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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DISCLAIMER

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.

Table of Contents

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 ASTRACT

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.

TABLE OF CONTENTS

2.0 LIST OF FIGURES

3.0 LIST OF TABLES

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	Ash, wt % dry	Volatile Matter, wt % dry
1.79	7.36	31.57

Carbon wt % dry	Hydrogen wt % dry	Nitrogen wt % dry	Sulfur wt % dry	Oxygen by difference
80.31	4.56	1.41	0.71	5.65

Vitrinite vol % mf	Liptinite vol % mf	Inertinite vol % mf	Mineral Matter vol % mf
57.2	8.3	30.3	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.

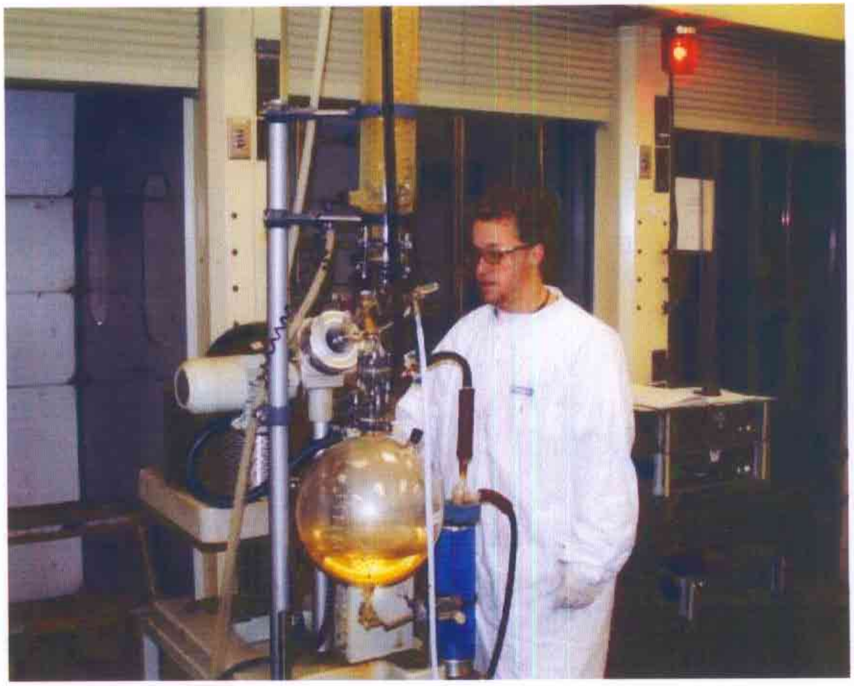

Figure 3. Rotary evaporation of NMP from coal extracts.

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.

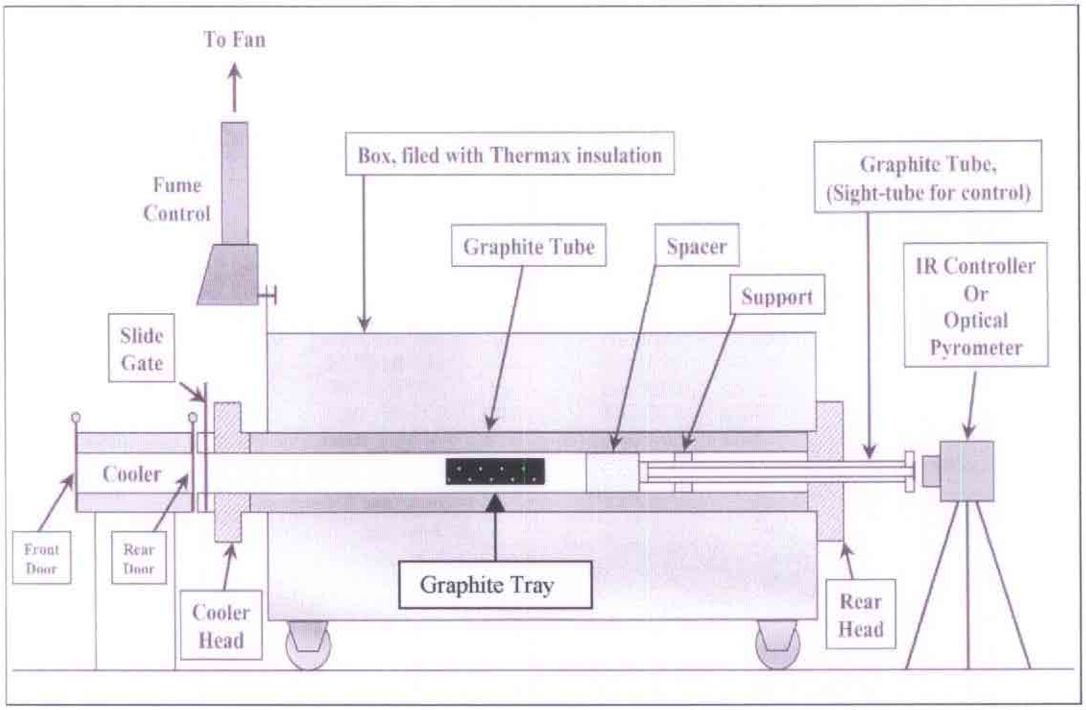

Figure 6. Schematic of the laboratory calciner.

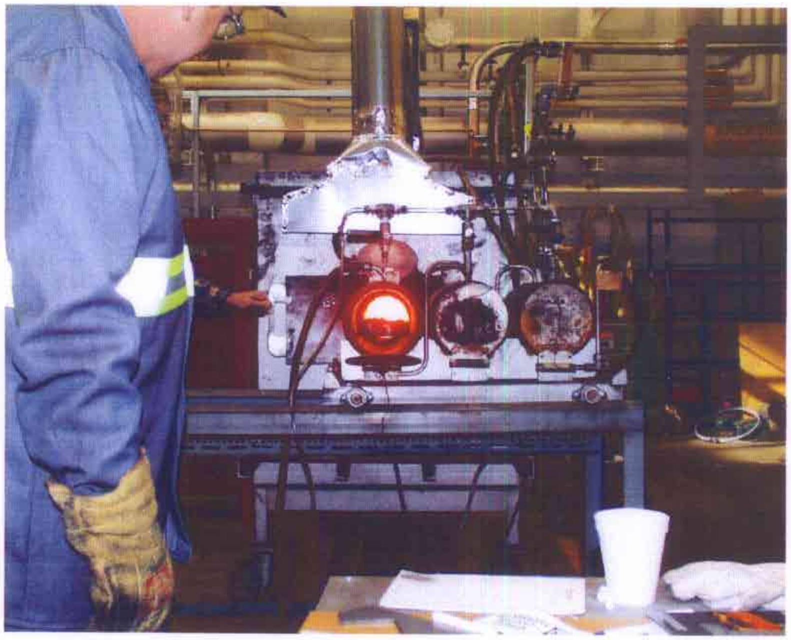

Figure 7. Insertion green coke into the hot zone of the laboratory calciner.

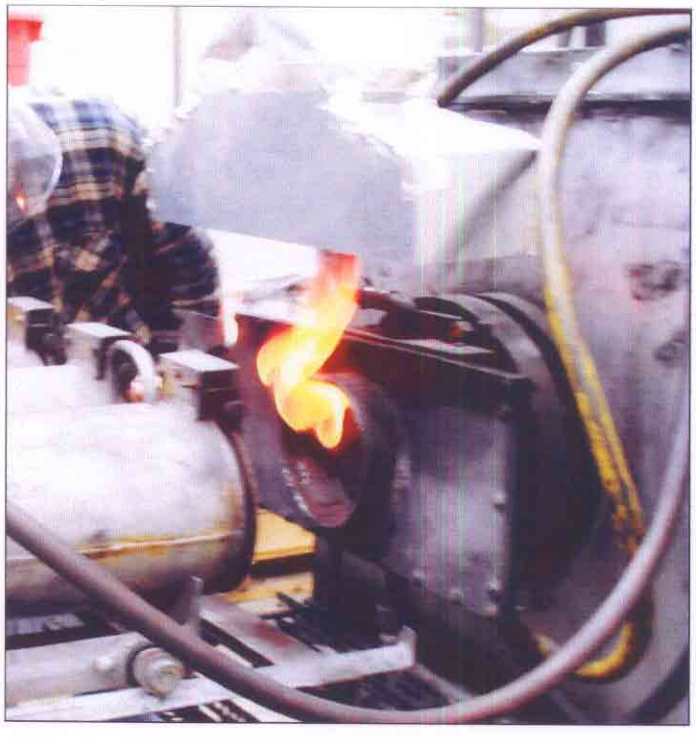

Figure 8. Flaring of coke volatiles during calcining operation.

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.

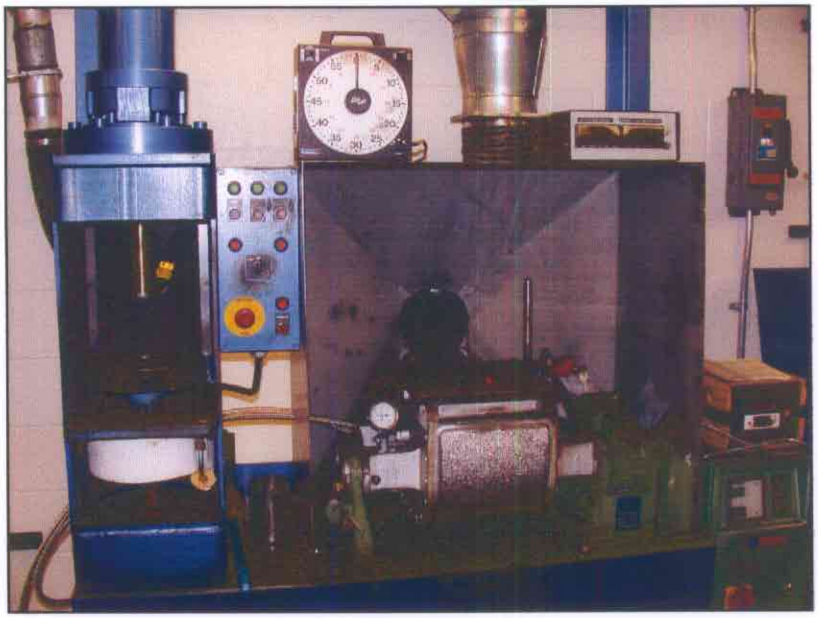

Figure 9. R&D Carbon RDC-161 Bench Scale Anode Paste Unit showing mixer (right) and test anode press (left).

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 isolated 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.

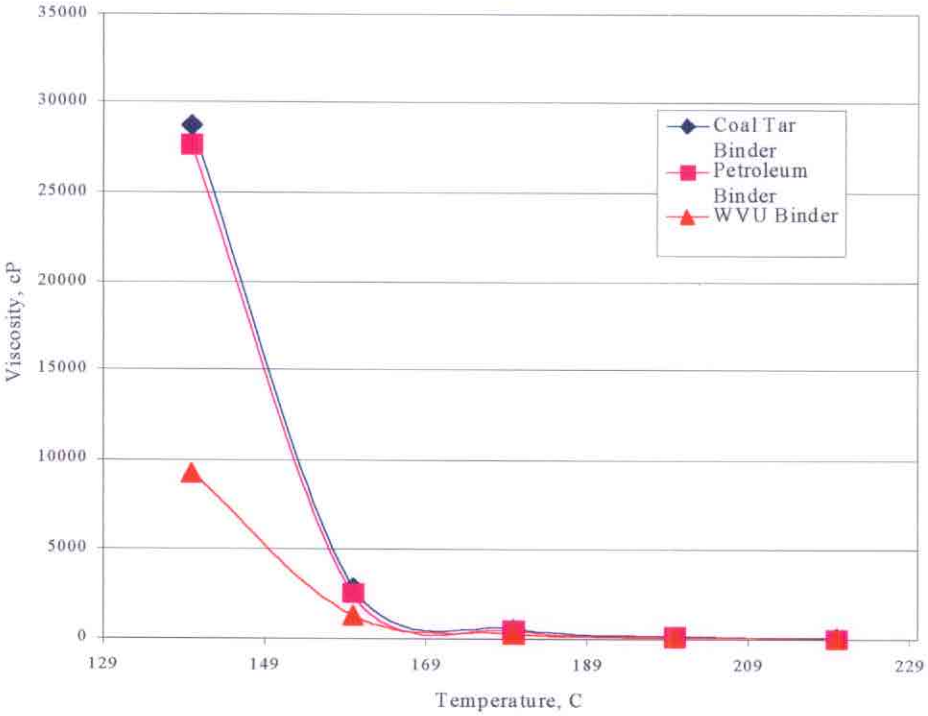

Figure 10. Viscosity as a function of temperature of selected binder pitches.

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.

				XRF								
Sample ID	HGI	Ash %	Vol %	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 calcincer. 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

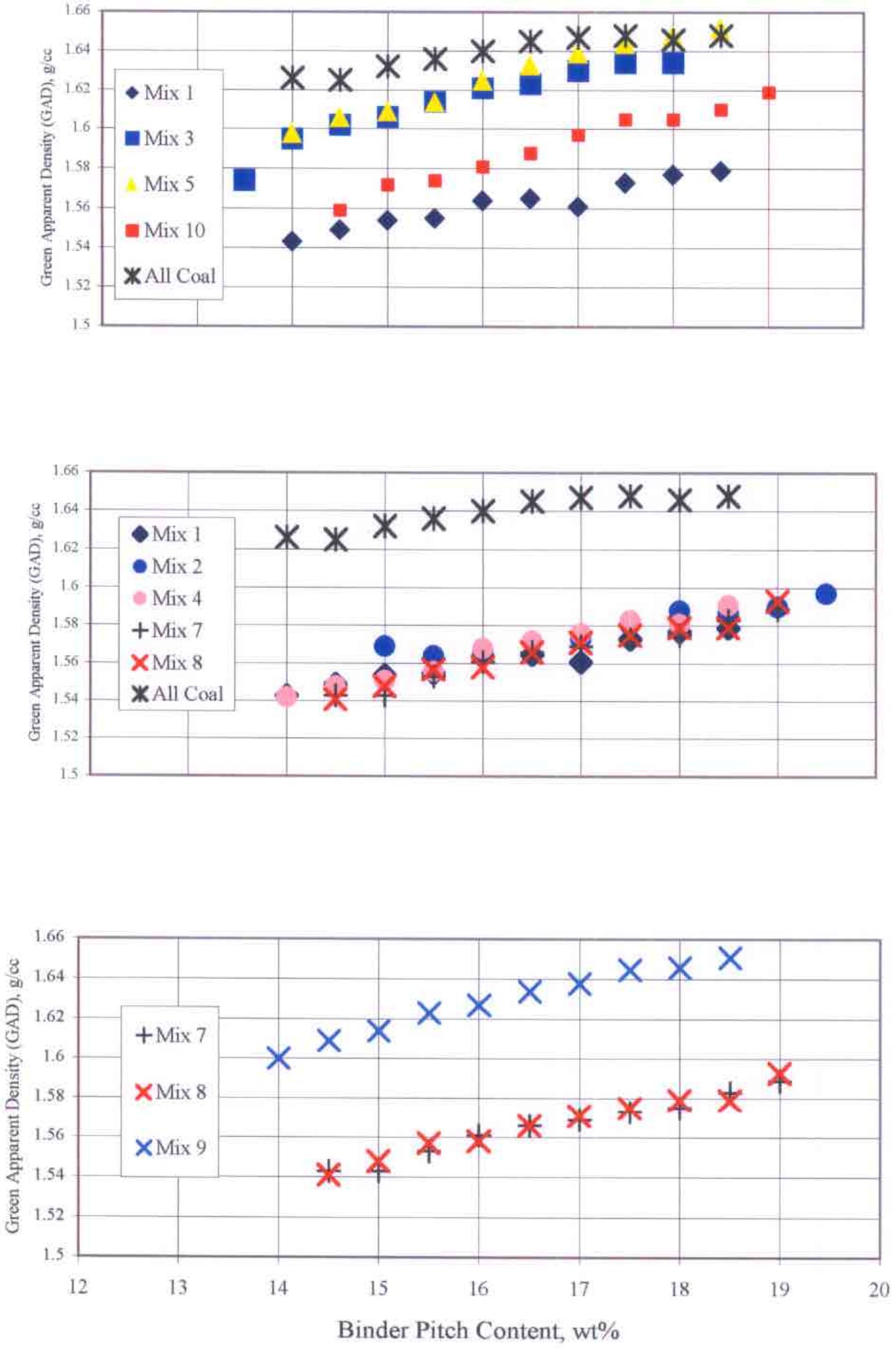

Figure 12. Green apparent density vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

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.

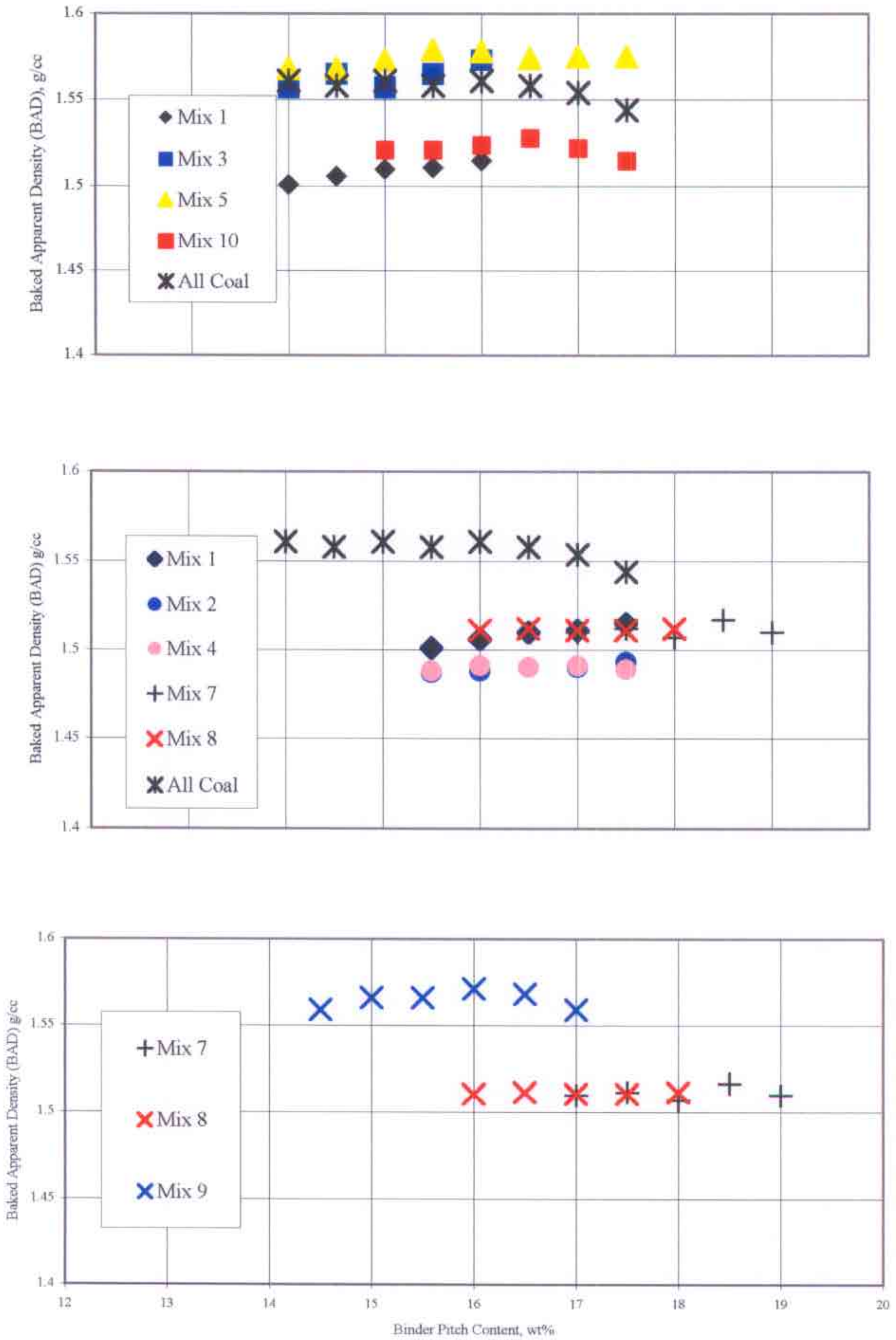

Figure 13. Baked apparent density vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

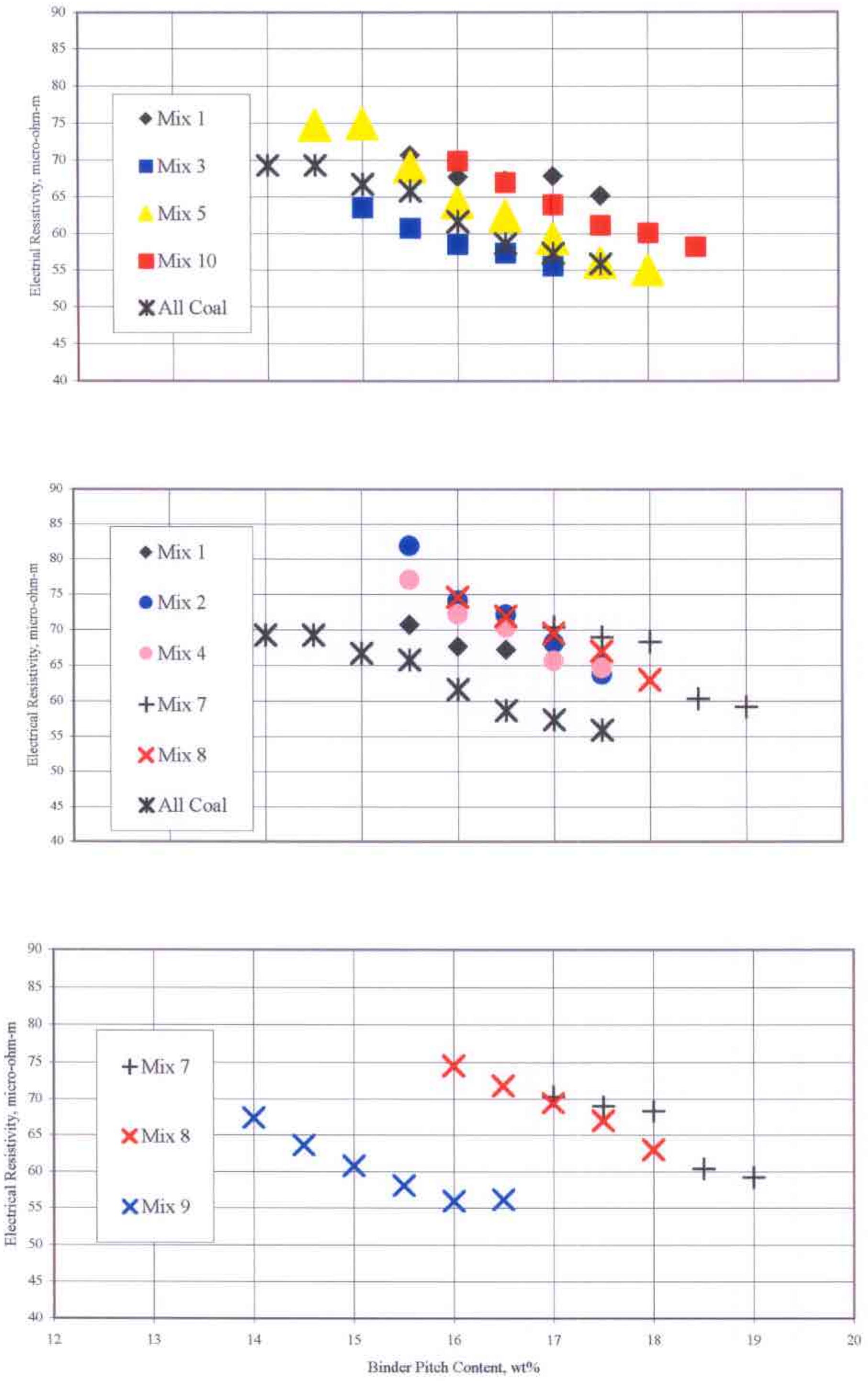

Figure 14. Electrical resistivity vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

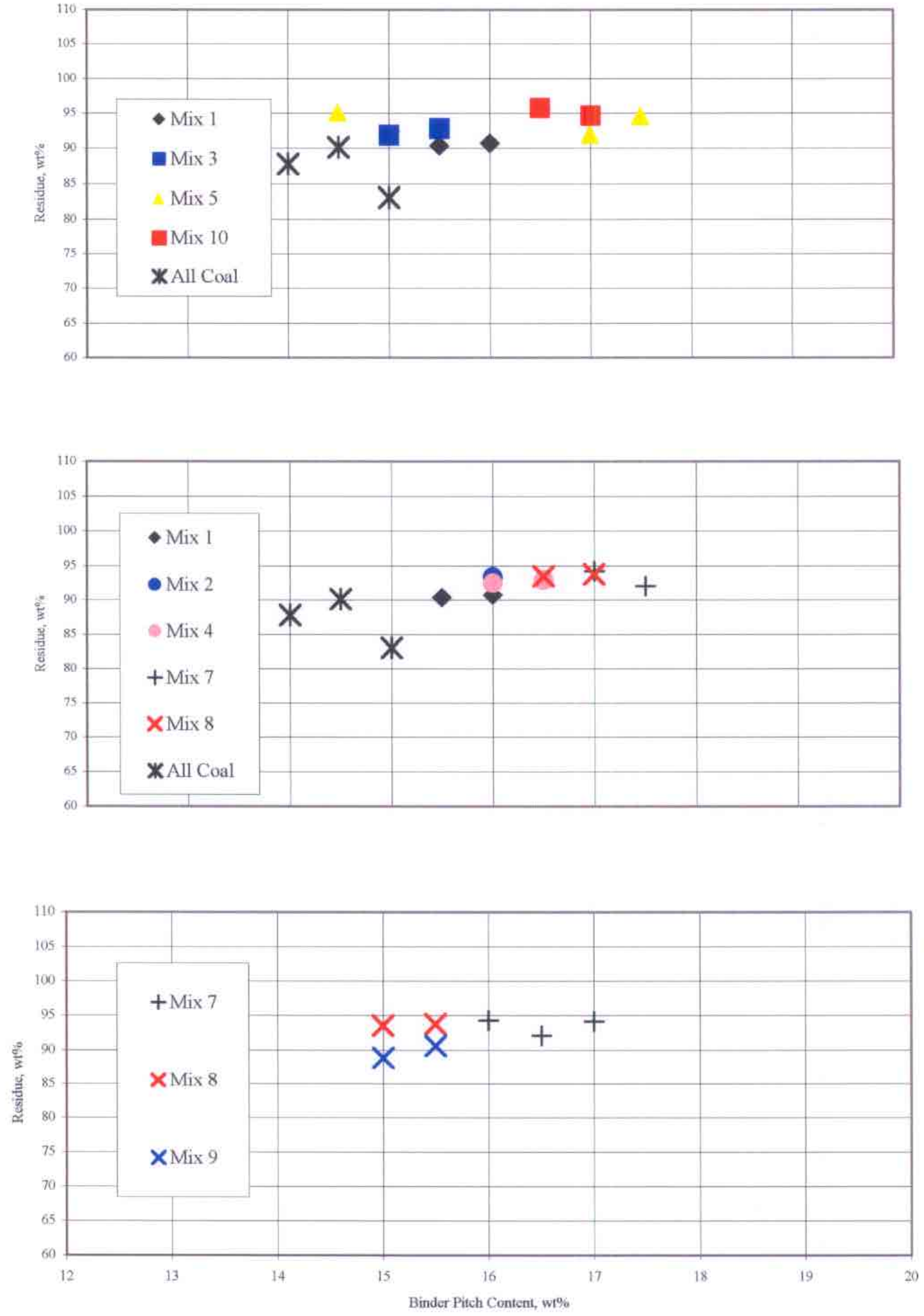

Figure 15. Carbon dioxide reactivity vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

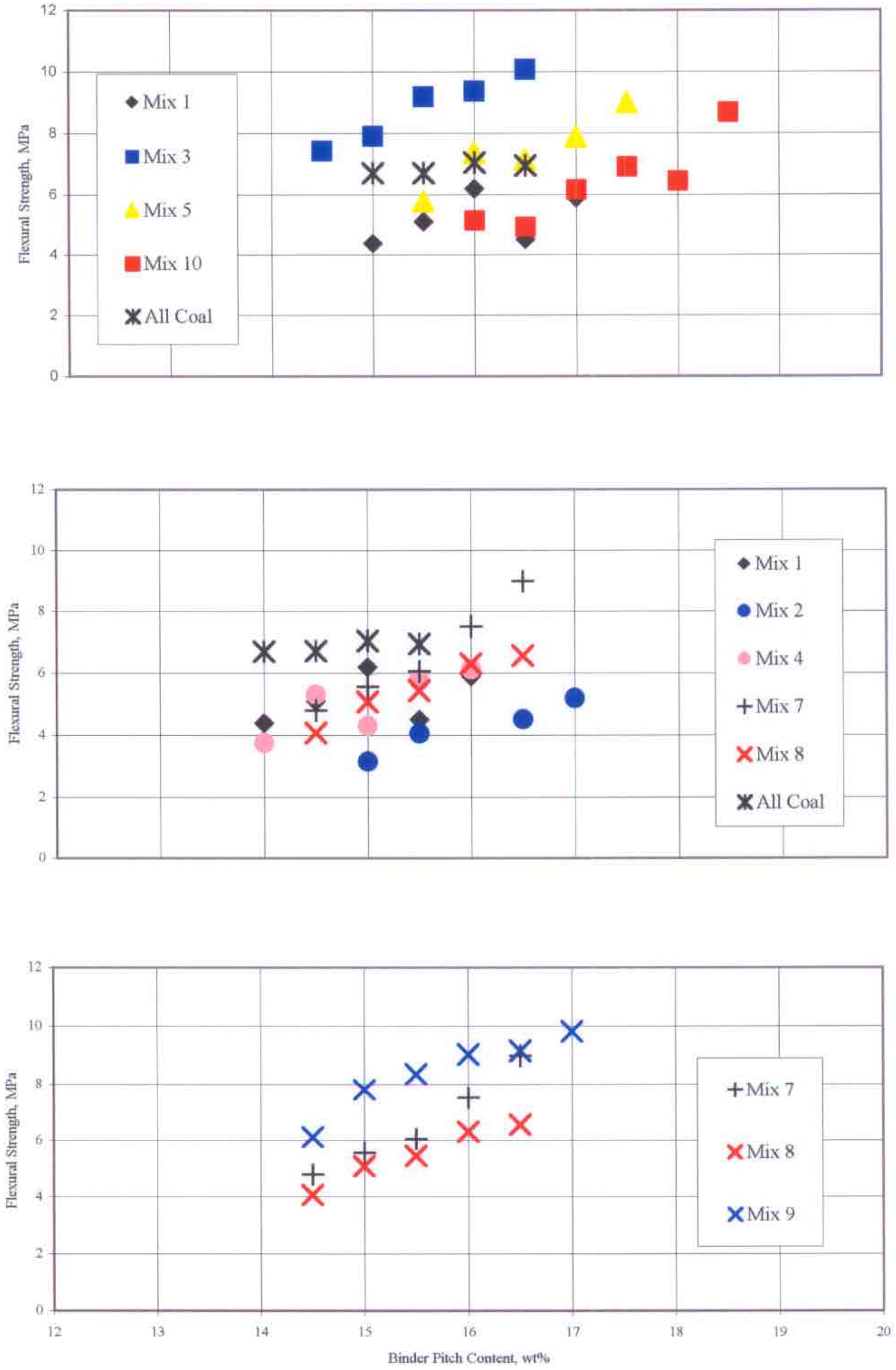

Figure 16. Flexural strength vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

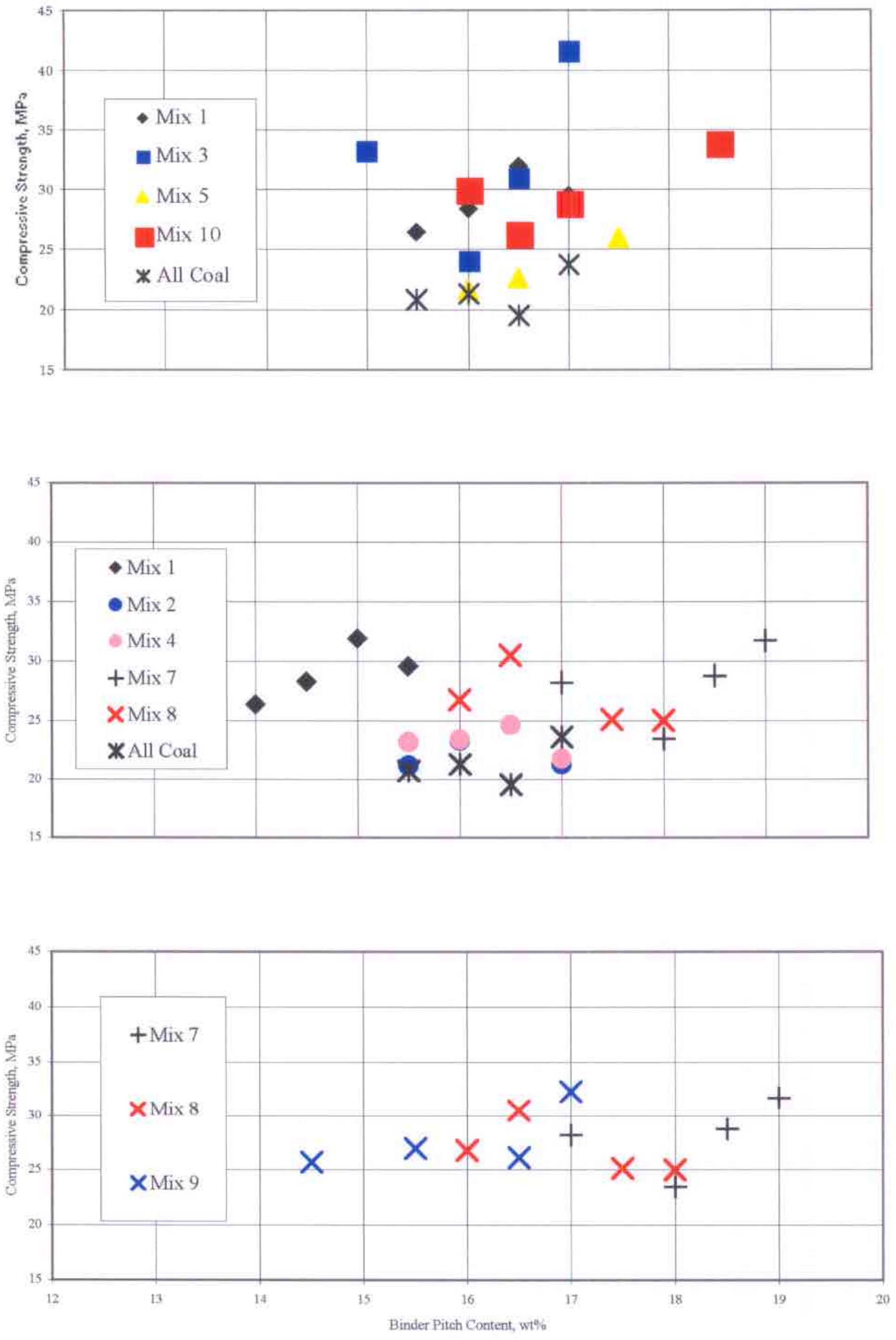

Figure 17. Compressive strength vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

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.

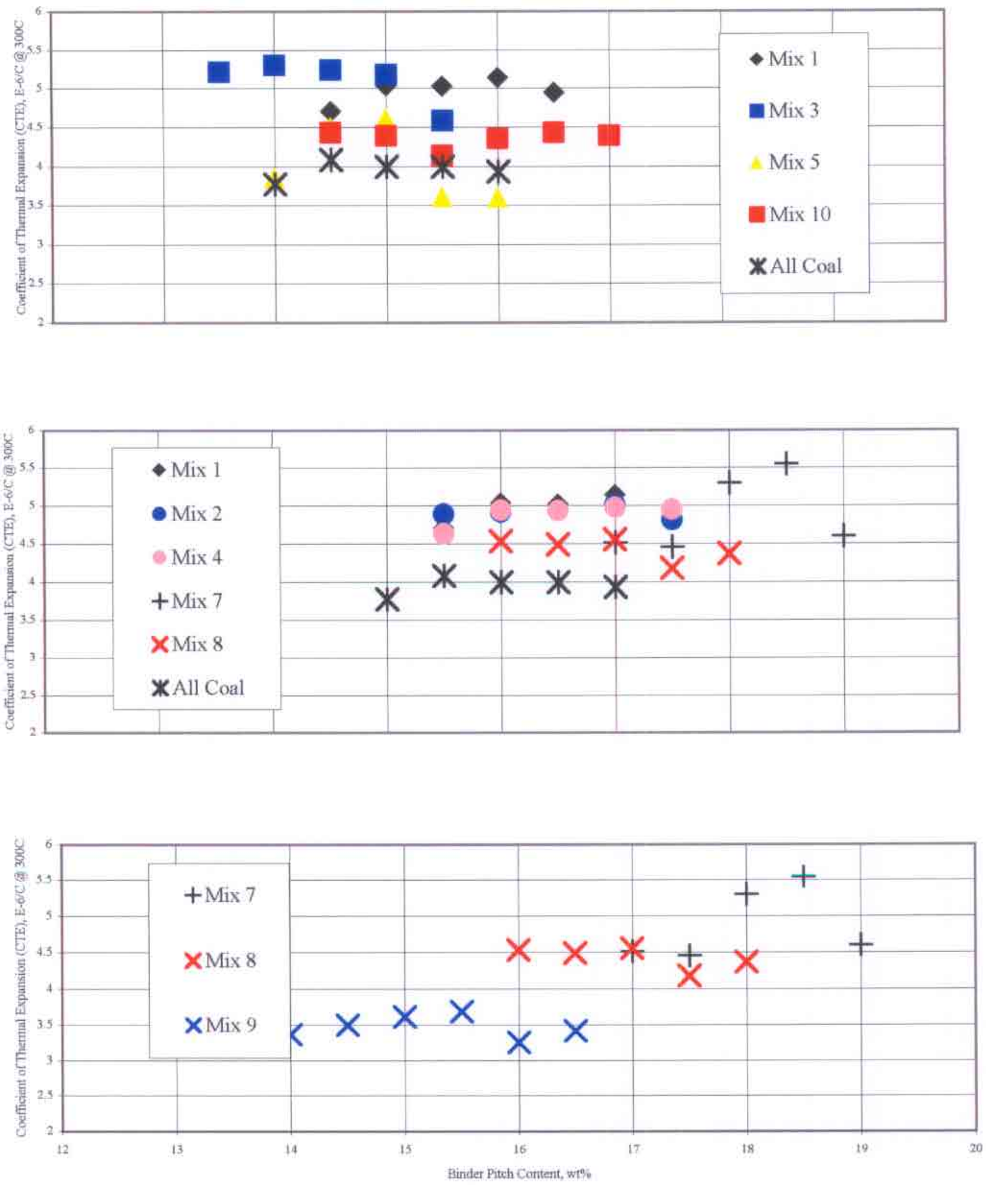

Figure 18. Coefficient of thermal expansion vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

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.

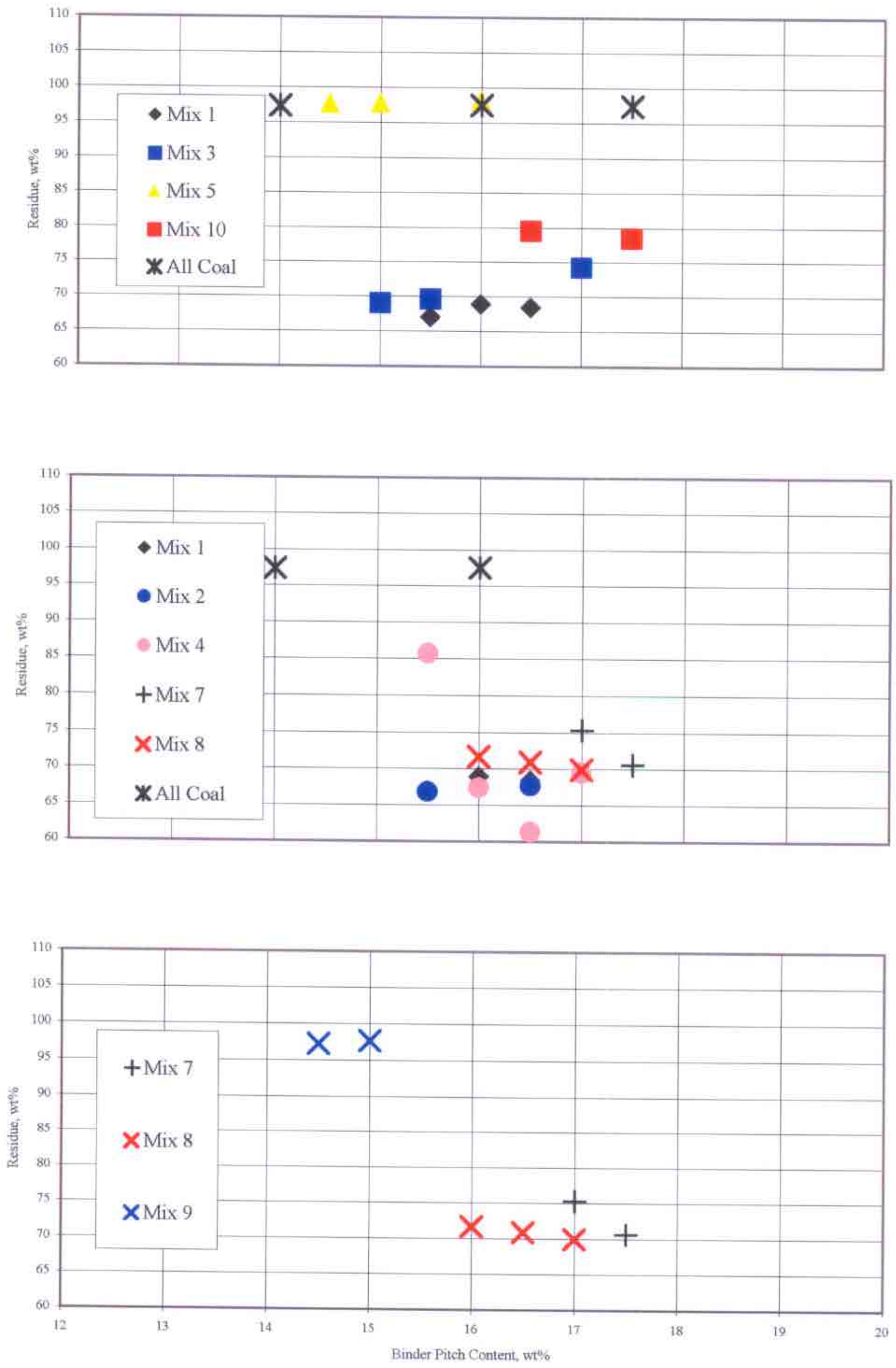

Figure 19. Air reactivity vs. binder pitch content. Top: effects of coke type with standard coal tar pitch. Middle: effects of binder type with conventional petroleum coke. Bottom: effects of calcined WVU and petroleum cokes with Type A binders.

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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