DESIGNED EXPERIMENT FOR EFFECTS OF NORMAL QI, CARRY-OVER QI, AND BETA RESIN IN PITCH ON PREBAKED ANODE PROPERTIES

Part I - Preparation and Testing of Experimental Pitches and Bench-Scale Anodes

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Abstract

To better understand the effects of normal QI, carry-over QI, beta resin, and their interactions on the performance of coal tar pitch as a prebaked anode binder, a designed experiment was performed. The design was a 2-level, 3-factor full factorial in which eight pitches having high and low levels of each of the variables were evaluated as binders. The pitches were produced from two coal tars having low and high concentrations of normal QI. Low levels of carry-over QI were obtained by centrifugation and high levels of beta resin by thermal treatment. Bench-scale anodes were produced using a single lot of coke having a size distribution typical for commercial anodes. Anode fabrication and baking conditions simulated commercial practices. Pitch content was varied over a wide range so that the optimum level for each pitch could be determined. All conventional anode properties were determined.

Introduction

Coal tar pitch, the binder pitch commonly used in the manufacture of carbon anodes, is produced by distilling coal tar recovered from coke ovens. Pitch constitutes about 15-18 wt% of a green anode and it is known that the characteristics of a pitch can have a significant effect on the performance of the anodes in the Hall-Héroult cell. The properties of pitch are usually determined by standard tests (ASTM and/or ISO) such as softening point (SP), quinoline insolubles (QI), toluene insolubles (TI), coking value (CV), ash, and distillate content to 360°C. The ASTM or ISO methods for QI give the total QI or solids present in the pitch; however, QI is composed of 3 basic types [1,2]:

a) Normal QI - formed in the coke oven by high-temperature reaction of coal volatiles; the diameter of the spherical normal QI particles is about 1 μm and generally <2 μm.

b) Carry-over QI - composed primarily of coal derived materials "carried over" in the tar especially during charging of the coke oven. These entrained particles are predominantly coke cenospheres which are hollow spheres formed by rapid melting and devolatization of small coal particles; cenospheres generally range in size from 10 to 200 μm. Carry-over QI also contains coal and coke dust, as well as mineral matter derived from coal and refractories. Often, the sum of normal and carry-over QI is referred to as primary QI (i.e. derived from the coke oven).

c) Mesophase and/or secondary QI - any QI that is formed by thermal treatment of tar or pitch during pitch manufacture is known as secondary QI. If the secondary QI has developed into liquid crystal spheres that are visible in the pitch using reflected polarized light microscopy (>2 μm) it is called mesophase.

The normal and carry-over QI content of pitch is set by the concentration of the QI materials in the tar. Normal QI in tar is determined mainly by the temperature and head space in the coke oven, while carry-over QI is a function of coal charging and tar decanting conditions. The tar distiller can only control normal QI by blending tars having various QI levels. Carry-over QI can be reduced by centrifugation, settling, or other techniques. The ASTM QI method gives the total amount of QI (normal, carry-over, and mesophase) present in the pitch. Carry-over QI can be determined by petrographic analysis of the pitch solids extracted with quinoline [3,4]. Mesophase is determined in the pitch by reflected polarized light microscopy [2].

Toluene insolubles or TI can be controlled by thermal treatment and tar blending [5,6]. Since all materials insoluble in quinoline are also insoluble in toluene, beta resin (BR) is used to describe the portion of pitch insoluble in toluene but soluble in quinoline. Beta resin is calculated by subtracting the QI value from the TI value.

The effect of pitch QI on performance has been discussed in the literature; some examples are given in References 7-11. It is generally agreed that normal QI contributes to improved performance; however, the recommended amount varies from about 5 to over 20 wt%. Since carry-over QI contains metallurgical coke cenospheres and accounts for the ash content of pitch, it is considered to be detrimental to anode performance. The effect of carry-over QI has not been well quantified; one study using 32-mm diameter anodes showed no detrimental effects due to usual concentrations of carry-over QI [12].

There is considerably less mention in the literature on effects of beta resin. Beta resin is usually thought of as the "glue" that holds the anode together [13]. High values of 18-20 wt% are believed by some to be beneficial; although, the effect of beta resin on anode performance has not been quantified. One thorough study by Wagner et al. [14] investigated the effect of 54 coal tar pitches on graphite electrode properties.

Experimental Design

After a review of the literature, it was clear to the authors that a quantitative assessment of normal QI, carry-over QI, and beta resin in pitch on prebaked anode properties could not be obtained from published data. Therefore, a decision was made to perform a designed experiment in which these 3 factors were

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	Normal QI			
	Low		High	
	Carry-Over QI		Carry-Over QI	
Beta Resin	Low	High	Low	High
Low	E	D	C	G
High	A	H	F	B

Figure 1: Diagram showing variable levels for the eight pitches of the designed experiment.

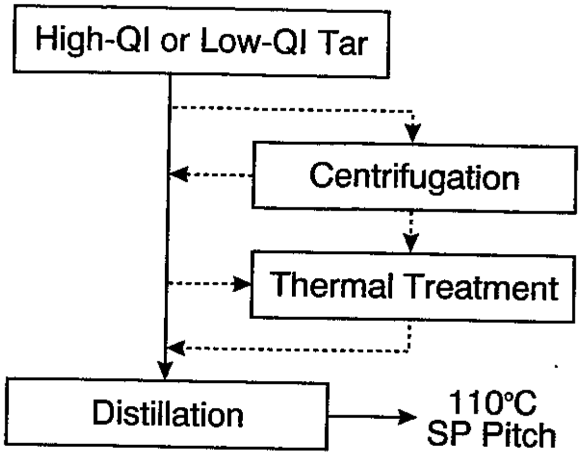

Figure 2: Processing scheme used to produce the eight experimental pitches.

controlled at high and low levels. The eight runs of the experiment are shown in Figure 1. Initially, a half-factorial experiment (pitches A-D) was conducted; however, analysis of the data indicated ambiguities resulting from missing information. Consequently, the other half of the experiment was completed (pitches E-H).

Pitch Preparation And Testing

A flow diagram depicting the preparation of the pitches is shown in Figure 2; about 5 Kg of each of the eight experimental pitches were prepared. To obtain high and low levels of normal QI, two tars were obtained from the same coke plant but at different times that corresponded to operating conditions that produced tars with about 6 and 9 wt% normal QI. Both of these tars had similar levels of carry-over QI (high level); therefore, portions of both tars were centrifuged to obtain tars with low carry-over QI content. The centrifugation conditions were such that only carry-over QI was removed. To increase beta resin, topped tars were thermally treated at about 390°C for 6 hours prior to vacuum distillation to nominal 110°C SP pitches. (Prior to thermal treatment, the tars were topped to remove the naphthalene fraction from the tar; the SP of the topped tar was about 40°C.) The properties of the eight laboratory-prepared experimental pitches along with a production pitch (pitch P - see next paragraph) are given in Table I. The range of values in the high and low levels of the experimental design is given in Table II. Most properties were determined by ASTM standard methods: SP - D3104, QI - D2318, Ash - D2415, Dist to 360°C - D2569, CV - D2416. Normal QI and carry-over QI were determined using reflected polarized light microscopy and a point count procedure; beta resin was calculated by subtracting the QI value from the TI value. None of the pitches used in the study contained mesophase.

In order to verify consistency of experimental anode fabrication procedures and to help identify any time-dependency of experimental results, a production pitch from the Aristech Tarben plant was also used. In general, properties were within the ranges in the experimental pitches but normal QI was lower, 8.2 wt% (Table I, pitch P).

Table II Range of values in the low and high levels of the experimental design.

	Low Level	High Level
Normal QI, wt%	11.4-12.9	16.8-18.9
Carry-over QI, wt%	0.3	2.2-4.2
Beta Resin, wt%	11.1-13.7	17.0-20.1

Anode Fabrication And Testing

Calcined petroleum coke from Venco, Inc. (Moundsville, WV) was used in anode fabrication. Because of a concern that dedust oil content might not be consistent throughout a given coke sample and that variability in dedust oil content could affect experimental results, coke without dedust oil was obtained.

Table I Properties of experimental and production pitches.

	A	B	C	D	E	F	G	H	P
Normal QI, wt%	12.0	18.9	18.2	12.9	11.4	17.3	16.8	12.2	8.2
Carry-over QI, wt%	0.3	2.3	0.3	2.7	0.3	0.3	4.2	2.2	2.6
Beta Resin, wt%	20.1	18.6	13.7	12.0	12.3	17.0	11.1	17.4	11.3
SP, °C	110.1	109.6	110.0	110.3	110.6	110.4	110.4	109.9	111.3
Total QI, wt%	12.3	21.2	18.5	15.6	11.7	17.6	21.0	14.4	10.8
TI, wt%	32.4	39.8	32.2	27.6	24.0	34.6	32.1	31.8	22.1
Ash, wt%	0.04	0.32	0.08	0.27	0.06	0.07	0.39	0.25	0.25
Dist to 360°C, wt%	0.0	3.5	2.9	1.5	0.9	0.9	1.8	0.0	2.5
CV, wt%	58.2	61.7	60.6	58.4	57.7	59.6	61.1	58.6	57.3

Also because of a variability concern, butts were not used in the anode mixes. Coke particle size distribution was 10% (by weight) -4+8 mesh, 18% -8+14 mesh, 16% -14+28 mesh, 11% -28+48 mesh, 10% -48+100 mesh, 14% -100+200 mesh, and 21% -200 mesh. (To minimize any variability in coke particle size distribution, the coke was actually separated into 16 narrowly cut fractions, and the additions made from these narrower fractions.) This particle size distribution is typical of that used in commercial anode production when the absence of coarse butt particles is taken into consideration.

For the first half fractional factorial experiment, five lots of anodes were produced using the production pitch (P), and three lots of anodes were produced using each of four experimental pitches. During the production of anodes, the pitches were used in the order: P, P, A, B, C, D, P, B, D, C, A, P, A, D, B, P. The same sequence was used in the second half factorial experiment using pitches P, E, F, G, and H to eliminate any variations that might be introduced with a different sequence.

Pitch levels tested were 15, 17, 18, 19, 20, 21, and 23 wt%. It was expected that maximum baked apparent densities would occur around the middle of this range. As a general rule, higher optimum pitch levels are found for bench-scale anodes than for commercial size anodes. In addition, the absence of recycled butt particles increases the optimum pitch level by about one percentage point, relative to the level required with the butt particle contents typically used in the plants.

Blending of coke and pitch was carried out in a bench-scale sigma blade mixer at 160°C. The initial mix with a given pitch was prepared using 3825 g of coke and 675 g of pitch, the amount corresponding to 15 wt% pitch. After blending for 30 minutes, sufficient mix for fabrication of one experimental anode was removed. Pitch was added to attain the next planned level, and additional blending was carried out. The process was continued until all the specimens were prepared.

A 400-gram quantity of mix at each level was placed in a cylindrical mold preheated to 135°C and pressed at 55 MPa (8000 psi) to form a green anode having a diameter of 50 mm and height of approximately 125 mm. Weights and dimensions of the green specimens were determined after removal from the mold and cooling.

Specimens were surrounded with packing coke and baked in a resistance heated furnace under a nitrogen purge at a heat-up rate of 10°C/h to 500°C and 25°C/h to 1125°C. Soak time at 1125°C was 15 hours. After cooling, specimens were removed from the furnace, tightly adhering packing coke was removed by sanding, and the baked specimens were weighed and dimensions were determined.

Using the weights and dimensional measurements, green apparent density, baked apparent density, and the in-situ pitch coking value were calculated. Electrical resistivities of the baked anodes at room temperature were calculated from measurements obtained using the four-point method. A current of 9 amps was passed through an anode and voltage drop determined using a fixture having contacts separated by 25 mm.

For the first half of the designed experiment, additional determinations were made on selected baked specimens. Included were air reactivity, CO_2 reactivity, air permeability, flexural strength, compressive strength, and Young's modulus by two techniques. Most of these determinations were conducted using R&D Carbon Ltd. (Sierre, Switzerland) test equipment and procedures. Since conducting these tests added to the time and expense of the experimental program and since a preliminary statistical analysis conducted after completion of the first half of the designed experiment indicated statistically significant correlations between these test results and either baked apparent density or electrical resistivity, the additional tests were not conducted on any baked specimens from the second half of the experiment.

Overall Results

Since densities, in-situ pitch coking values, and electrical resistivities were determined for 238 anodes, and since additional properties were determined for 119 anodes, individual results will not be given; rather, averaged data are presented in graphical form.

Consistency Of Results Among Replicate Runs

Despite great care in maintaining a uniform coke and invariant mixing, pressing, and baking conditions, there was variability with regard to replicate specimens. As an example, Figure 3 shows baked apparent densities for all the specimens prepared using the production pitch. The range was as large as 0.015 g/cm^3, with 23 wt% pitch, and as narrow as 0.010 g/cm^3 around the optimum level.

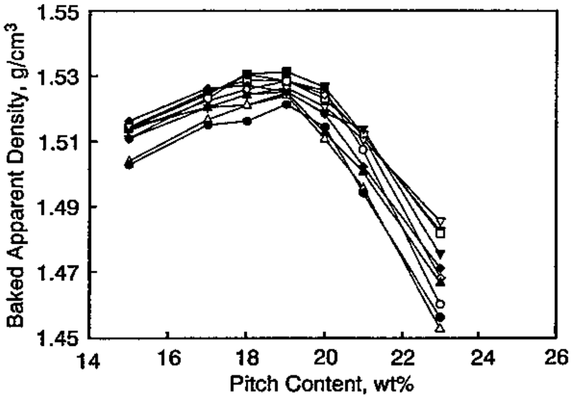

Figure 3: Baked apparent densities of all individual anodes made using the production pitch.

No differences between the two halves were found by an analysis of variance using paired observations for the two experimental halves indicating that the first half of the designed experiment with the production pitch was not significantly different from the second half with respect to baked density. However, electrical resistivities for baked anodes produced using the production pitch differed significantly. At the 19 wt% pitch level, for example, average for the first half of the designed experiment was 62.5 μΩ·m, and average for the second half was 63.1 μΩ·m. An analysis of variance with paired observations for the two halves indicated that this difference was statistically significant. However, this difference did not complicate the analysis of results since the two experimental halves were blocked on the three-factor interactions of the three main variables. It was still possible to analyze main effects and two-factor interactions as will be shown in Part II.

Agreement in properties among the three runs with each experimental pitch was reasonable. As examples, Figure 4 shows baked apparent densities with two of the pitches, one for

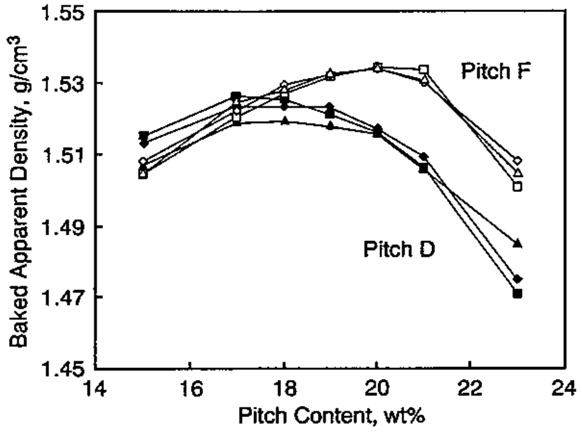

Figure 4: Baked apparent densities of individual anodes made using experimental pitches D and F.

which variability was largest (Pitch D) and one for which variability was smallest (Pitch F). Most of the statistical analyses given in this paper deal with average values for the three runs with each experimental pitch and for the 10 runs with the production pitch (Pitch P).

Average Results With Experimental Pitches

Figure 5 shows averages of the three replicate green apparent densities at each pitch level with the eight experimental pitches. Standard deviation for the three replicate anodes for each pitch at each level averaged 0.002 g/cm^3, while standard deviation for all 24 anodes at each pitch level averaged 0.006 g/cm^3, indicating that there were differences due to the different pitches.

Baked apparent densities are shown in Figure 6. Standard deviation for the three replicate anodes for each level averaged 0.003 g/cm^3, while standard deviation for all 24 anodes at each pitch level averaged 0.008 g/cm^3, again indicating that there were differences due to the different pitches. Note that there are relatively small differences among the maximum baked apparent density values (1.522 to 1.533 g/cm^3), but an appreciable range in the amount of pitch required to produce the maximum density (~18 to over 20 wt%).

Electrical resistivities are given in Figure 7. Comparison of standard deviation for replicate anodes from a given pitch and all anodes again indicates that the differences are significant (0.6 μΩ·m average for replicates versus 2.4 μΩ·m average for all specimens at each pitch level). Comparison of Figure 7 with the previous figure shows that for each pitch, the level resulting in minimum electrical resistivity is greater than the level resulting in the maximum baked apparent density. Since, from an operational standpoint, anodes containing more pitch than required to achieve maximum baked apparent density would be difficult to handle and bake, data analysis with regard to electrical resistivity used the resistivity values for anodes having maximum baked apparent densities rather than the resistivity values at the pitch levels giving minimum resistivities.

In-situ pitch coking value in an anode as a function of pitch level is shown in Figure 8. The behavior with pitch level varied somewhat from pitch to pitch. The reason for this is not certain, but at least part of it might have to do with variability in removing packing coke. This procedure involves sanding away tightly adhering packing coke, allowing the potential for variability from

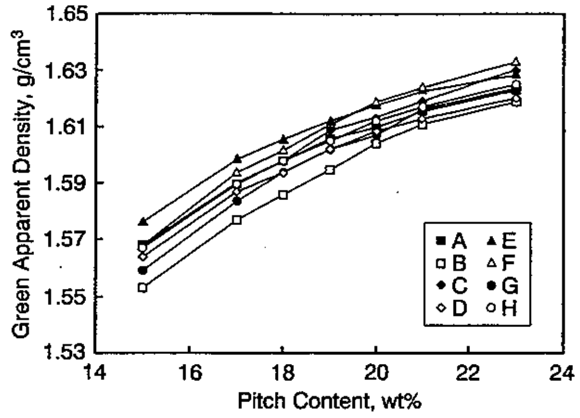

Figure 5: Average green apparent densities of anodes made using the experimental pitches.

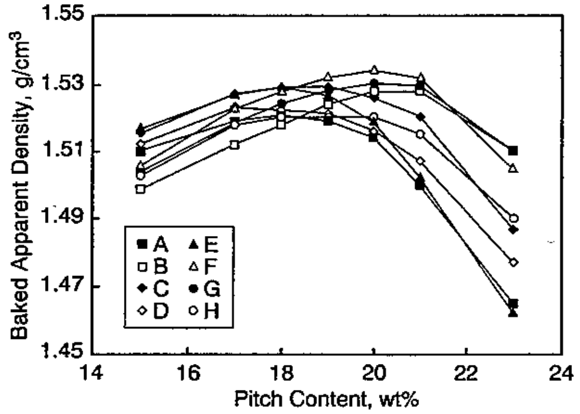

Figure 6: Average baked apparent densities of anodes made using the experimental pitches.

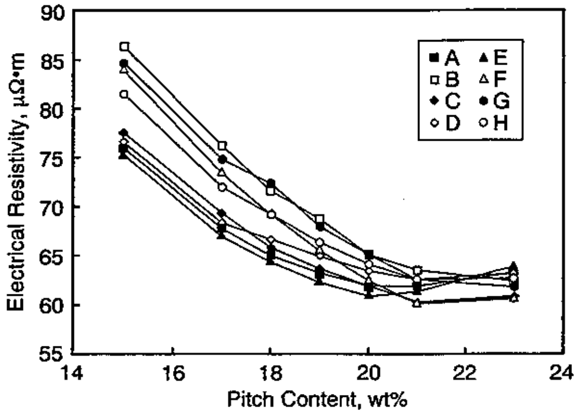

Figure 7: Average electrical resistivities of anodes made using the experimental pitches.

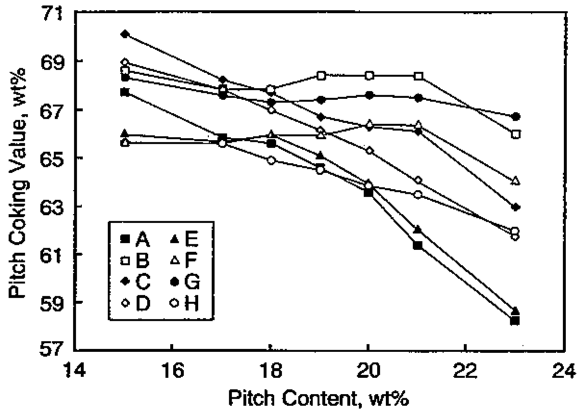

Figure 8: Average in-situ pitch coking values in anodes made using the experimental pitches.

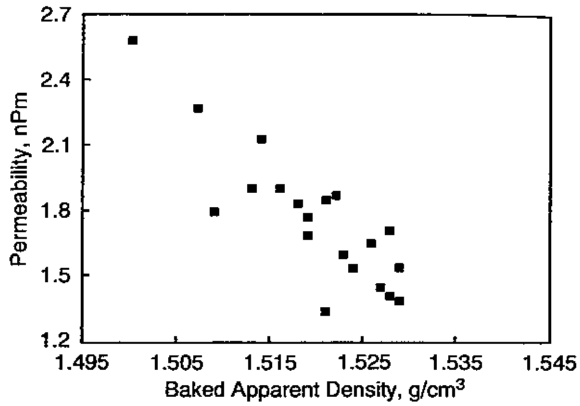

Figure 9: Relationship between air permeability and baked apparent density for anodes made using experimental pitches A-D.

insufficient sanding (leaving some packing coke) or excessive sanding (removing some of the anode surface). These differences would affect the apparent weight of the baked anode, which would erroneously be attributed to differences in coking value from the pitches.

The averaged interpolated values of maximum baked apparent density for each of the experimental pitches are given in Table III. The optimum binder concentration for the maximum baked apparent density is also given along with the resistivity and in-situ coking value of the anode at maximum baked apparent density.

As mentioned earlier, generally good correlations were found between either baked apparent density or electrical resistivity and each other property measured in the first half of the designed experiment. Figure 9 exemplifies one of the better correlations with baked apparent density, that with air permeability. (Air permeabilities were only determined for anodes containing 17-21 wt% pitch.) Figure 10 shows one of the better correlations with electrical resistivity, that with flexural strength. (Flexural strengths were only determined for anodes containing 17, 19, and 21 wt% pitch.)

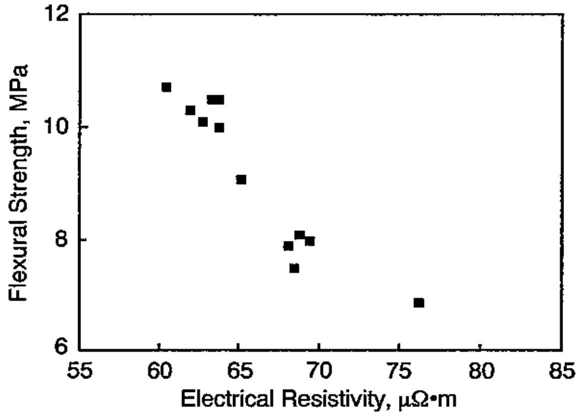

Figure 10: Relationship between flexural strength and electrical resistivity for anodes made using experimental pitches A-D.

Table III Interpolated values for baked apparent density (BAD), optimum binder concentration (OBC), electrical resistivity, and in-situ pitch coking value (CV) for the experimental pitches and anodes.

Pitch	Maximum BAD g/cm³	OBC @ max BAD wt% pitch	Resistivity @ max BAD µΩ·m	In-situ CV @ max BAD wt%
A	1.522	17.6	66.1	65.9
B	1.525	19.8	66.0	68.1
C	1.531	18.1	65.6	67.6
D	1.524	17.8	67.1	67.0
E	1.530	17.6	65.4	65.9
F	1.533	19.1	65.0	66.2
G	1.529	19.5	66.4	67.4
H	1.522	18.5	67.3	64.7

Part I Summary

A 2-level, 3-factor full factorial experiment was conducted (in two halves) to determine effects of normal QI, carry-over QI, and beta resin in coal tar pitch on prebaked anode properties.

The three factors investigated were varied by tar selection, centrifugation, and thermal treatment.

Bench-scale anodes were fabricated using a typical calcined petroleum coke and sufficient levels of each experimental pitch to determine the optimum level with each.

Baked apparent densities, electrical resistivities, and in-situ pitch coking values were determined for all (238) individual bench-scale anodes made using the experimental pitches.

Other physical properties determined as part of the first half of the factorial experiment tended to correlate with either baked apparent density or electrical resistivity, so were not determined in the second half of the factorial experiment.

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