DEVELOPMENT OF ANODE BINDER PITCH LABORATORY CHARACTERIZATION METHODS

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Abstract

Typical anode binder pitch characteristics, such as softening point and quinoline insoluble content, are used to monitor quality assurance. More meaningful laboratory characterization methods that can be used to predict the performance of binder pitches are being developed. A pitch carbon yield measurement designed to follow pilot-scale anode baking rates is proving to be more informative than routine laboratory methods. The pitch carbon from this measurement is used to determine relative reactivity values of carbons from a variety of pitches. A four-inch diameter vibrated anode is permitting comparison studies of binder pitches and anode forming variables; for example, temperature, vacuum vs. atmospheric pressure and binder level. The results from these non-routine characterization procedures are assisting in the development of feedstock sources and processing.

Introduction

We primarily use ASTM standard tests for the characterization of Industrial Pitches used as binders for aluminum cell carbon anodes. These test methods are summarized in Table 1.

Table 1. Standard Pitch Testing Methods

Property	Test Method
Softening Point (SP), °C	ASTM D-3104
Toluene Insoluble (TI), wt.%	ASTM D-4072
Quinoline Insoluble (QI), wt.%	ASTM D-2318
β-resin, wt.%	(TI-QI)
Modified Conradson Carbon (MCC), wt.%	ASTM D-2416
Alcan Coking Value (ACV), wt.%	ASTM D-4715
Ash, wt.%	ASTM D-2415
Sulfur, wt.%	Leco*
Relative Density, 25°C/25 °C	ASTM D-71
Viscosity, cps	ASTM D-5018
Distillation to 360°C wt.%	ASTM D-2469
Metals, ppm	AA**
* Leco Sulfur Analyzer	
** Atomic Absorption Spectroscopy	

A detailed discussion of these methods is provided in a paper published at the 1992 Australasian Aluminium Smelter Workshop[1]. The softening point and viscosity data can be used to guide temperature selection for green mixing and forming. The insoluble values can be related to binder levels, coking value and wetting. However, most people appear to use these routine property values only to assure consistent quality.

Many metallurgical and foundry coking operations in the USA have closed during the last decade because of economic and environmental reasons; therefore, the amount of coal tar available for binder applications was reduced[2]. Consequently, new pitch processes and pitches with different properties are being developed[3]. In order to understand the effect of feedstock and processing changes on carbon anode properties and performance, we have began to develop more meaningful laboratory characterization methods that relate to product application.

Development And Experimental Results

Pitch Carbon Yield and Coke Studies

The routine pitch coke value is determined by standardized empirical methods; e.g., Modified Conradson Carbon (CCV) and ALCAN (ACV). These methods estimate the carbon yield of pitch; however, the actual values obtained by the two methods on a given sample differ by two to four weight percentage points. The pitch coking value (carbon yield) obtained in anodes during the baking process can exceed the routine pitch coke test value by five to fifteen weight percentage points. This latter process carbon yield is commonly referred to as "in-situ coking value"; for brevity, we will also refer to it as "baked coking value" (BCV). In order to better estimate the BCV, we have developed a new laboratory test where the pitch is placed in nested ceramic crucibles and heated at our pilot-scale anode baking rate; this method is labeled the "Koppers Coking Value" (KCV)[4]. A short description of the four coking value methods is shown in Table 2.

Table 2. Comparison Of Pitch Coking Value Methods

Method	Apparatus	Heating Program
Modified Conradson (ASTM D-2416)	A 3-g sample placed in porcelain or silica crucible that is set in a 2-piece Skidmore crucible. This assembly is placed in a metal crucible with lid.	30-minutes at 900°C in a muffle furnace
Alcan (ASTM D-4715)	A 1-g sample placed in a porcelain crucible with lid that is set on a bed of calcined petroleum coke in a 2-piece nickel crucible	2-1/2 hours at 550°C in an electric furnace
Koppers	A 70-g sample placed in a 100 ml covered porcelain crucible that in turn is placed in a 300-ml covered porcelain crucible. The assembly is placed in a nitrogen purged electric furnace and packed in fluid coke.	10°C/hour to 600°C and 25°C/hour from 600° to 1125°C. A soak time of 13 hours at 1125°C completes the cycle.
In-Situ (Baked Coking Value)	At Koppers, pilot scale anodes are placed in a nitrogen purged electric furnace and packed in fluid coke.	10°C/hour to 600°C and 25°C/hour from 600° to 1125°C. A soak time of 13 hours at 1125°C completes the cycle.

Figure 1 confirms that the Modified Conradson, Alcan, Koppers and baked coking values for three typical pitches follow the above projections. The correlation of KCV with BCV is shown in Figure 2.

Figure 1. Coking Values

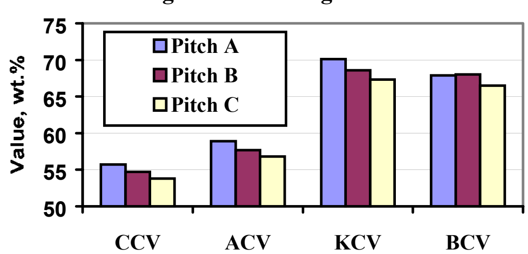
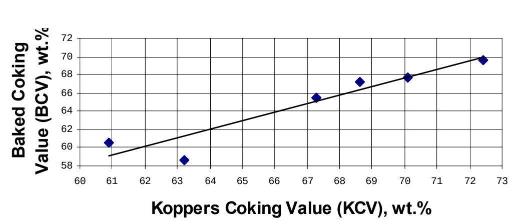


Figure 2. KCV vs. BCV



We reported our initial results on 27 pitches and the derived pitch cokes in 1997[4]. Since that time we have expanded the study to 53 pitches. Pitches were first analyzed by ASTM methods and metals were determined by atomic absorption spectroscopy. The pitch coke samples were obtained by the KCV method. Air reactivity of the pitch coke was determined by heating four grams of 10- X 18- mesh particles in a ceramic boat for 24 hours at 525°C in a controlled stream of air. (See the air and carbon dioxide granular test apparatus in Figure 3.) Helium density was determined on a 10-gram sample of minus 10-mesh coke using a gas-pycnometer. Reflected polarized light microscopy was used to quantify the anisotropic coke structure. The range of properties for the pitches and resultant cokes prepared by the KCV method, are given in Table 3.

Table 3. Range of Properties of 53 Pitches and Derived Pitch Cokes

Pitch Properties	**Minimum**	**Maximum**
Softening Point, °C	102.6	205.2
Toluene Insolubles, wt%	3.3	47.6
Quinoline Insolubles, wt%	0.0	21.2
Beta Resin, wt%	3.2	26.4
Conradson Coking Value, wt%	43.7	80.0
Ash, wt%	0.00	0.28
Sulfur, wt%	0.46	2.95
Specific Gravity, 15°C/15°C	1.207	1.377
Viscosity @ 160°C, cps	1,110	21,600
Distillation to 360°C, wt%	1.0	7.1
Ca, ppm	<5	260
Na, ppm	5	263
V, ppm	<5	8
Pitch Coke* Properties		
Yield, wt%	52.1	87.0
Sulfur, wt%	0.32	2.54
Air Reactivity Loss, wt% **	0.8	98.5
Helium Density, g/cc ***	1.963	2.068
Anisotropic Structure, vol% ****	64	100

* Obtained from Koppers Coking Value method
** 525°C/24 hours/10 X 18 mesh
*** Quantachrome Penta-Pycnometer
**** Reflected Polarized Light Microscopy

Figures 4-6 show that pitch coke yield, density and anisotropy are functions of the original pitch QI content. It appears that from Figure 7, pitch sodium content below 100 ppm is desired. These relationships can be used in the design of binder systems for carbon manufacture. For example, a more anisotropic coke structure will be produced from low QI pitches

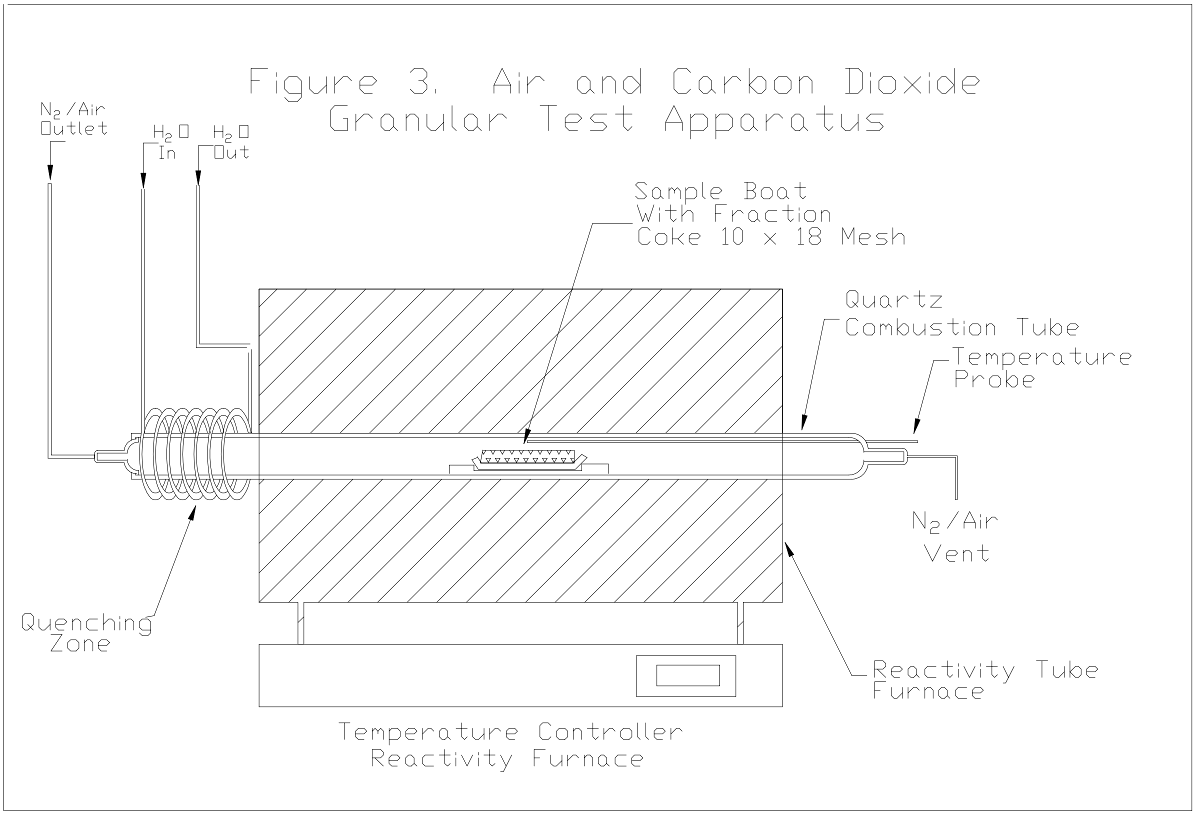


Figure 3. Air and Carbon Dioxide Granular Test Apparatus

Figure 4. Pitch Coke Yield vs Pitch QI
r = 0.83

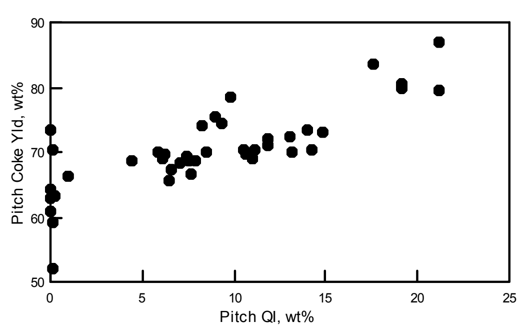


Figure 5. Anisotropic Coke vs Pitch QI
r = -0.93

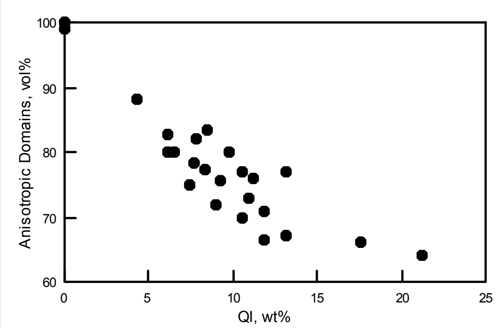


Figure 6. Pitch Coke Density vs Pitch QI
r = -0.92

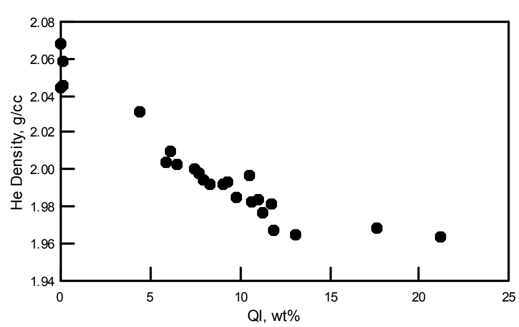


Figure 7. Pitch Coke Air Rx vs Pitch Sodium Content r = 0.93

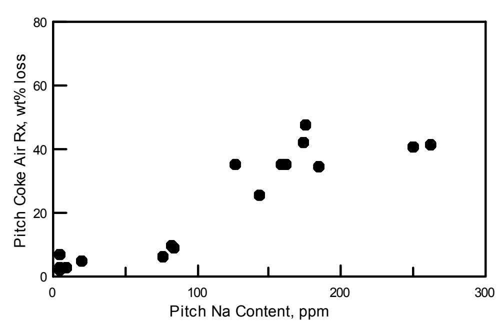


Figure 8. VIBRATED ANODE FABRICATION EQUIPMENT

(VACUUM and ATM)

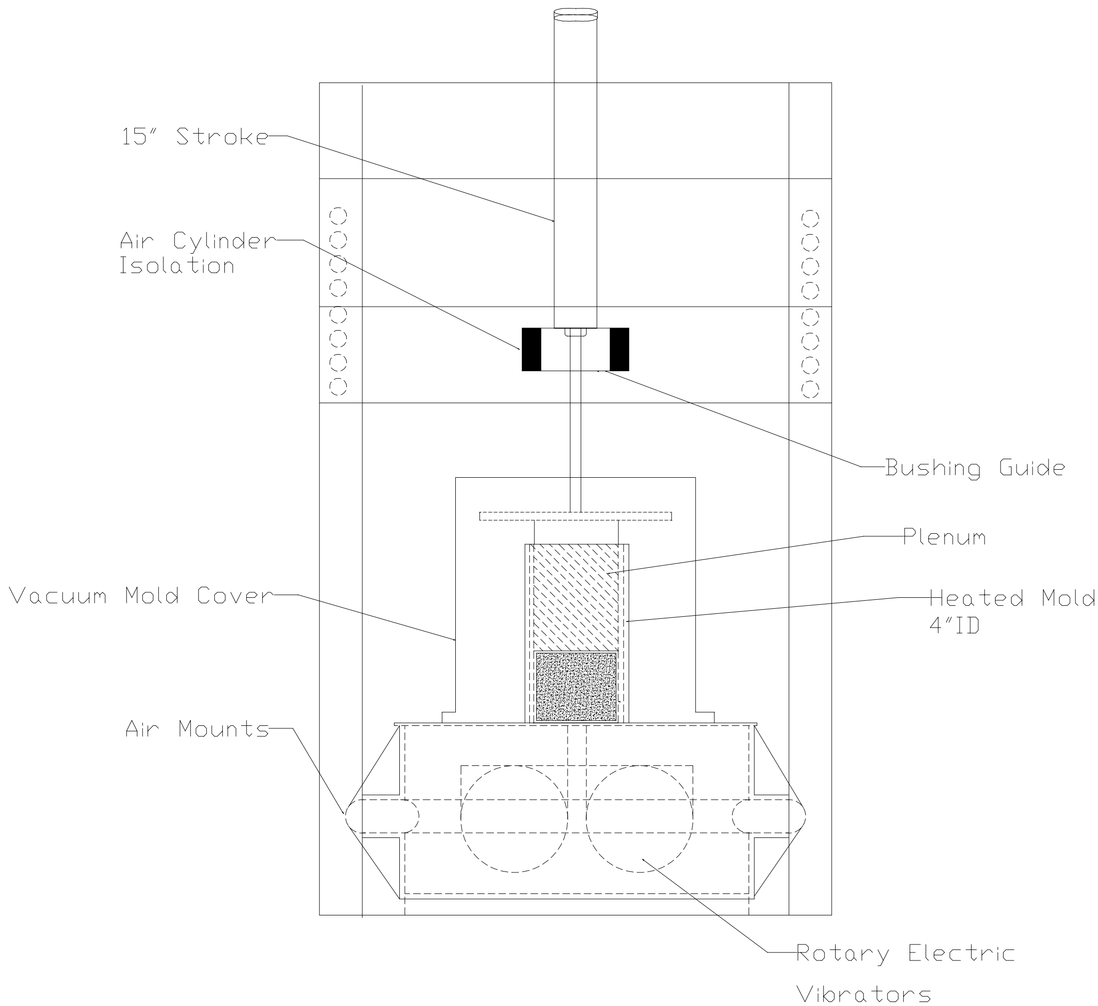


Figure 9. Core Baked Apparent Density

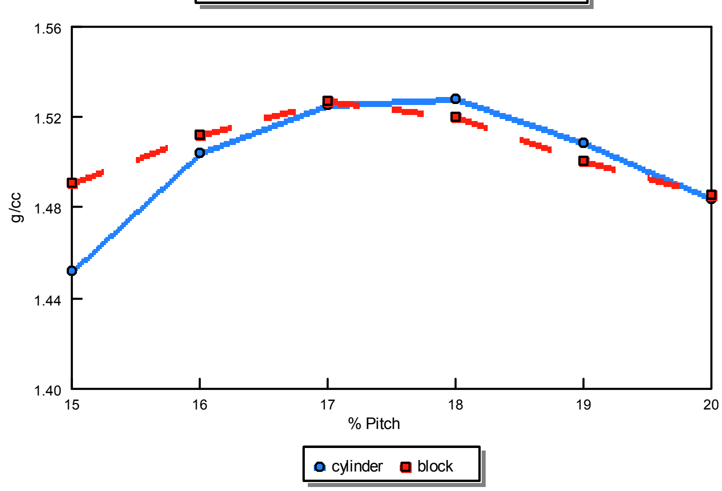
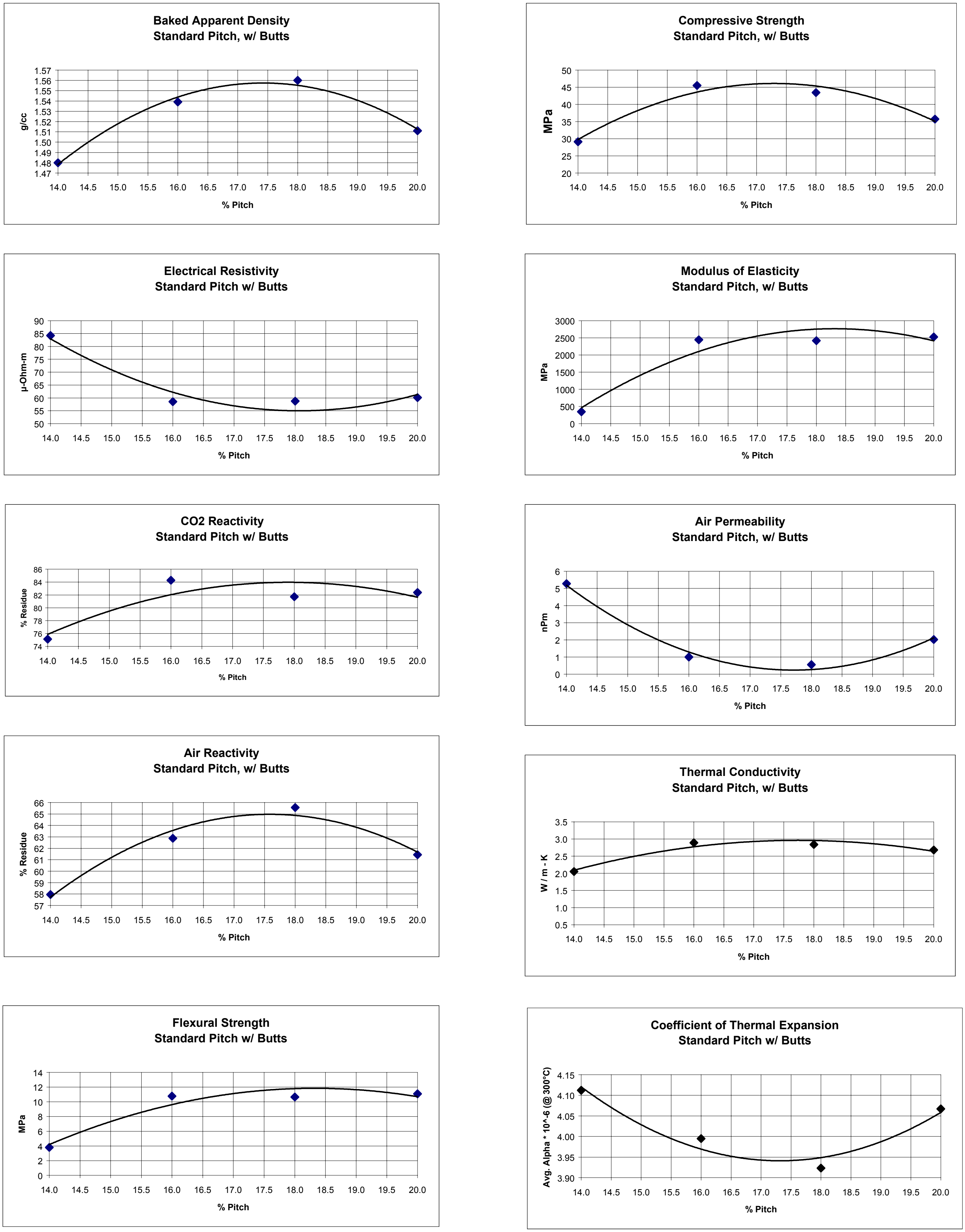


Figure 10. Core Tests Performed as a Function of Binder Level



Anode Optimization for Various Binders

For the past eight years, Koppers has produced 6- x 9- x 12-inch pilot scale vibrated anodes to evaluate pitch and other carbon processing variables. The properties of these large pilot scale anodes correlate with production scale anodes from various smelters. In order to have a more uniform structure, enable easy binder level studies and provide vacuum forming options, a four-inch diameter vibrated anode molding system was designed and constructed. A schematic drawing of the four-inch diameter vibrated anode fabrication equipment is presented in Figure 8. The applied weight, amplitude and frequency are variables in controlling the vibration process. A cylindrical dome over the mold enables the alternate use of vacuum. Using the same raw materials and mix design, 6- x 9- x 12-inch and four-inch diameter anodes were compared. As illustrated in Figure 9, core baked apparent densities were found to be almost equivalent for both size anodes.

Approximately 30 of the four-inch diameter anodes can be baked to about 1100°C in an electric furnace. The anodes are bulk packed in fluid coke and a nitrogen purge is used throughout the temperature controlled baking cycle (typically three and half days each for heating and cooling).

Examples of potential anode variables that can be studied with this pilot scale processing are listed.

- Coke
- Butt Material Recycle
- Pitches
- Binder Level
- Mix Design
- Mix Temperature
- Mix Time
- Vibration (Applied Weight, Amplitude and Frequency)
- Vacuum Vs. Atmospheric Molding
- Bake Temperature Program

Fifty-mm diameter cores are cut from each anode for carbon testing. Figure 10 illustrates the variety of testing we can perform on the carbon cores as a function of binder level. The various property plots confirm a preferred binder level in the 17-18 weight percent ranges; a more detailed study from 17-18 weight percent will provide the optimum value.

Summary and Conclusions

The following correlations were established in this study:

1. Pitch QI content correlates with pitch coke yield, anisotropic structure and density.
2. Pitch coke air reactivity correlates with pitch sodium content.
3. The Koppers coking value measurements are similar to the anode binder baked coking value.
4. The four-inch diameter anode properties are comparable to the established 6- x 9- x 12-inch anode properties.

The four-inch diameter vibrated anode equipment enables significant study of raw materials and processing of carbon fabrication.

Future Studies

1. Develop additional and new correlation data for pitch, pitch coke and anodes:
   - Pitch feedstock-sourcing effect on coking value, reactivity and coke microstructure
   - Pitch coke air and carboxyl reactivity versus anode core reactivity
2. Correlate pilot scale and production anode processing variables.

Acknowledgements

P. K. Sickels, S. A. McKinney, T. A. Mutschler, W. E. Saver and G. D. Wall assisted the authors in providing data and preparing this report. Their contributions are gratefully appreciated.

References

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[2] "Coping with the Tightening Coke Supply: Is a Crisis Looming?" Coke Supply Conference, Charlotte, NC, March 5-7, 1997.
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