on May 13-14, 2002. Approximately 50 people attended the spring meeting 2002.

The Summer Tutorial was held at the Hampton Inn, Hazleton, PA on July 16, 2002 focusing on the use of carbon in the water treatment industry. Approximately 20 people attended this year's Tutorial.

The Fall 2002 meeting that was to be held at the Penn State Conference Center at State College on October 21-22, 2002 was postponed due to a change of directorship of the CPCPC. On November 15, 2002 Dr. John M. Andresen replaced Dr. Frank Rusinko Jr. as director.

The Winter 2003 Consortium meeting was held at the Penn State Conference Center on January 13-14, 2003. Approximately 60 people attended the spring meeting 2002.

RESULTS AND DISCUSSION

During Budget Period 5 eleven projects were supported and sub-contracted were awarded to seven organizations. Six subcontracts received no-cost extensions for their work and will report in Budget Period 6. Two projects were completed, where one is reported in Appendix while the other was withheld to include additional data and will appear in the report for Budget Period 6. Three subcontracts are ongoing and will appear in the Budget Period 6 technical report.

List of final reports for Budget Period 5 to be included in Budget Period 6:

“Production of Bulk Carbon Fibers and Activated Carbon Fibers via Centrifugal Melt Spinning (CMS)”, Principal Investigator Dr. Rodney Andrews, University of Kentucky, KY. No-cost extension.

“Tailoring the Electrical Performance of Coal-Based Carbon Foams for Radar and Shielding Applications”, Principal Investigator Dr. Janusz Plucinski, Touchstone Research Laboratory Ltd., PA. No-cost extension.

“Preparation of the West Virginia University Coal-to-Pitch Process for Commercialization”, Principal Investigator Dr. George Keller, New Carbon, Inc., WV. No-cost extension.

“Nuclear-Grade Isotropic Graphite from Coal”, Principal Investigator Dr. John Zondlo, West Virginia University, WV. Withheld to include additional data.

“Low Cost Carbon Fibers from Coal-Based Precursors-4th year”, Principal Investigator Dr. Jim Withers, MER Corporation, AZ. No-cost extension.

“Low Cost Coal-Based Carbon Electrodes for Batteries and Fuel Cells-2nd year”, Principal Investigator Dr. Witold Kowbel, MER Corporation, AZ. No-cost extension.

“Designed Wear Properties of Coal-Based Products”, Principal Investigator Dr. Janusz Plucinski, Touchstone Research Laboratory Ltd., PA. No-cost extension.

“Value-Added Carbon Products from PCC and IGCC Byproducts”, Principal Investigator Dr. Rodney Andrews, University of Kentucky, KY. Ongoing project.

“Tailoring Coal-Based Activated Carbon to Remove Tastes, Odors, and Other Trace Organic Contaminants from Drinking Water”, Principal Investigator Dr. Fred Cannon, Pennsylvania State University, PA. Ongoing project.

“Recovery of Carbon from Coal-Fired Power Plant Ash Using a Jet Mill”, Principal Investigator Dr. Thomas Weyand, Pittsburgh Mineral & Environmental Technology, Inc., PA. Ongoing project.

CONCLUSIONS

As we move into Budget Period 6 we are working constantly to increase our membership and involve a range of industries that can benefit from using and/or producing premium carbon products from coal, as well as facilitate academic institutions to educate future leaders in the coal to carbon field.

REFERENCES

None.

Appendix I

Anthracite Filler and Coal-Extract Binder for the Development of Isostatically-Molded Graphite

FINAL REPORT

Reporting Period
March 1, 2002 to February 28, 2003

Report Prepared by

Peter G. Stansberry
Department of Chemical Engineering
College of Engineering and Mineral Resources
P. O. Box 6102
West Virginia University
Morgantown, WV 26506-6102

Report Issued
March 15, 2003

DOE Award Number DE-FC26-98FT40350

Other Contributors

Harold H. Schobert
The Energy Institute
College of Earth and Mineral Sciences
C211 Coal Utilization Laboratory
The Pennsylvania State University
University Park, PA 16802

&

David P. Struble and Leo Lanzel
Carbone of America
Graphite Materials Division
215 Stackpole Street
Saint Marys, PA 15857

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

1.0 ABSTRACT

Conventional isostatically-molded graphite is produced from petroleum coke and coal-tar binder pitch. The current project sought to demonstrate that isotropic graphite could be obtained entirely from coal-based feeds, which are not reliant on petroleum sources or coke oven byproducts. A West Virginia bituminous coal (Bakerstown, WVGS 13407) was hydrogenated and then deashed by extraction in N-methyl pyrrolidone to produce a pitch material for trial use as a binder. Hydrogenations were conducted for two hours at 450°C in batch reactors. Reactions were repeated until sufficient coal-derived binder was made to fulfill the objectives of the project. The pitch-like product had a Mettler softening point of 112.2°C, toluene insoluble content of 32.7wt%, coking value of 50.3wt%, ash content of 0.2wt%, and a density of 1.25g/cm³. These characteristics are found within the range of values for commercial binder pitches. Also, the WVU coal-derived binder contained less carbon and more hydrogen than a conventional coal-tar binder pitch with a carbon-to-hydrogen atomic ratio of 1.21 and 1.81, respectively. A Pennsylvania anthracite coal (LCNN) was calcined to between 1,315 and 1,427°C. Following calcination, the anthracite was milled to an average particle size of 27.4µm, with a median particle size of 23.3µm. The coal-extract binder and calcined anthracite were mixed, milled, and isostatically molded up to 20,000psi into 5 x 5 x 12 inch billets. The billets were baked to 950°C and then graphitized inductively to 2,700°C. The green, baked, and graphitized billets were tested following standard industrial practice. Graphite made from calcined petroleum coke and coal-tar binder pitch was used as controls. The results of this work demonstrate that synthetic graphite is possible based on feed materials entirely from coal. In many respects the overall characteristics of the coal-based graphites did not meet or exceed the corresponding products made from conventional feeds, vis-à-vis, petroleum coke and coal tar pitch. The results indicate that considerable improvements to the coal-based materials might be possible especially as they relate to the development of increased density starting with the green state and ending at the graphitization stage.

TABLE OF CONTENTS	Page
Disclaimer	8
1.0 Abstract	9
Table of Contents	10
2.0 List of Figures	11
3.0 List of Tables	12
4.0 Executive Summary	13
5.0 Introduction	14
6.0 Experimental	15
6.1 Preparation of Coal-Extract Binder	15
6.2 Characterization Methods for Coal-Extract Binder	19
6.3 Preparation and Characteristics of LCNN Anthracite Filler	22
6.4 Preparation of the Isostatically-Molded Graphite Specimens	23
7.0 Results and Discussion	24
7.1 Characteristics of the WVU Coal-Extract Binder Pitch	24
7.2 Characteristics of the Isostatically-Molded Graphite Specimens ...	25
7.3 Confirmation of Isotropy	28
7.4 Examination of Overall Billet Properties	30
7.5 Characteristics of Billets at 46 and 50pph Binder Pitch Level	32
7.6 Effects of WVU Coal-Extract Binder Pitch Content on Graphite Properties	34
8.0 Conclusions	37
9.0 References	37
Appendix A Green Stock	38
Appendix B Baked Stock	39
Appendix C Graphitized Stock	40

2.0 LIST OF FIGURES	Page
Figure 1 Simplified flow diagram of coal-extract binder production	17
Figure 2 Left, WVU coal-extract binder after dissolution and NMP solvent extraction of Bakerstown coal; Right, Bakerstown coal prior to extraction	18
Figure 3 Preparation of WVU coal-extract binder for shipment to Carbone.	18
Figure 4 Viscosity vs. temperature of WVU coal-derived binder and coal-tar pitch.....	26
Figure 5 Photograph of representative graphite billets.....	27
Figure 6 Coefficient of thermal expansion with vs. against the grain.....	28
Figure 7 Flexural strength with vs. against the grain.....	29
Figure 8 Resistivity with vs. against the grain.....	30
Figure 9 Effects of green apparent density on baked apparent density.....	31
Figure 10 Effects of baked density on graphite density.....	31
Figure 11 Effects of volume change on baked apparent density.....	32
Figure 12 Effect of green apparent density on baked and graphite density at 46 pph binder level.....	33
Figure 13 Effect of green apparent density on baked and graphite density at 50 pph binder level.....	33
Figure 14 Effects of binder pitch level on graphite density and CTE.....	34
Figure 15 Effects of WVU coal-extract binder content on graphite density and CTE.....	35
Figure 16 Effects of WVU coal-extract binder content on graphite density and resistivity	35
Figure 17 Effects of WVU coal-extract binder content on graphite density and strength.....	36
Figure 18 Effects of WVU binder pitch content on graphite density and hardness	36

3.0 LIST OF TABLES	Page
Table 1 Characteristics of bituminous coal.....	16
Table 2 Methods for measuring pitch properties.....	19
Table 3 Characteristics of as-received and calcined LCNN anthracite.....	23
Table 4 Comparison of WVU coal-extract binder with commercial binders...	24
Table 5 Elemental composition of WVU and coal tar binder pitches.....	25
Table 6 Composition and grade designation of test billets.....	27

4.0 EXECUTIVE SUMMARY

The primary ingredients in conventional synthetic graphite are calcined petroleum coke filler and coal-tar binder pitch, byproducts from petroleum refining and metallurgical coke manufacturing. There is motivation to find alternate sources of these materials because petroleum crudes are containing increasingly higher amounts of sulfur and metals, which are concentrated in cokes after carbonization of refinery residues. In addition, because of the diminishing demand for steel and, consequently, metallurgical coke, and stringent environmental regulations, adequate future domestic supplies of coal tar pitch are uncertain. Other sources of materials that can supplement, supplant, or augment fillers and binders used in synthetic graphite production are being sought. Thus, the focus of the present work was the fabrication and evaluation of isostatically-molded graphite made entirely from coal feeds: calcined anthracite used as filler and coal extract used as binder pitch.

Pennsylvania anthracite (Lehigh Coal and Navigation, LCNN) was chosen based on its ability to graphitize under laboratory conditions. The anthracite was calcined up to 1,427°C and then milled to an average particle size of about 27µm. The calcined anthracite had the following characteristics in weight percent: moisture, 0.09; ash, 8.76; volatile matter, 0.45; fixed carbon, 90.70; sulfur, 0.24.

A West Virginia bituminous coal (Bakerstown, WVGS 13407) was extracted batch-wise in tetralin at 450°C for two hours. The coal product was dissolved in the organic solvent N-methyl pyrrolidone (NMP) followed by centrifugation to remove mineral matter and unconverted coal. After removal of NMP, the pitch-like product had a Mettler softening point of 112.2°C, coking value of 50.3wt%, ash content of 0.2wt%, and density of 1.25g/cm³. These qualities are not outside the realm of commercial binder pitches. Enough coal was processed until about 29kg of coal-extract binder was made.

The calcined anthracite and coal-extract binder were sent to Carbone of America where they were mixed, isostatically molded into 5x5x12 inch billets, baked, and then graphitized up to 2,700°C. A variety of mixes at different binder levels was examined. Formulations with conventional calcined petroleum coke and standard coal-tar pitch were used as controls. The green, baked, and graphitized stock were subjected to conventional testing protocols.

The results show that substituting anthracite for petroleum coke or the coal-extract binder for coal-tar pitch generally produced billets with lower green, baked, and graphitized densities than the corresponding controls. When both coal-derived materials were used together the effects were accentuated. Examination of the results show that high density, from the green through the graphitized stage, is required for optimal performance. Nevertheless, without any effort at optimization, all of the coal-based billets graphitized successfully. With further refinement, it might be possible to develop all-coal graphite suitable for special applications.

5.0 INTRODUCTION

A goal of the CPCPC is to develop coal-based products of high value. To meet this goal, efforts are being undertaken to examine whether coal and coal extracts can perform satisfactorily as both pitch binders and precursors for coke fillers, two key ingredients in the manufacture of industrial carbons. The current project is timely in that the DOE and the CPCPC have recognized the need for carbon-product precursors that do not rely solely on sources traditionally obtained from the byproduct recovery coke oven and the petroleum delayed coker.

In previous CPCPC-sponsored work, a bituminous coal was hydrogenated and solvent extracted to produce a pitch-like material low in mineral matter and sulfur content. The results of blending the coal-derived pitch with conventional coal-tar pitch in the fabrication of laboratory carbon anodes indicated that coal extracts can perform satisfactorily as binders⁽¹⁾. In another CPCPC project coal extracts were successfully evaluated for both pitch binders and coke fillers in the laboratory testing of an all coal-derived carbon anode⁽²⁾.

The CPCPC has also sponsored work to examine the use of anthracite filler material in synthetic graphite manufacture⁽³⁾. In laboratory testing, it was determined LCNN (Pennsylvania) anthracite exhibited a high propensity to graphitization as determined by the sharpness of the characteristic (002) peak for graphite. The anthracite was used as filler with a conventional coal-tar pitch binder to produce graphite test specimens. Evaluation of the resultant billet showed that the anthracite-based product falls in the range of specifications for specialty graphite. Thus, the current effort is a

natural extension of previous successes and has as its goal the development of an all coal-derived isotropic graphite made from coal-extract binder and anthracite filler.

6.0 EXPERIMENTAL

6.1 Preparation of Coal-Extract Binder

A West Virginia bituminous coal was selected for extraction. Characteristics of the coal are provided in Table 1. About 55kg of as-received coal was ground in a hammer mill to about 20 mesh (Tyler sieve) top size and then dried in a vacuum oven overnight under a nitrogen purge at 100°C to remove excess moisture. The dried coal was then sealed in 4L glass bottles and stored under refrigeration until ready for use.

Coal-derived pitches were produced in batches by placing 600g of coal along with 1.5L of tetralin into a pair of 1gal reactors. Similarly, 3kg of coal along with 7.5L of tetralin were added to a 5gal reactor. For all reactions, the tetralin to coal mass ratio was approximately 2.5. Each reactor was purged of air with hydrogen gas and then pressurized hydrogen at room temperature to 400psig with molecular H₂. The reactor contents were stirred while heating and brought to 450°C for 2 hours. Following reaction the reactors were cooled overnight to room temperature and vented. The products were removed from each reactor and combined in a holding vessel. The contents of the holding vessel were then transferred to a pilot-size rotary evaporation apparatus to remove tetralin from the dissolved coal. Afterward, enough N-methyl pyrrolidone (NMP) was added to form a low-viscosity slurry and stirred for about 2 hours at 110°C. The mixture was transferred to 750mL centrifuge bottles and centrifuged for 1 hour at

Table 1. Characteristics of bituminous coal.

West Virginia Geological Survey Designation	WVGS 13407
Coal Bed	Bakerstown
State County	West Virginia Barbour
ASTM Rank	h _v Ab
Mean-Max Vitrinite Reflectance	1.059
Proximate Analysis, as received	
Moisture	0.68
Fixed Carbon	55.15
Volatile Matter	28.23
Ash	15.94
Petrographic Composition, vol%	
Vitrinite	59.6
Exinite	3.9
Inertinite	27.0

2000 times the force of gravity (2000G) to separate unconverted coal and other insoluble material. The supernatant liquid was decanted and placed in the pilot-scale rotary evaporator to remove the NMP. Finally, the coal-derived product was placed in a vacuum oven at about 150°C overnight while maintaining a slow purge of nitrogen. The process of coal and NMP-solvent extraction was repeated until about 29kg of coal-extract binder was made. Figure 1 is a block flow diagram of the process steps followed.

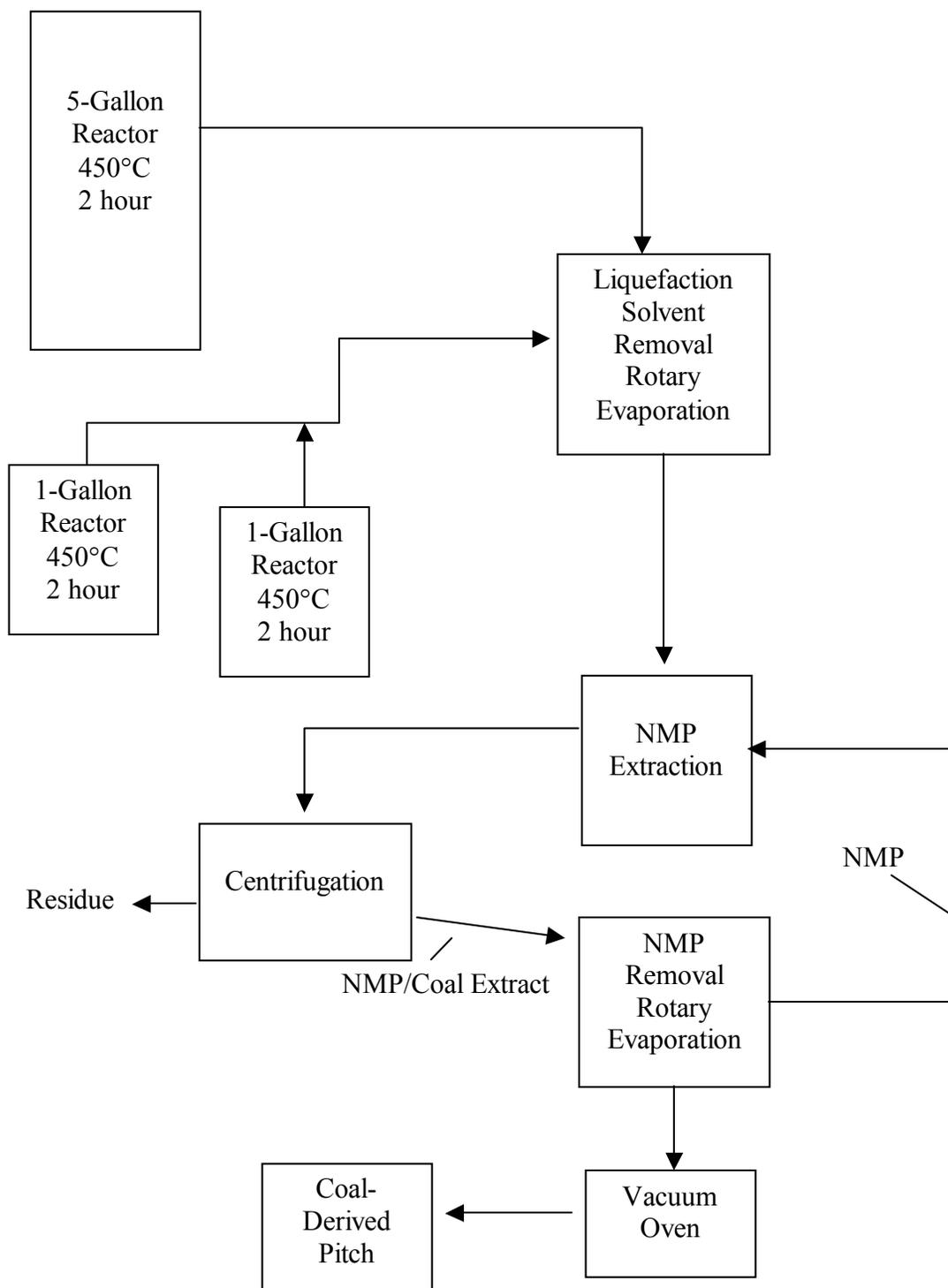


Figure 1. Simplified flow diagram of coal-derived pitch production.



Figure 2. Left, WVU coal-extract binder after dissolution and solvent extraction of Bakerstown coal; Right, Bakerstown coal prior to extraction.



Figure 3. Preparation of WVU coal-extract binder for shipment to Carbone.

6.2 Characterization Methods for Coal-Extract Binder

The WVU coal-extract binder was evaluated according to the testing methods listed in Table 2. The softening point was determined in duplicate using a Mettler FP80HT central processor and a Mettler FP83HT dropping cell apparatus. The sample holder was laden with sample and heated on a hot plate until melting occurred. Additional pitch was added until the sample holder was filled. The specimen was inserted into the Mettler apparatus initially warmed to 80°C and then heated at 2°C/min. The softening point was determined to be the temperature at which the pitch sample flowed a prescribed distance through the orifice on the bottom of the sample holder. Interruption of a light beam by the pitch was detected and displayed automatically as the softening point temperature.

Table 2. Methods for measuring pitch properties.

Characterization	Method
Softening Point, °C	ASTM D 3104
Toluene Insolubles, wt%	Soxhlet Extraction
Conradson Carbon, wt%	ASTM D 189
Density, g/cm ³	ASTM D 4892
Ash Content, wt%	ASTM D 2415
Viscosity, cP	ASTM D 5018
C, H, S, N Content, wt%	In-House Elemental Analyzer

Toluene insoluble content was determined in duplicate using a Soxhlet extraction procedure. About 5 grams of <20 Tyler mesh pitch were digested by stirring in 150-200mL of hot toluene for 30 minutes. The mixture was poured into a tared ceramic extraction thimble while at the same time allowing the soluble portion to drain into a tared 250mL Pyrex round-bottom flask. The ceramic thimble was inserted into the Soxhlet apparatus and a water-cooled condenser attached to the top of the unit. The

round-bottom flask was placed on a heating mantle and fitted to the Soxhlet extractor. Extractions were carried out at the normal boiling point of toluene until the toluene condensate was nearly colorless, usually about 12-16 hours. Following extraction, the toluene was removed from the soluble portion by rotary evaporation and then dried in a vacuum oven, along with the ceramic thimble containing the toluene insolubles, overnight at about 150°C. The percentage of toluene insolubles was calculated using the following equation:

$$\% \text{Toluene Insoluble} = \frac{[(\text{weight thimble} + \text{weight insoluble}) - (\text{weight thimble})]}{(\text{weight pitch})} \times 100$$

The Conradson carbon test is a measure of the amount of solid coke a particular tar or pitch material will produce after heating under standardized conditions and environment. In this test the sample was heated to a high temperature using a gas-fired burner. A high flame was directly applied to a tared porcelain crucible that contains a sample of pitch for 11.5 minutes in order to drive off volatiles and tars. The burner was positioned to burn the emanating matter with a moderate flame for 13 minutes. Finally, the specimen was again subjected to high flame directly for 7 minutes. After cooling to room temperature, the crucible and coke were weighed. On duplicate runs, the Conradson carbon residue was determined using the following equation:

$$\% \text{Conradson Carbon} = \frac{[(\text{weight crucible} + \text{coke}) - (\text{weight crucible})]}{(\text{weight pitch})} \times 100$$

Density is useful in characterizing and specifying the properties of pitches as an aid in the selection of their potential application. The density of the pitch was determined by a Micromeritics AccuPyc 1330 Helium Pycnometer. A sample of pitch was ground to pass through a 2.36mm sieve. The fines were then removed by passing through 0.6mm sieve and the material collected on this sieve was used for density testing. After calibration of the pycnometer, a known weight of pitch was loaded into the instrument. The density and the standard deviation of five runs were obtained.

The ash in pitch is the inorganic oxides of the mineral matter found after the pitch is combusted in air under standard conditions. The ash is considered as an impurity for most carbon products. In duplicate determinations, about 1 gram of pitch was placed in a tared porcelain crucible and the sample set inside of a temperature-programmable furnace equipped with a fan for the circulation of air. The furnace was programmed to heat at 8°C/min to 500°C and then 4°C/min to 900°C. The sample was then maintained at that temperature for 2 hours. After cooling, the sample was weighed to determine ash content according to the following equation:

$$\% \text{ Ash} = \frac{[(\text{weight crucible} + \text{ash}) - (\text{weight crucible})]}{(\text{weight of pitch})} \times 100$$

Viscosity of the pitch was determined by a Brookfield Model DV-III Programmable Rheometer. Approximately 10 grams of pitch were placed in the sample holder. The holder was placed into the heating cell and purged with an inert gas. The sample was heated to approximately 20°C above its Mettler softening point temperature.

Once thermal equilibrium was achieved, the viscosity was determined over the largest possible shear-rate range. This process was repeated for higher temperatures at 10°C increments. The average viscosity at each shear rate was calculated using computer software supplied by the manufacturer of the instrument.

The elemental composition of the pitch was determined by a ThermoQuest Flash EA 1112 elemental analyzer. A 1-3mg of sample was encapsulated in a tin-foil cup. The mass of the sample was recorded and the specimen placed in the autosampler. The instrument then dropped the sample cup into an oxygen-filled combustion reactor in which the pitch was converted into carbon dioxide, water, nitrogen oxides, and sulfur trioxide. The oxides of nitrogen and sulfur were reduced catalytically to molecular nitrogen and sulfur dioxide. The gases then were conveyed to a chromatographic column for separation and quantification. The combustion products were detected by a thermal conductivity detector to give percentages of nitrogen, carbon, hydrogen, and sulfur. Three determinations were conducted and the average composition reported.

6.3 Preparation and Characteristics of LCNN Anthracite Filler

Approximately 1 ton of the LCNN anthracite was calcined to between 1,315 and 1,427°C by NAC Carbon in Punxsutawney, PA. The calcined anthracite was then milled by Asbury Graphite in Kittanning, PA to an average particle size of 27.4µm. The median particle was determined to be 23.3µm. Characteristics of the as-received and calcined anthracite are provided in Table 3.

Table 3. Characteristics of as-received and calcined LCNN anthracite.

Weight Per Cent	As-Received LCNN	Calcined LCNN
%Moisture	2.26	0.09
%Ash	7.08	8.76
%Volatile Matter	30.61	0.45
%Fixed Carbon	87.05	90.70
%Sulfur	--	0.24

6.4 Preparation of the Isostatically-Molded Graphite Specimens

Carbone of America in St. Marys, PA processed the anthracite into graphite test specimens. A conventional coal-tar binder pitch (110°C softening point) and a calcined petroleum coke were used as control feed materials. The appropriate proportion of filler and binder was stirred at 150°C in a mixer for 2 to 3 hours. The blend was cooled to room temperature and then pulverized in a mill to 100µm top size. The material was transferred to a mold and isostatically pressed up to 20,000psi for 2h at 25C to form a green billet. The billet was removed from the mold and placed in a sagger with silica sand used as packing. Thirty days was required to reach a temperature of 950°C during baking of the green billet. Finally, the baked billets were heated to 2,700°C by inductive graphitization over a period of 1 to 2 days. The green, baked, and graphitized billets were weighed and their geometric dimensions measured. The volume of each billet was determined by a water displacement method. Carbone conducted evaluation and characterization tests using established industrial methods the results of which are tabulated in the appendices.

7.0 RESULTS AND DISCUSSION

7.1 Characteristics of the WVU Coal-Extract Binder Pitch

Table 4 compares some of the properties of the WVU coal-extract binder with commercially available binder pitches. Because of the processing steps involved in the manufacture of the WVU binder to remove ash forming material and other solids, the quinoline insoluble content is generally low⁽⁴⁾. Also, the softening point temperature of the WVU coal-extract binder as well as its ash content and coking value compare favorably to the other binder pitches.

Table 4. Comparison of WVU coal-extract binder with commercial binders.

	WVU Coal- Extract Binder	Coal-Tar Pitch	Petroleum Pitch	General Pitch Specifications
Softening Pt, °C	112.2	110.2	120.9	108-115
Toluene Insol wt%	32.7	27.2	4.05	24 min
Quinoline Insol wt%	nil	13.2	0.26	8-17
Coking Value, wt%	50.3	57.1	50.5	53 min
Ash Content, wt%	0.2	0.19	0.02	5 max
Density, g/cm ³	1.25	1.33	1.23	1.30 min

Table 5 provides the elemental analyses for the WVU coal-extract binder and a conventional coal-tar binder pitch. Because of the extreme temperature conditions in the recovery coke oven, coal-tar binder pitches are high in carbon and low in hydrogen contents, as indicated by its high carbon-to-hydrogen atomic ratio. The WVU coal-

extract binder is lower in nitrogen and slightly higher in sulfur compared to the conventional coal tar pitch.

Table 5. Elemental composition of WVU coal-extract and coal-tar binder pitches.

Element, wt%	WVU Coal-Extract Binder	Coal-Tar Pitch
C	87.7	93.5
H	6.1	4.3
N	1.7	2.3
S	1.0	0.71
C/H atomic	1.21	1.81

Figure 4 shows the viscosity versus temperature of the WVU coal-extract binder. A conventional coal-tar binder pitch is included for comparison. Despite similar softening points, the WVU coal-extract binder exhibits appreciably higher viscosity at temperatures below 185°C.

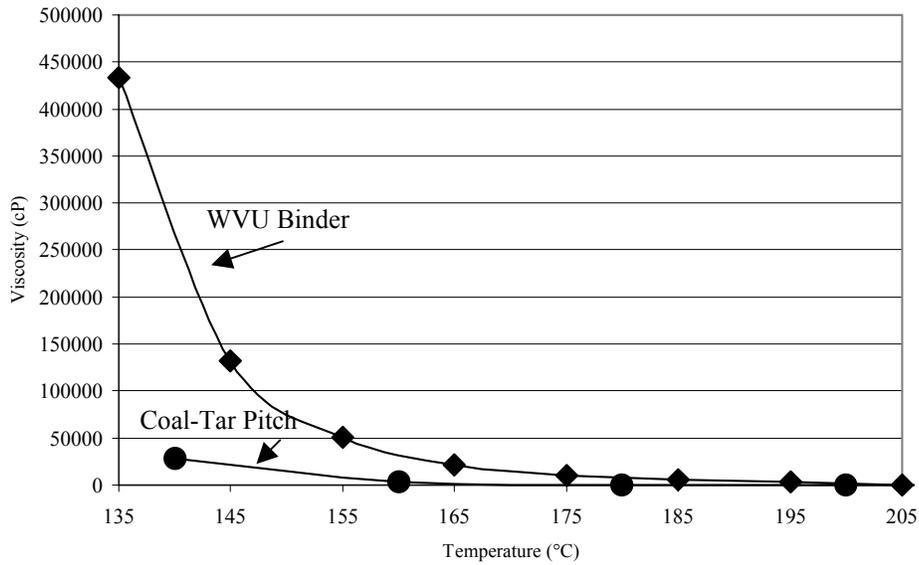


Figure 4. Viscosity vs. temperature of WVU coal-extract binder and coal-tar pitch.

7.2 Characteristics of the Isostatically-Molded Graphite Specimens

A total of eight graphite samples were produced. Table 6 outlines the mix composition and molding plan undertaken in the fashioning of 5 x 5 x 12-inch billets using the coal-extract binder pitch and calcined LCCN anthracite. Details on the measured properties of the green, baked, and graphitized stock are provided in Appendices A, B, and C, respectively. Grade P42 is a control sample, consisting of calcined petroleum coke and coal-tar binder pitch at the lower binder pitch level, while Grade P46 is the control sample at the higher binder pitch level.

Table 6. Composition and grade designation of test billets.

Grade ID	Calcined Anthracite (AN)	Calcined Petroleum Coke (PC)	WVU Coal-Extract Binder Content (WVU), pph	Coal-Tar Binder Pitch Content (CTP), pph
P40	X			46
P41	X		46	
P42		X		46
P43	X		48	
P44	X		50	
P45		X	50	
P46		X		50
P47	X		52	

pph = parts per hundred



Figure 5. Photograph of representative graphite billets.

7.3 Confirmation of Isotropy

Ideally isostatic-molding procedures impart no preferred orientation in bulk properties. In other words density, resistivity, coefficient of thermal expansion (CTE), and other properties should not vary throughout the dimension of the graphite specimen. Nevertheless, in practice, the long dimension of the billet is designated as “against the grain” and the cross section dimension as “with the grain”.

Verification of isotropy is evident by examining some pertinent data. For example Figure 6 shows the CTE with and against the grain for all of the graphite samples. It can be seen that the data points lie very nearly on a straight line. A similar linear relationship is also depicted when examining flexural strength as shown in Figure 7.

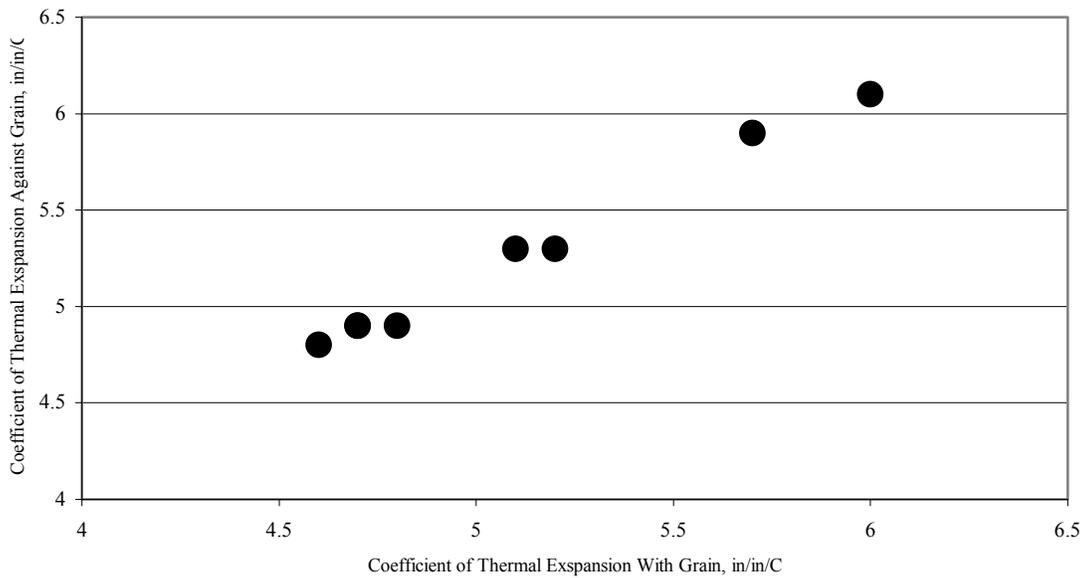


Figure 6. Coefficient of thermal expansion with vs. against the grain.

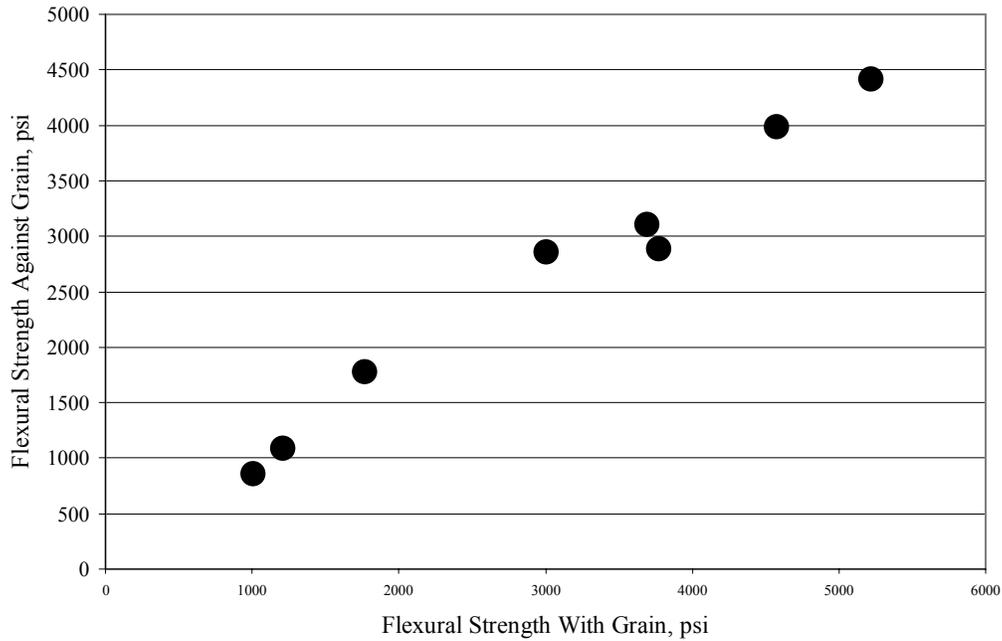


Figure 7. Flexural strength with vs. against the grain.

Isotropic behavior is also evident in the resistivity of the graphites as shown in Figure 8. However, the resistivity of sample Grade P42 is highly anisotropic. It is not clear at this time the origin of the discrepancy. Since the other measurements of Grade P42 indicate that isotropy is established, the resistivity result might be the consequence of an anomalous measurement.

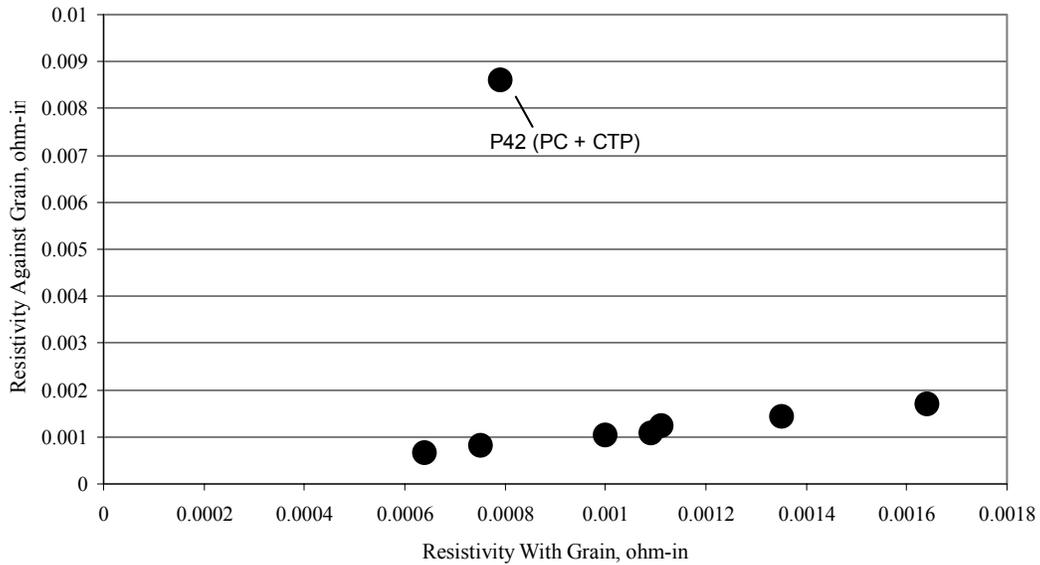


Figure 8. Resistivity with vs. against the grain.

7.4 Examination of Overall Billet Properties

Figure 9 shows how green apparent density affects the density of the billets after the bake cycle. The development of high density at the green article stage is essential since many of the resultant properties are determined at this point and are carried over during graphitization, as shown in Figure 10. The results indicated in Figure 11 suggest that density is at least in part related to shrinkage or dimensional changes. Moreover, physical attributes such as flexural strength, Rockwell and Shore hardness increase as the density of the graphite increase, Appendix C.

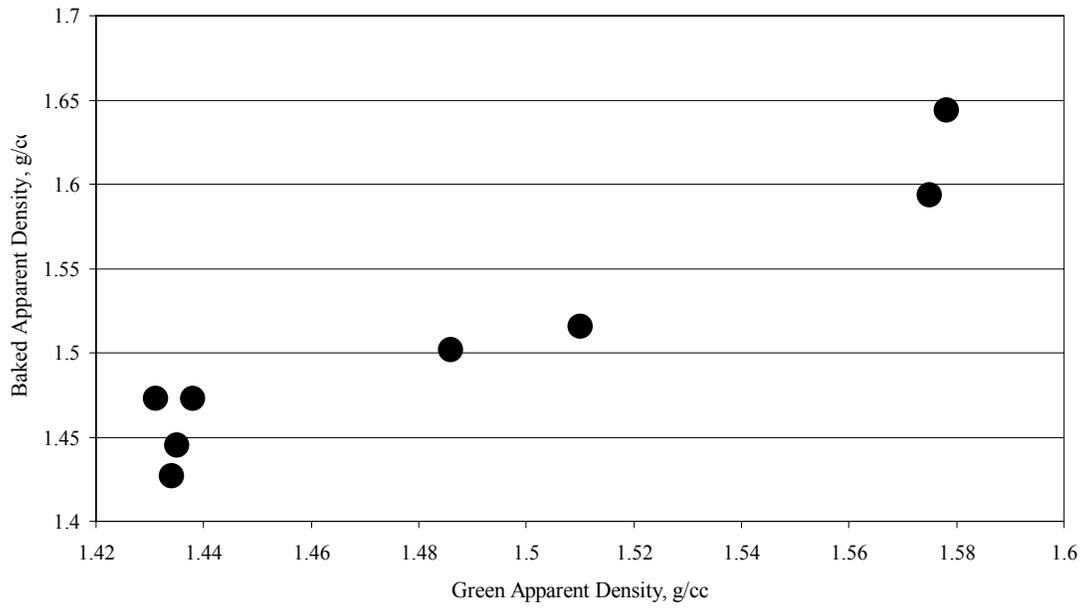


Figure 9. Effects of green apparent density on baked apparent density.

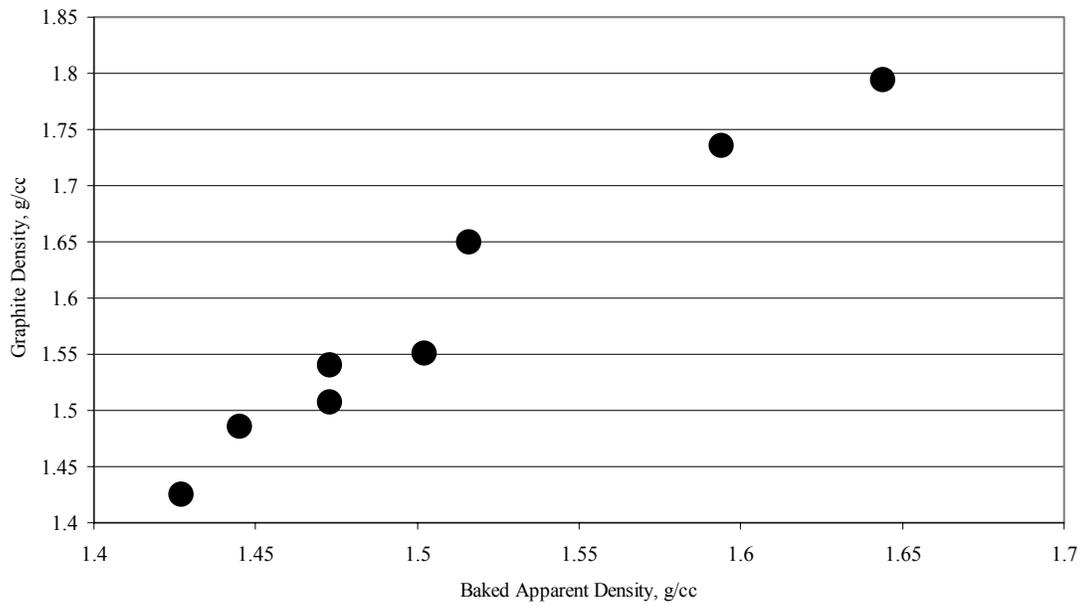


Figure 10. Effects of baked density on graphite density.

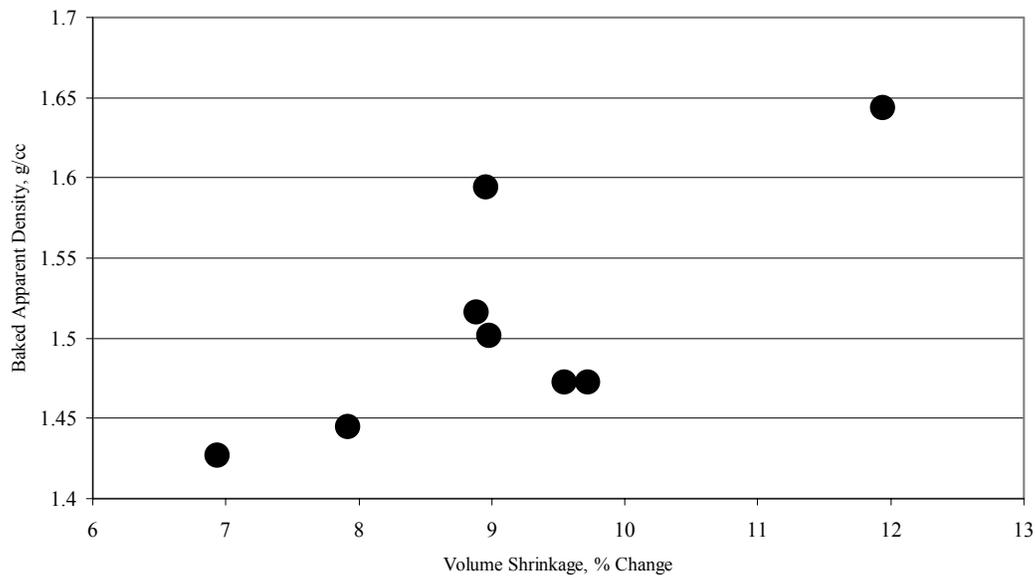


Figure 11. Effects of volume change on baked apparent density.

7.5 Characteristics of Billets at 46 and 50pph Binder Pitch Level

Conventional coal-tar binder pitch contains solids known as quinoline insoluble (QI) matter. This material consists of soot-like particles, ash, and other solids entrained in the carbonization products during the production of metallurgical coke. The presence of QI leads to binder pitches with densities greater than would be possible had the QI been removed. Since the WVU coal-extract binder has no QI because of processing, it is not unexpected that the green apparent density of Grade P40 (CTP binder) is greater than Grade P41 (WVU binder) using the same anthracite filler, as shown in Figure 12. Reduction in green density is more pronounced when the anthracite and WVU binder are combined together compared to the standard formulation, Grades P41 and P42, respectively. The observation indicates that the calcined anthracite is significantly less dense than the calcined petroleum coke. As noted previously, low green densities result

in low baked and graphite densities. Similar conclusions can be made at the 50pph binder pitch level, Figure 13.

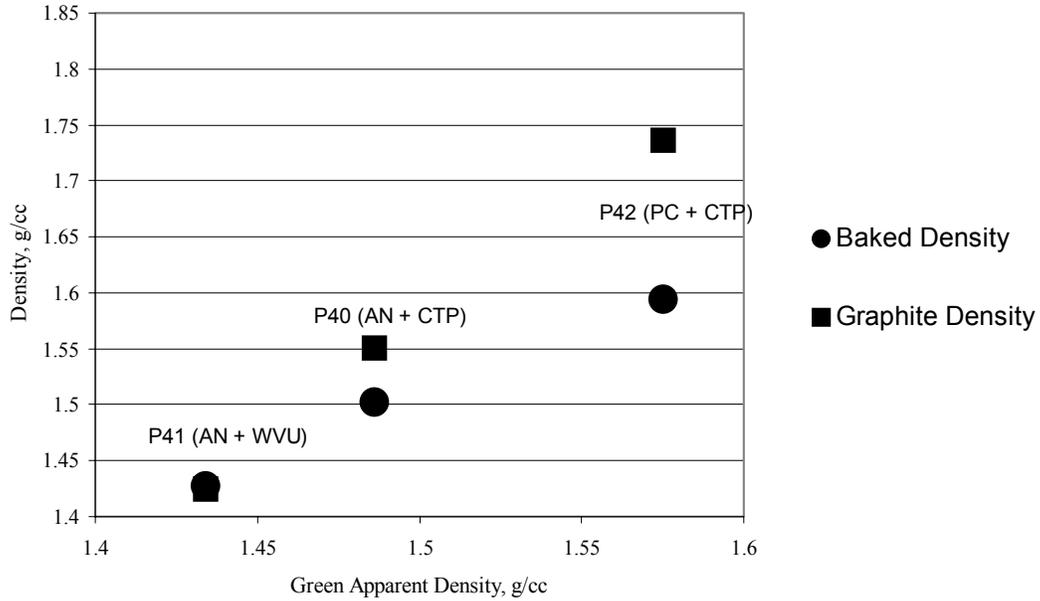


Figure 12. Effect of green apparent density on baked and graphite density at 46 pph binder level.

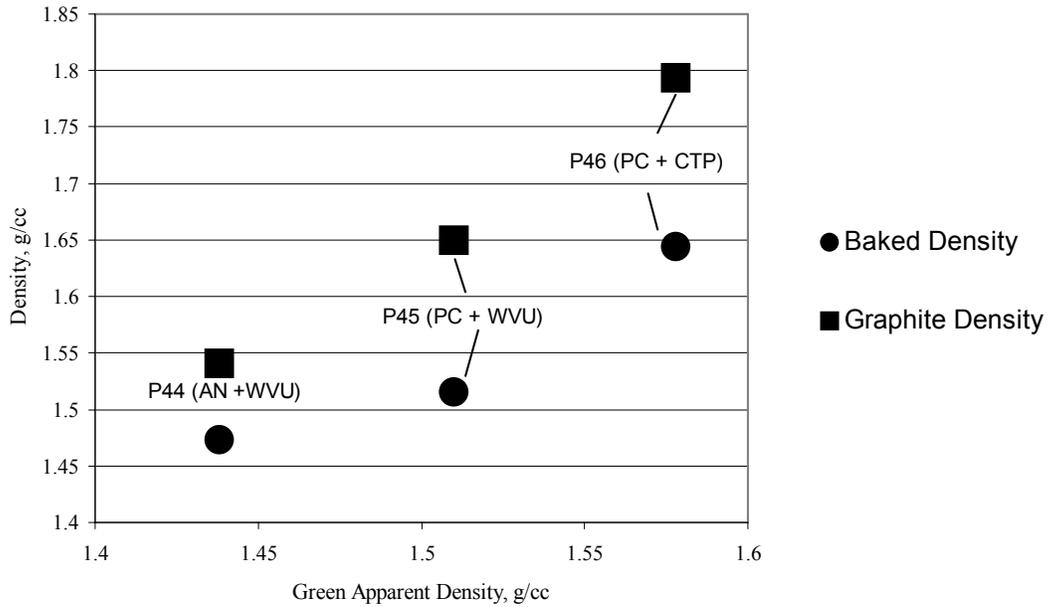


Figure 13. Effect of green apparent density on baked and graphite density at 50 pph binder level.

For a given filler material, the effect of increasing the binder level from 46 to 50 pph in general increases green apparent, baked, and graphite density, reduces resistivity, and increases strength and hardness. As illustrated in Figure 14, the effect of increasing binder level is seen also to increase the coefficient of thermal expansion.

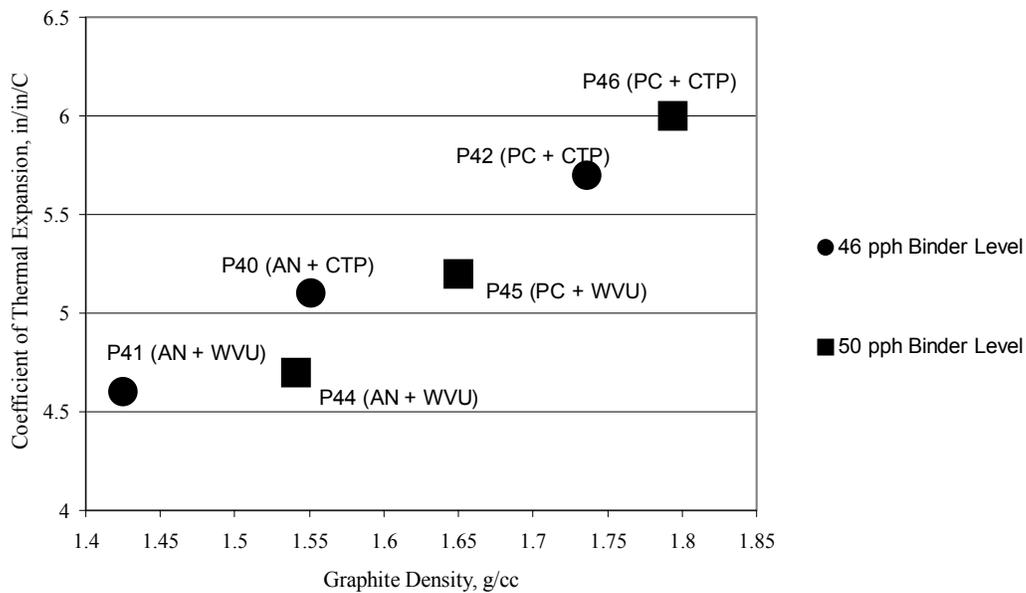


Figure 14. Effects of binder pitch level on graphite density and CTE.

7.6 Effects of WVU Coal-Extract Binder Content on Graphite Properties

The graphite Grades P41, P43, P44, and P47 were made with WVU coal-extract binder at different levels using the calcined anthracite as filler. Increasing the binder level from 46 to 52pph shows that there is a maximum in CTE at the 52pph WVU binder level, Figure 15. On the other hand Figure 16 shows a minimum in resistivity at the 52 pph binder level. Although there is a considerable range of graphite density, the affect of

the WVU binder pitch content is only slight on the CTE and resistivity values in absolute terms.

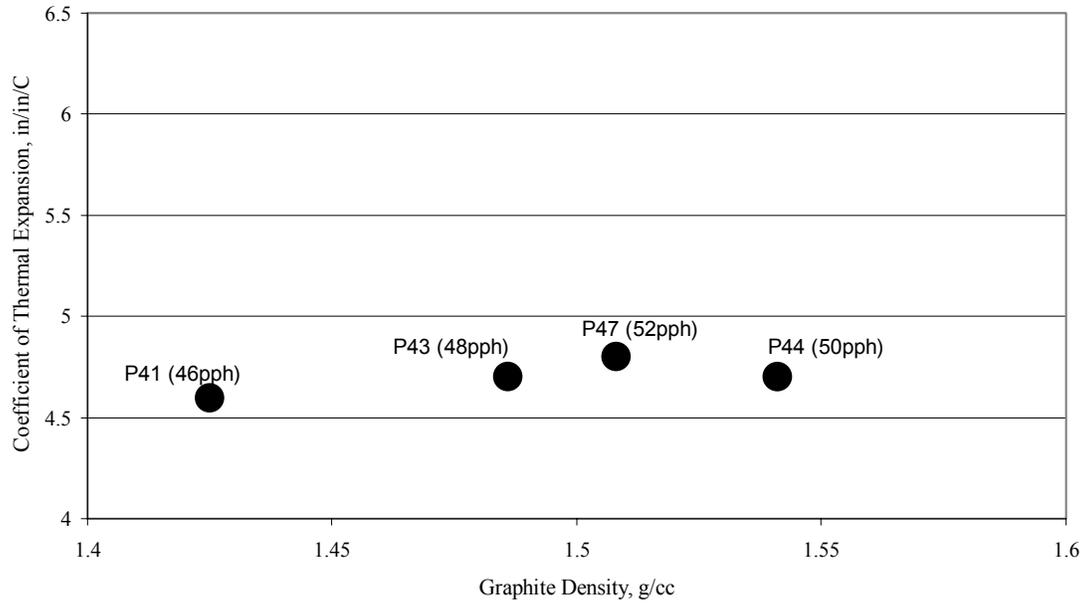


Figure 15. Effects of WVU coal-extract binder content on graphite density and CTE.

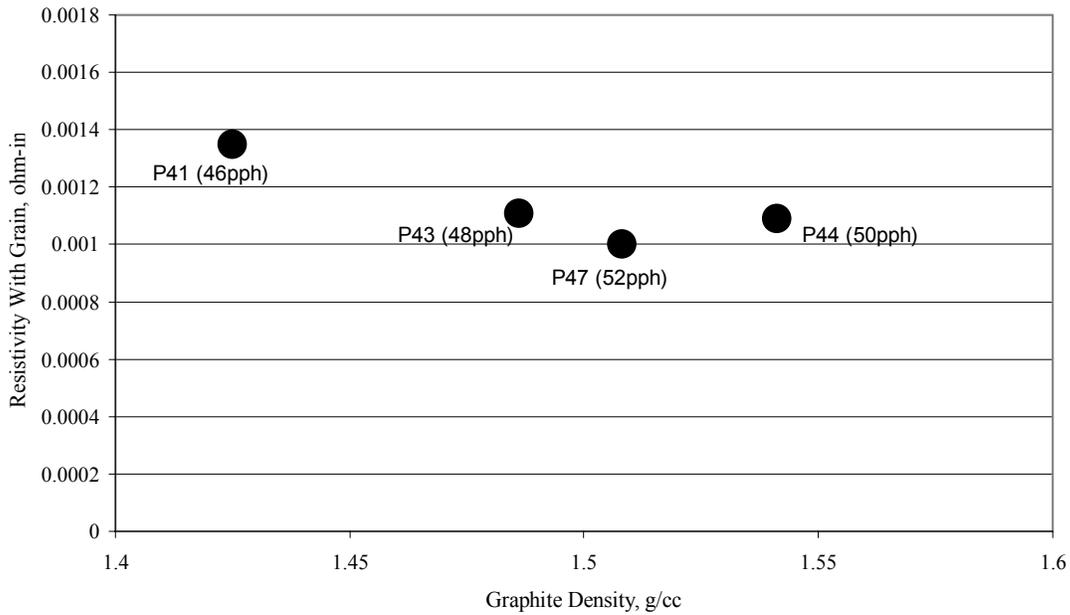


Figure 16. Effects of WVU coal-extract binder content on graphite density and resistivity.

The effects of varying the WVU coal-extract binder content are most prevalent on the mechanical properties coal-based graphites. Figures 17 and 18 show that the greatest flexural strength and hardness are obtained at the intermediate WVU binder level of 50pph.

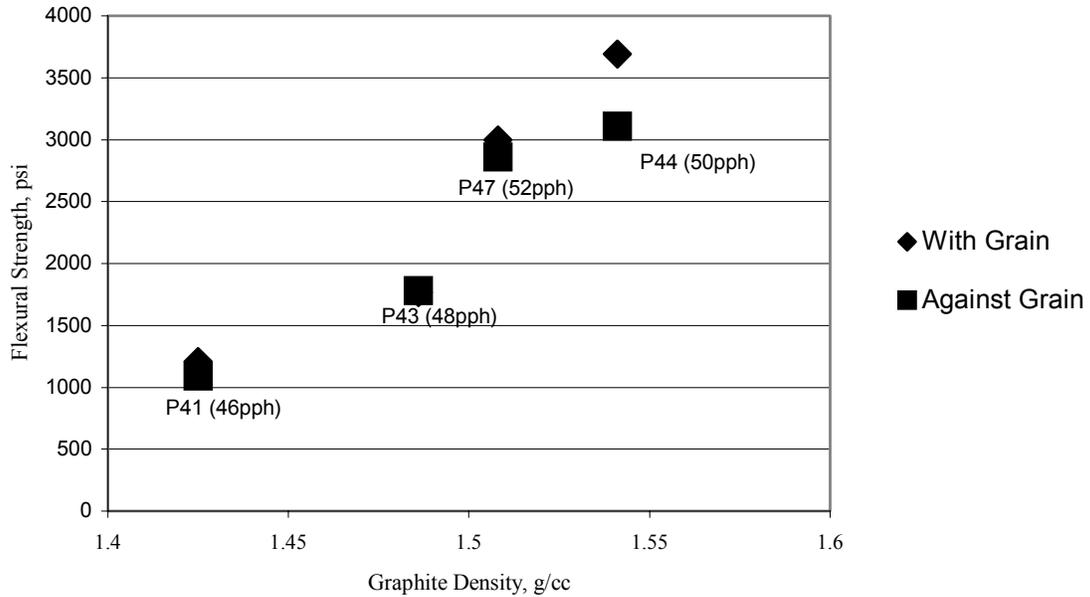


Figure 17. Effects of WVU coal-extract binder content on graphite density and strength.

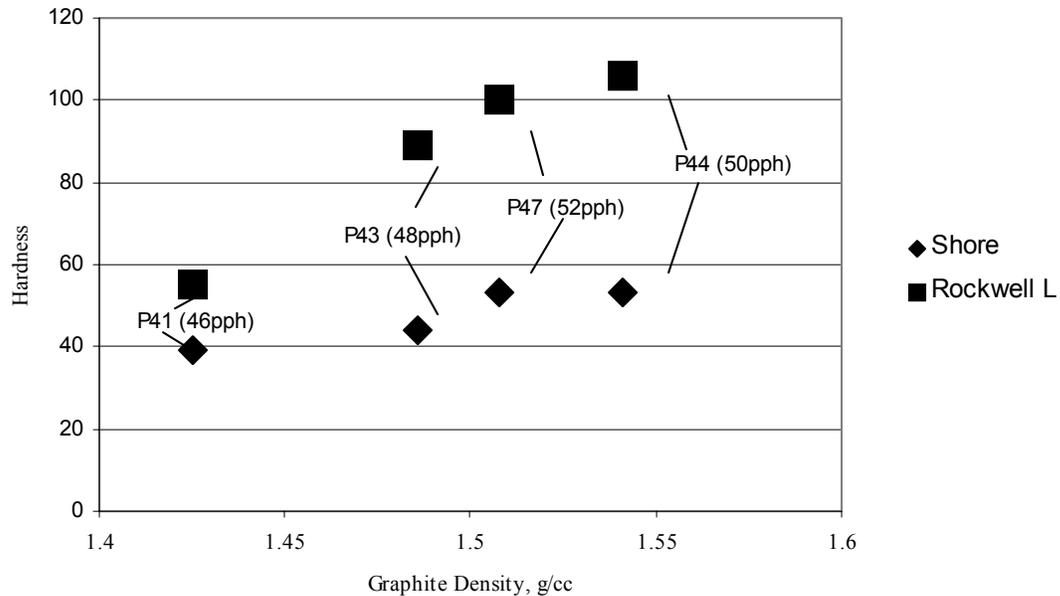


Figure 18. Effects of WVU coal-extract binder content on graphite density and hardness.

8.0 CONCLUSIONS

A series of isostatically-molded graphite was successfully fabricated using coal-extract as a binder pitch and calcined anthracite as filler. Control specimens were also made from calcined petroleum coke and conventional coal tar binder pitch at two binder levels. The results of this work demonstrate that synthetic graphite is possible based on feed materials entirely from coal. In many respects the overall characteristics of the coal-based graphites did not meet or exceed the corresponding products made from conventional feeds, vis-à-vis, petroleum coke and coal tar pitch. However, this initial work clearly demonstrates that properties of all-coal graphites could be dramatically improved after optimization of the feed material. The results indicate that considerable improvements to the coal-based materials might be possible especially as they relate to the development of increased density during the green state through graphitization.

9.0 REFERENCES

- 1) Stansberry, P. G., Zondlo, J. W., and Wombles, R. H., "Development of Binder Pitches from Direct Coal Liquefaction and Coal-Tar Pitch Blends," CPCPC final report to the U. S. DOE, contract DE-FC26-98FT40350, June 30, 2001.
- 2) Stansberry, P. G., Zondlo, J. W., Racunas, B., Wombles, R. H., "The Development of an All Coal-Derived Anode," DOE Award Number DE-FC26-98FT40350, Final Report April 15, 2002.
- 3) Pappano, P. J., Mathews, J. P., and Schobert, H. H., *Proc. Eurocarbon 2000*, 2000, **1**, 165.
- 4) Stansberry, P. G., Zondlo, J. W., and Wombles, R. H., "Development of Binder Pitches from Coal Extract and Coal-Tar Pitch Blends," *Light Metals*, 581-585, 2001.

Appendix A
Properties of Green Molded Stock

Green Stock													
Grade	Grade Composition				A			B		C		A/C	
	Calcined Anthracite	Calcined Petroleum Coke	WVU Binder	pph Coal Tar Binder	Dry Weight	Wet Weight	Volume	Wet Weight	Volume	Volume	Green Density	Green Density	1 cubic inch =
				grams	grams	cc	grams	cc	cc	g/cc	g/cc	inches	inches
P40	X			7280	2380	4900	1.486	4.9375	4.9375	1.486	4.9375	4.9375	12.125
P41	X		46	7860	2380	5480	1.434	5.125	5.0625	1.434	5.0625	5.0625	12.4375
P42		X	46	8440	3080	5360	1.575	5.0625	5.0625	1.575	5.0625	5.0625	12.5
P43	X		48	7980	2420	5560	1.435	5.0625	5.0625	1.435	5.0625	5.0625	12.8125
P44	X		50	8280	2520	5760	1.438	5.125	5.125	1.438	5.125	5.125	12.9375
P45		X	50	9180	3100	6080	1.51	5.25	5.25	1.51	5.25	5.25	13
P46		X	50	8460	3100	5360	1.578	5.0625	4.9375	1.578	5.0625	4.9375	12.8125
P47	X		52	8100	2440	5660	1.431	5.125	5.0625	1.431	5.125	5.0625	12.9375

Appendix B Properties of Baked Stock

		Baked Stock															
		Grade Composition															
Grade	Anthracite	Calcined	pph	pph	Baked												
		Petroleum Coke	WWU Binder	Coal Tar Binder	Density g/cc	Apparent Density	Width Shrinkage %	Thickness Shrinkage %	Length Shrinkage %	Weight Shrinkage %	Volume Shrinkage %	BAD Minus GAD					
P40	X			46	1.502		-2.532	-2.532	-3.608	7.967	8.98	0.016					
P41	X		46		1.427		-2.439	-1.235	-2.513	7.379	6.934	-0.007					
P42		X		46	1.594		-2.469	-2.469	-3.5	7.82	8.955	0.019					
P43	X		48		1.445		-2.469	-2.469	-2.927	7.268	7.914	0.01					
P44	X		50		1.473		-2.439	-2.439	-3.382	7.488	9.722	0.035					
P45		X	50		1.516		-2.381	-2.381	-3.365	8.497	8.882	0.006					
P46		X		50	1.644		-3.704	-3.797	-4.39	8.274	11.94	0.066					
P47	X		52		1.473		-2.439	-2.469	-3.865	6.914	9.541	0.042					

Appendix C Properties of Graphitized Stock

Grade	Grade Composition	Calcined	pph WWU	pph Coal Tar	Binder Pitch	Binder Pitch	Density A		Density C		Resistivity A		Resistivity C		Three Point Method		Flex Ratio	Hardness Shore L	Hardness Rockwell L	CTE A	CTE C	CTE Against Grain	CTE C/A	Ash wf%
							With Grain	Against Grain	With Grain	Against Grain	With Grain	Against Grain	With Grain	Against Grain	Flexural Strength A	Flexural Strength C								
P40	X				46		1.552	1.549	1.551	0.00075	0.00082	1.083	4573	3983	0.871	57	73	5.1	5.3	1	0.64			
P41	X				46		1.425	1.424	1.425	0.00135	0.00144	1.087	1207	1090	0.903	39	55	4.6	4.8	1	0.16			
P42		X			46		1.735	1.737	1.736	0.00079	0.00086	10.886	3770	2890	0.767	62	89	5.7	5.9	1	0.04			
P43	X				48		1.484	1.488	1.486	0.00111	0.00125	1.126	1763	1780	1.01	44	89	4.7	4.9	1	0.19			
P44	X				50		1.543	1.538	1.541	0.00109	0.00108	0.991	3693	3110	0.842	53	106	4.7	4.9	1	0.016			
P45		X			50		1.652	1.647	1.65	0.00164	0.00171	1.043	1007	857	0.851	47	81	5.2	5.3	1	0.019			
P46		X			50		1.795	1.792	1.794	0.00064	0.00067	1.047	5217	4413	0.846	66	102	6	6.1	1	0.014			
P47	X				52		1.503	1.512	1.508	0.001	0.00103	1.03	3000	2860	0.953	53	100	4.8	4.9	1	0.17			