

COKE CALCINATION LEVELS AND ALUMINUM ANODE QUALITY

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Summary

The calcination temperature of petroleum coke for aluminum anode applications has been generally increased during the past 10 years. This change by coke suppliers has often been done at the request of anode manufacturers (smelters) who seek special quality requirements for the calcined coke. Such an increase in calcining temperatures not only affects coke properties, but also has an effect on calciner operations and may have some unexpected effects on anode quality.

One high and one low sulphur coke were calcined industrially at two different levels. The four individual calcined cokes were characterized. Then laboratory scale anodes were produced with each individual calcined coke. These all-coke anodes were first evaluated for optimum pitch content. Then the anodes were baked over a range of temperatures (920 to 1260°C) in order to evaluate the influence of this heat treatment on anode properties.

The results show the influence of calcining temperature on coke properties and anode properties, including the most important influence of the anode baking level.

Introduction

The objective in calcining delayed petroleum coke is to produce a product at the desired level of real density (or electrical resistivity or L_c) with the highest purity, minimum porosity, and minimum reactivity. Obviously, calciners have other objectives such as minimizing costs or maximizing throughput, depending on market conditions. When heat recovery is a vital part of a calcination plant, additional objectives apply to this part of the plant.

Calciners may evaluate the "optimum" quality via kiln optimization, according to reference [6]. Smelters typically define the level of calcination (real density, L_c or electrical resistivity) and other calcined coke properties desired. Many smelters demand low reactivity which often requires high calcination levels, resulting in real density values of 2.09 to 2.10 g/cc. However, calcining to higher real density results in higher fuel consumption and lower throughput at the kiln. Beyond reactivity, the effects of high levels of calcination on anode properties have not been well-defined.

An important consideration when setting calcined coke specifications today is the increased level of sulphur. When calcining,

it is normal for about 10% of the sulphur content to be evolved during the process. That is, calcined coke sulphur content is about 10% lower than green coke sulphur content. For nearly 50% of the world's calciners, green coke feedstocks in excess of 2.5% sulphur are routinely used. As sulphur content increases, thermal sulphur evolution accelerates. For cokes as high as 5% sulphur, a 15% loss of sulphur is quite common. This evolution rapidly accelerates at calcination temperatures of 1300°C, a level theoretically desired to reach a real density of 2.09 g/cc or L_c of greater than 32Å. As has been well-documented [5], such sulphur evolution will result in lower density (higher porosity) and diminished anode properties. As will be shown in this paper, such over-calcined cokes will also tend to desulphurize more easily during anode baking.

From the viewpoint of the anode producer, a calcination level which optimizes the quality of the resulting anodes is the best. It will be seen that this calcination level should be dependent on the coke quality (sulphur level), the specific smelter needs and the anode quality requirements.

BackgroundInfluence of Coke Calcining Temperature on Coke Properties

A number of studies have been published on this topic [1 to 12]. There has been overall agreement on the following results.

When the calcination level increases:

- **L_c**: the crystallite height rises.
- **Resistivity**: decreases
- **Porosity**: increased due to thermal sulphur evolution. It first leads to prepuffing, i.e. formation of closed pores without macroscopic expansion of coke grains and subsequent puffing with a decrease in apparent density.
- **Real density**: typically increases, but due to desulphurization, real density may not serve as a good indicator of the calcination level, especially for high sulphur cokes. [1, 3, 11]
- **Air reactivity** typically decreases over the normal range of calcination.
- **CO₂ reactivity** decreases until desulphurization occurs, when it again increases [16, 19].
- **Coefficient of thermal expansion**: decreases [12].

Influence of Coke Calcining Temperature on Anode Reactivity

There are a number of different views about the relationship between coke reactivity and anode reactivity. For example, both air and carboxy reactivities of cokes were correlated with anode reactivities in reference [18]. In another study [19], anode properties were correlated to many coke properties such as degree of calcination, impurity levels and carboxy reactivity, but not to coke air reactivity. Other researchers [21] stated that anode reactivity is related to the combination of coke reactivities and coke structure (feedstock type).

Influence of Calcined Coke Quality on Carbon Consumption

While it is fully accepted that calcined coke quality ultimately affects net carbon consumption, there are a number of different views as to what is important. Considering calcination temperature, an early study [15] found increased carbon consumption with increased calcination level. Another study [20] found no such correlation. Both of these studies did cite baking temperature of anodes as the more influential factor in anode consumption. A recent study [13] identified the effects of baking conditions on the properties of anodes containing a mixture of high and low sulphur cokes; this study further identified the dramatic effects of desulphurization during baking on anode properties. As will be seen, this paper now links calcination temperature of coke to desulphurization during anode baking, particularly with high sulphur cokes.

Studies have been published on the influence of coke calcining temperature on the physical and mechanical properties of anodes [20,21]. These papers showed that coke heat treatment had little influence on the anode physical and mechanical properties, but these studies were limited to low sulphur (less than 1.75%) cokes which were less susceptible to desulphurization during either calcining or baking. The current paper will also address this topic, but using both low sulphur and high sulphur (over 4%) cokes, the latter of which was much more susceptible to desulphurization.

Finally, net carbon consumption is generally accepted to be a function of anode quality and cell design and operating conditions. Again, different views are presented in the literature. For example, one study [17] correlated net carbon to measured anode properties, such as air reactivity residue and CO₂ reactivity residue, plus cell current efficiency and bath temperature. Another study [19] stated net carbon consumption was primarily influenced by so-called "electrolytic consumption," then corrected for air and CO₂ oxidation. In any case, the anode performance within smelters is dependent on good anode physical, mechanical, and chemical properties. It is the intention of this current work to more clearly define how to achieve these properties.

Coke Characterization

General Characteristics

Two different cokes, A and B, each calcined at two different levels (+, -) were used to carry out the study. Their main characteristics are described in Table I:

Table I Coke Characteristics

Coke	A-	A+	B-	B+
Apparent density (g/cm ³)	1.75	1.74	1.74	1.67
Helium real density (g/cm ³)	2.079	2.138	2.073	2.049
L _c (Å)	26.9	44.4	32.6	35.7
Sulphur (%)	1.82	1.79	4.52	4.23
Vanadium (ppm)	160	160	360	350
CTE (10 ⁻⁶ /K)	2.90	2.77	3.52	3.36
Granular resistivity (Ωcm)	0.103	0.079	0.100	0.089
Air reactivity (%/min)	0.28	0.06	0.13	0.12
CO ₂ reactivity (%)	13.6	5.1	6.0	5.9

A⁻ and A⁺ were produced from identical green cokes calcined at different temperatures. A⁺ was calcined at a much higher temperature than A⁻. The same designation was used for the B coke. Both cokes are US Gulf Coast-produced. The key distinctions are the sulphur and vanadium contents.

The data in Table I show that an increase in the heat treatment temperature led to several expected changes in characteristics:

- L_c increased.
- Sulphur content decreased, especially for the higher sulphur coke.
- Granular resistivity and CTE diminished significantly.
- Helium real density increased for the low sulphur A coke but decreased for the high sulphur B coke.
- Apparent density decreased, especially for the high sulphur coke.
- Air reactivity and CO₂ reactivity decreased, especially for the low sulphur coke.

These results are consistent with past observations. Thermal sulphur evolution caused the development of internal closed porosity which resulted in lower real density and apparent density for coke B. This conclusion was verified by investigating the real density results obtained after a more severe grinding procedure for the B coke. These results are presented in Table II.

Table II Effect of Sulphur Evolution and Pore Development on the Real Density Measurement

Coke	B ⁻	B ⁺
Real density in helium (g/cm ³) (normal grinding)	2.073	2.049
Real density in helium (g/cm ³) (extra grinding)	2.086	2.077

Similar results were previously described [15, 16]. A more severe grinding procedure caused some closed pores to open. (This may still not be enough to allow total penetration of the measuring fluid [helium in this case] into all porosity.) Therefore, real density results must be considered with great care when evaluating the calcination level of high sulphur cokes.

Structural Characterization

The structural characteristics of the carbons described in this paper were obtained by refining X-ray powder diffraction patterns with the computer program Carbon X [22]. This full profile refinement program, analogous to the usual Rietveld method but dedicated to the analysis of carbons, allows the quantification of the finite size, strain and disorder present in disordered carbons. The parameters of the structural model incorporated into the program are schematically described in Figure 1.

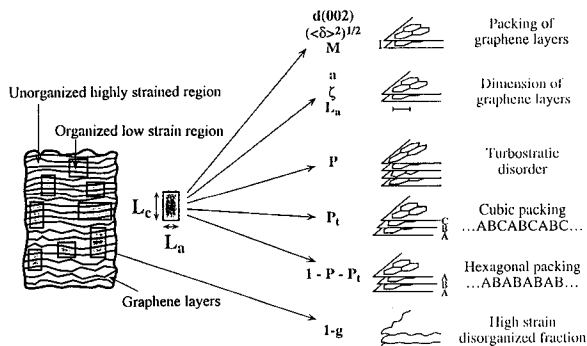


Figure 1: Characterization of the Fraction of Unorganized and Organized Carbon Material.

It was observed that the following parameters varied significantly with the type of coke and with the heat treatment temperature.

- L_c : crystallite size
- L_a : lateral extension of the sheets of carbon
- a : in-plane lattice constant
- g : high-strain organized fraction.

The results for the two different cokes calcined at two different levels are given in Table III.

Table III Structural Characteristics of the Four Cokes

Coke	A-	A+	B-	B+
L_c (Å)	26.9	44.4	32.6	35.7
L_a (Å)	16.6	26.9	21.3	26.9
a	2.438	2.447	2.442	2.449
g	0.598	0.660	0.610	0.670

For both cokes A and B, the organized fraction g increased with the calcination level. Likewise, both L_c and L_a increased. As compared to the L_c results, the L_a and the g fraction showed there was no significant difference in graphitization due to calcining between A^+ and B^+ cokes. All measurements, L_c , L_a and g , showed that coke A^- had a lower level of graphitization than coke B^- .

Experimental

Bench scale anodes were manufactured from each of the four cokes, A^- ; A^+ ; B^- ; B^+ following the standard method described

Experimental

Bench scale anodes were manufactured from each of the four cokes, A^- ; A^+ ; B^- ; B^+ following the standard method described in reference [23]. Particle size distribution was identical to that in use in industrial anode plants. Binder pitch content was optimized for each coke in order to give maximum baked geometrical density, so that the optimum level as a function of the type of coke could be tested. Four batches of bench scale anodes were manufactured with pure cokes A^- ; A^+ ; B^- ; B^+ .

Anodes were baked in a resistance-heated furnace and in packing coke at five different maximum temperatures: 920°C, 1000°C, 1080°C, 1160°C and 1260°C. Heat-up rate was 35°C/h and a soak time of 56 hours was applied.

The resulting baked lab scale anodes were characterized for:

- baked apparent density
- real density in helium
- resistivity
- Young's modulus
- permeability
- coefficient of thermal expansion
- BET surface area
- oxy and carboxy reactivity
- sulphur content.

Results

Optimum Pitch Content and Anode Properties

Figure 2 shows the baked apparent density versus the binder pitch content for each of the four cokes. For any given pitch content, the bench scale anodes manufactured with the A type coke reached higher densities than those obtained with the B type coke. For both cokes A^- and B^- (the lower calcination level), the maximum densities were achieved with a lower binder pitch content than for A^+ and B^+ cokes.

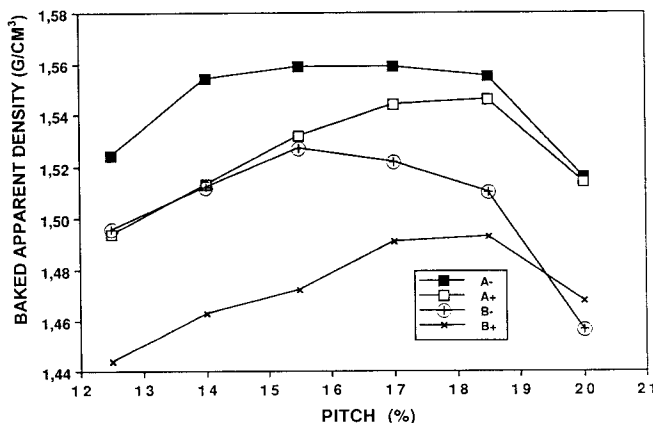


Figure 2: Baked Apparent Density VS Pitch Content.

Table IV summarizes the optimum pitch content and accessible porosity values (based on mercury porosimetry measurements) for each of the four cokes tested.

Table IV
Accessible Porosity and Pitch Optimization

Coke	A-	A+	B-	B+
Vo (X 10 ³ cm ³ /g)	41	34	41	33
V1 (X 10 ³ cm ³ /g)	57	50	62	47
Optimum pitch content (%)	16.3	18.0	15.5	18.0

Vo = porosity between 90µm and 15µm pore diameter.
V1 = porosity between 15µm and 0.5µm pore diameter.

Note that optimum pitch content increased for both coke A and B as a function of the calcination level. The increased demand in binder pitch obviously cannot be linked to an increase in porosity between A⁻ and A⁺ or B⁻ and B⁺ since Vo and V1 both decreased for each coke. No clear explanation for this increase in pitch demand can be given at this time.

The evolution of the other physical characteristics are presented in Figures 3 to 8.

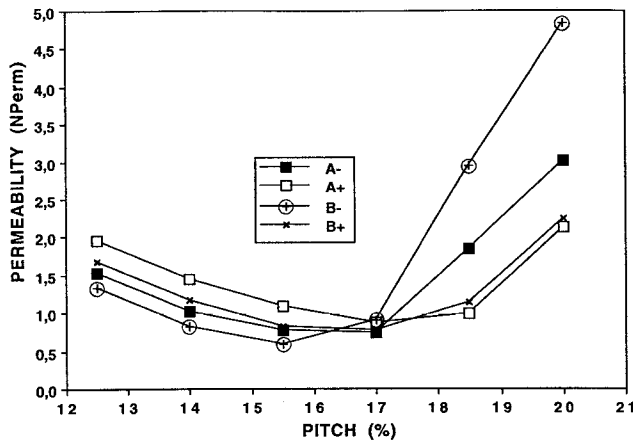


Figure 3: Permeability VS Pitch Ratio.

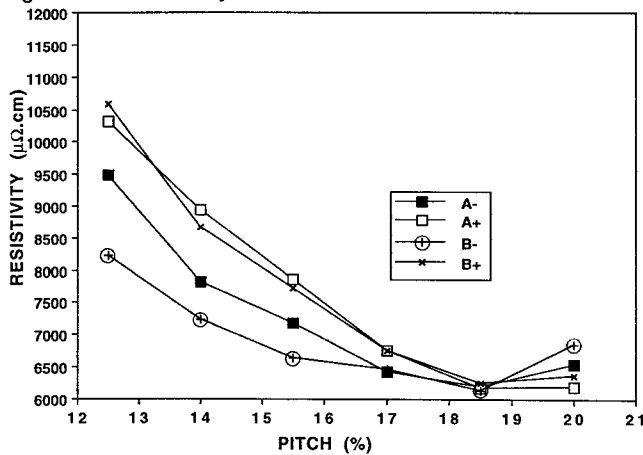


Figure 4: Resistivity VS Pitch Ratio.

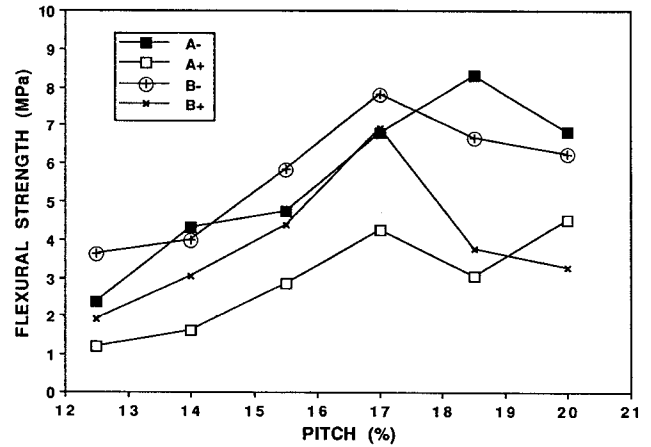


Figure 5: Flexural Strength VS Pitch Ratio

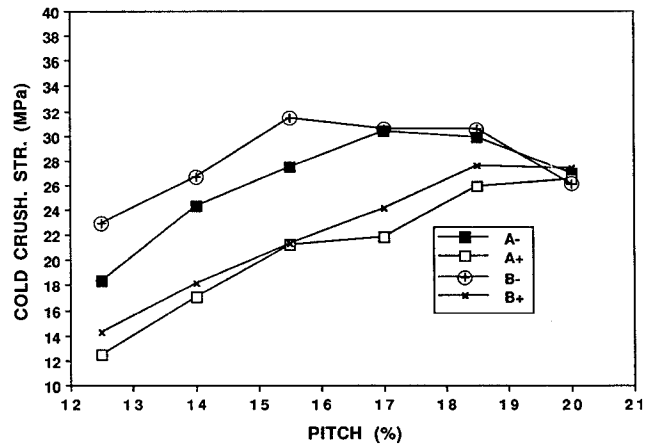


Figure 6: Cold Crushing Strength VS Pitch Ratio.

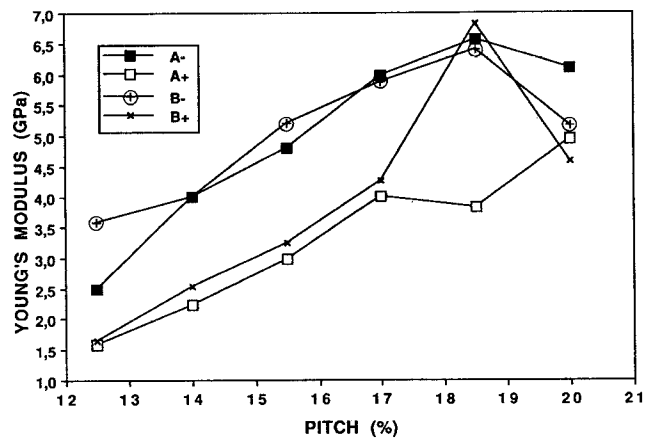


Figure 7: Young's Modulus VS Pitch Ratio.

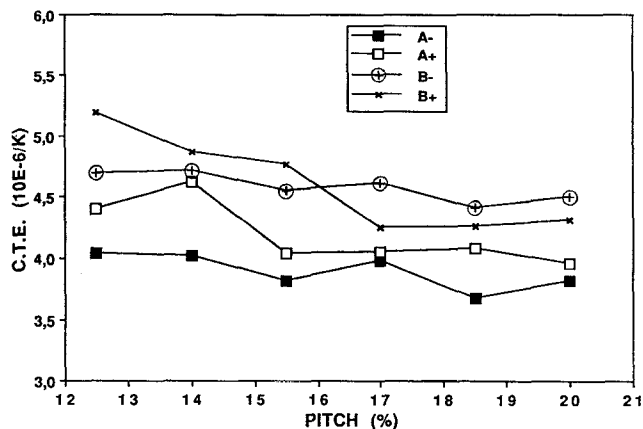


Figure 8: Coefficient of Thermal Expansion VS Pitch Ratio

Based on the study of the pitch content as a function of each coke, it was determined that bench scale anodes manufactured with highly calcined cokes resulted in less advantageous physical and mechanical properties. In particular:

- Resistivity was higher with highly calcined coke, but at optimum pitch content, not significantly different.
- Flexural and compressive strength, as well as Young's modulus, were lower.
- The coefficient of thermal expansion of anodes prepared with high temperature calcined cokes was not significantly different from the low temperature calcined cokes.
- The calcining of cokes at high temperature leads to an unexplained additional demand in pitch in order to reach the optimum baked apparent density. In any case, the less calcined cokes produced anodes of higher baked density.

Influence and Importance of the Baking Level

Figure 9 shows that sulphur release of the anodes manufactured with the high sulphur B coke was very high above 1100°C.

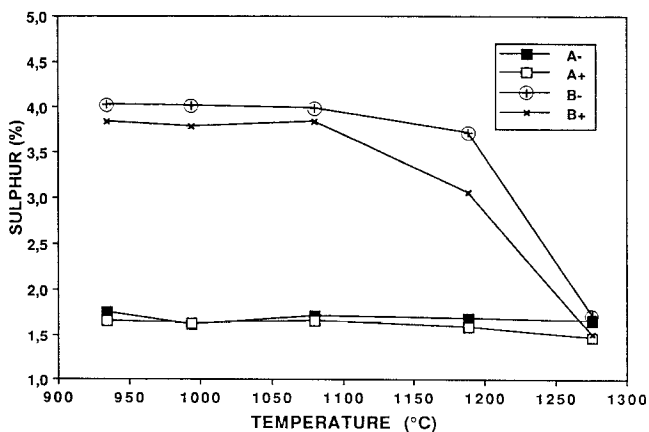


Figure 9: Sulphur Content VS Baking Temperature.

Limited sulphur losses occurred for the low sulphur content A coke; such sulphur losses appeared to occur only with the A⁺ coke. It was more surprising to see that for both cokes A and B, the higher the coke was calcined, the sooner the sulphur escaped during anode baking. Thermal sulphur release seemed to be the key phenomenon affecting almost every anode characteristic.

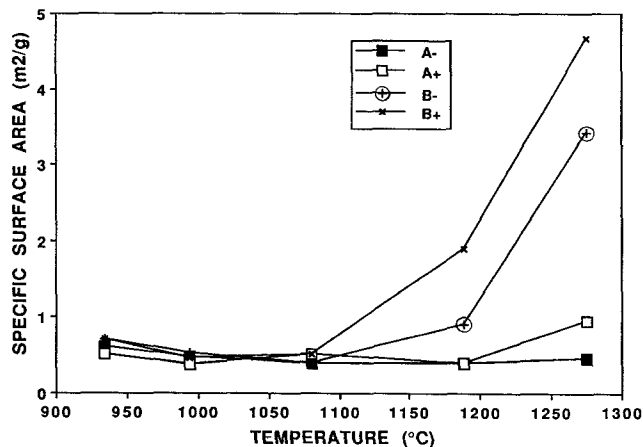


Figure 10: Specific Surface Area VS Baking Temperature.

- BET surface area increased rapidly with the sulphur loss in the anodes produced with the higher sulphur B coke. (See Figure 10.)

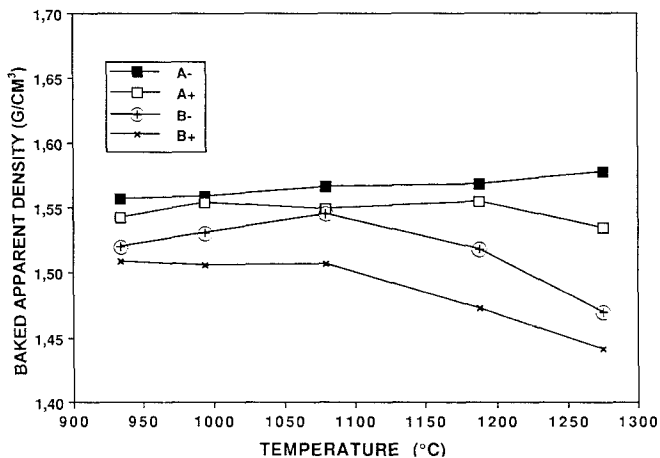


Figure 11: Baked Apparent Density VS Baking Temperature.

- Baked apparent density was higher for the low sulphur A⁻ and A⁺ cokes; baking temperature had an influence only on A⁺ coke at 1260°, when desulphurization was noted. The effect of desulphurization was quite prominent for the high sulphur B⁻ and B⁺ coke. Baked apparent density dropped notably for both as the temperature increased; for B⁺ it was especially noteworthy. (Figure 11.)

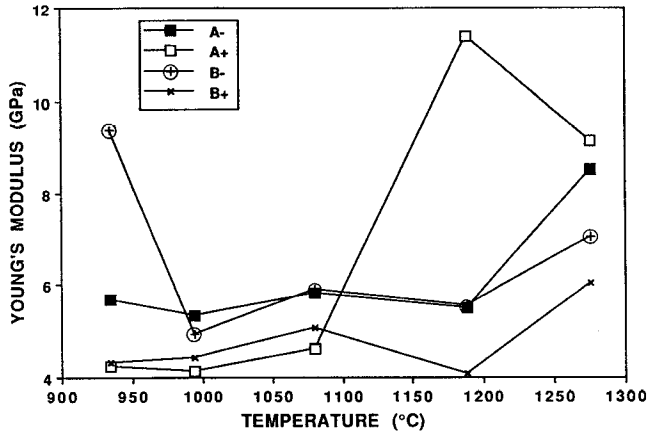


Figure 12: Young's Modulus VS Baking Temperature.

- Young's modulus increased slightly with increased baking temperature for all anode samples. (Figure 12.)

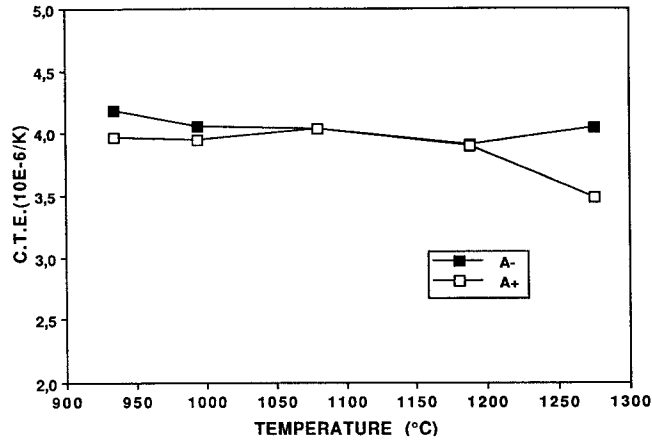


Figure 13: Coefficient of Thermal Expansion VS Baking Temperature (Coke A)

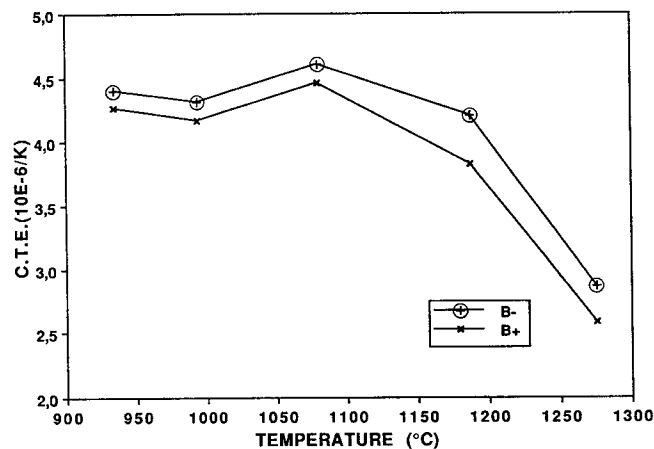


Figure 14: Coefficient of Thermal Expansion VS Baking Temperature (Coke B)

- The coefficient of thermal expansion of the anodes dropped rapidly when desulphurization began. (Figures 13 and 14.)

Anodes manufactured with highly calcined high sulphur coke B+ were those affected earlier and to a greater extent. The baking process, or more exactly, the combined effect of temperature and soaking time may have affected, to a large extent, the coefficient of thermal expansion of the final product.

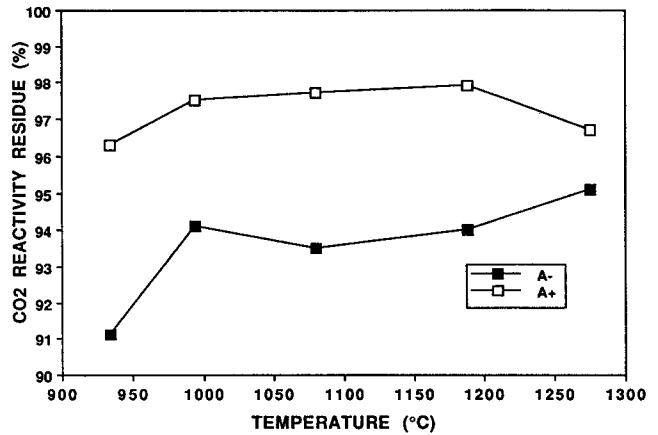


Figure 15: CRR VS Baking Temperature (Coke A)

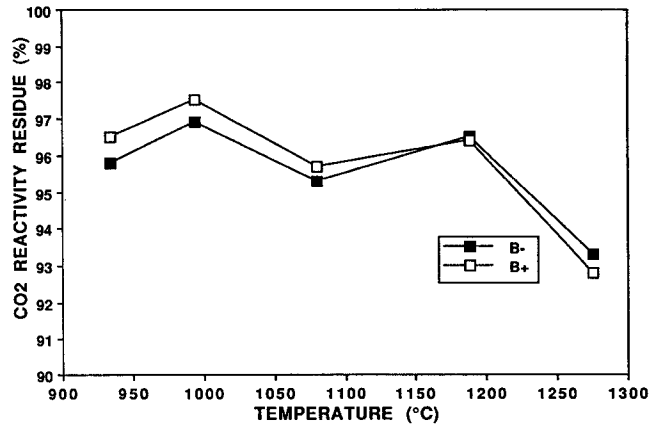


Figure 16: CRR VS Baking Temperature (Coke B)

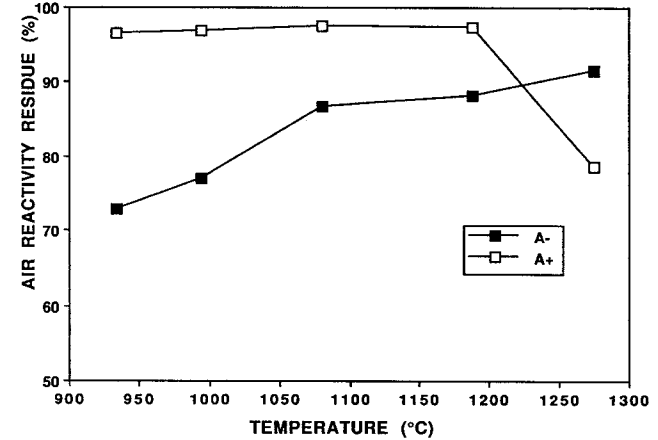


Figure 17: ARR VS Baking Temperature (Coke A)

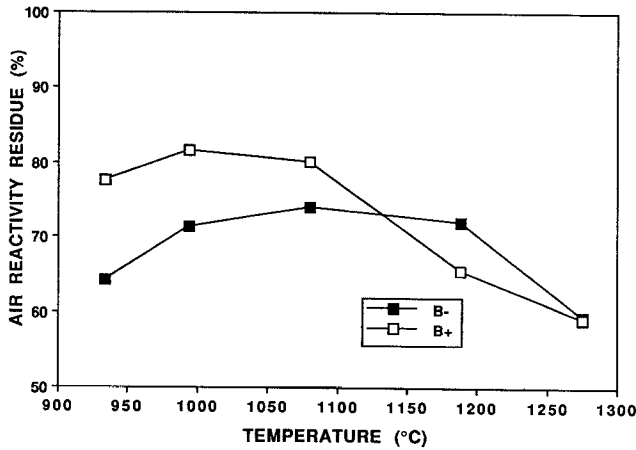


Figure 18: ARR VS Baking Temperature (Coke B)

- Figures 15 through 18 show that the highly calcined cokes had generally higher reactivity residues. As expected, reactivity residue deteriorated rapidly as desulphurization occurred, particularly with the high sulphur B cokes.

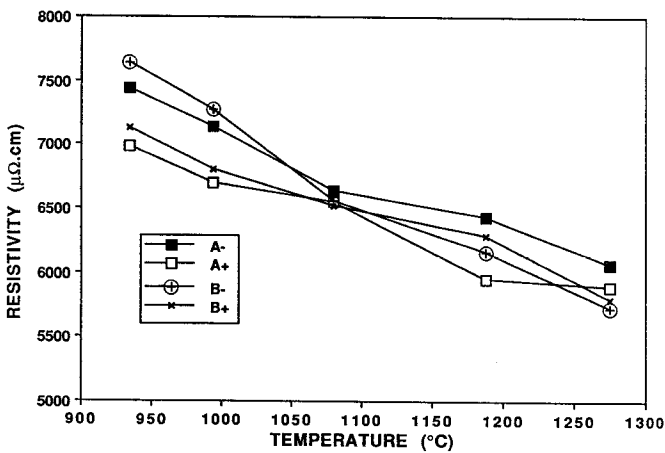


Figure 19: Resistivity VS Baking Temperature.

- Desulphurization did not affect resistivity which continuously decreased with the increase in baking level. Resistivity was not much affected by the calcination degree of the cokes. (Figure 19)

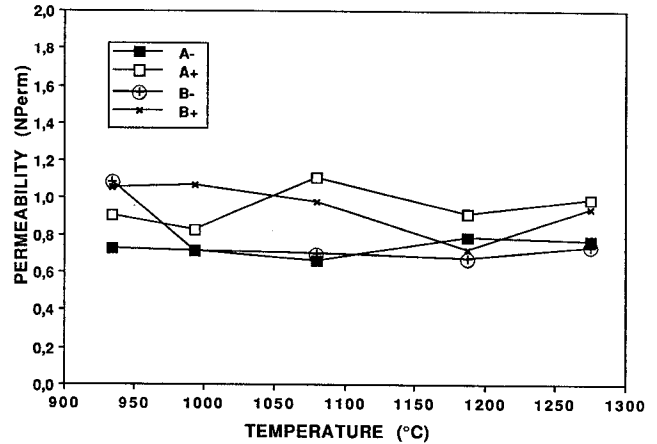


Figure 20: Permeability VS Baking Temperature

- Desulphurization did not affect permeability. This result implies that the sulphur evolution led to formation of closed microporosity in grains. (Figure 20)

Conclusions

This work coupled with other recent studies showed that the degree of coke calcination affects chemical, physical and mechanical properties of anodes. The degree to which such properties are affected is strongly related to the sulphur content of the coke.

Generally, highly calcined cokes result in anodes which are less reactive but with poorer mechanical and physical properties. These anodes have less resistance to desulphurization under excessive baking conditions. In other words, there appears to be a direct link between anode desulphurization during baking and coke calcination level.

The physical and mechanical properties of the anodes produced with the lower calcined cokes were better than those produced with the highly calcined cokes.

If anode reactivity is of prime importance and the coke is low in sulphur, higher levels of coke calcination may be desired.

For higher sulphur cokes or for applications where anode reactivity is less critical than mechanical properties, lower levels of calcination may be desired.

In the case of anodes produced with high sulphur cokes, when strong sulphur evolution starts, most of the characteristics of the anodes diminished rapidly. Only the CTE improved.

The optimum baking level, defined by the maximum temperature and minimum soaking time, should be chosen as close as possible to the level for which the desulphurization process starts to diminish the anode properties. Correct baking level adjustment is especially important with high sulphur content cokes and seems to have farther reaching consequences than the level of coke calcination.

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