# ANODE DESULFURIZATION ON BAKING

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## Abstract

The phenomenon of sulfur loss during the calcining of petroleum cokes and the subsequent impact on anode quality has been widely reported in the literature. However, the fact that these same petroleum cokes undergo a further extensive heat treatment during anode baking, which can also lead to sulfur loss, has not been as well documented. Although anodes are subjected to lower maximum temperatures during baking than are petroleum cokes during calcining, the exposure time in the baking operation is much greater. In this study, the combined effect of baking furnace time and temperature have been examined and found, under certain conditions, to result in anode desulfurization leading to poorer anode quality.

## Background

The objective of anode baking in any given smelter is to produce anodes of uniform quality with respect to common measurements such as air and $CO_2$ reactivity, air permeability and strength (compressive and tensile). To achieve uniformity of properties, the best baking furnaces can achieve a uniform baking temperature (typically 1100-1150°C) with a variation of $\pm$25°C. Older furnaces can operate with variations of $\pm$50°C if properly maintained and well-controlled. Such minimization of baking temperature variability is commonly thought to produce the desired objective.

In an effort to improve baked anode properties, a smelter supplied with low sulfur and high sulfur cokes (which were precisely blended) had methodically increased baking severity. Average anode baking temperature had been increased to near 1200°C with a soak time of 56 hours. While anode properties were generally good, some baked cores showed greatly diminished properties. High air reactivities, $CO_2$ reactivities and permeability were frequently coincident with abnormally low sulfur levels (<2.0% S as compared to >2.3% normal). At first, the lower than normal sulfur was attributed to inconsistent blending of the incoming cokes. But a consistent history of poor physical properties with the lower sulfur cores led the technical people to believe that desulfurization during the baking was responsible for these observed results. This concern became the basis for this investigation.

## Introduction

Garbarino and Tonti[1] describe three ways in which sulfur can be released from petroleum cokes during calcining:

1. sulfur released with volatile matter during thermal devolatilization.
2. sulfur lost or burned in association with either the kiln coke bed or coke particle entrainment in the kiln exhaust gases, and
3. sulfur thermally dissociated from the coke during calcination.

This study will focus on the last method of sulfur loss due to thermal dissociation which has traditionally been referred to as "desulfurization."

Gehlbach et al.[2], in a laboratory calcining study investigating desulfurization, identified a "critical temperature," Tc, corresponding to the initial release of sulfur and the creation of micropore volume (pore diameters < 0.1mm). This critical temperature was found to be coke specific and ranged from 1300°C for the highest sulfur coke to 1500°C for the lowest sulfur coke in their test group. Hardin et al.[3] also carried out laboratory calcinings, finding similar results and reporting that the severity of thermal desulfurization appears to be directly related to the sulfur content of the green coke. Calcining times in the two studies were 45 minutes and 30 minutes respectively.

Two points bear mentioning about such test work:

1. The soak times are typically less than one hour.
2. The so-called critical temperature is the temperature at which sulfur loss becomes detectable for the given soak time.

This means that sulfur could still be lost at temperatures lower than the so-called critical temperature but, due to the much lower evolution rates, this loss will only become measurable with longer soak times. This is just the situation found in anode baking where the blocks are exposed to elevated temperatures for many hours. Unfortunately, this point is often overlooked by anode manufacturers who bake anodes at target temperatures 1100-1150°C which are well below the "critical temperatures" and therefore do not consider the possible detrimental effects of desulfurization due to extended soak times. Fischer et al.[4], for example, have shown that anode



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desulfurization during anode baking, particularly with high sulfur cokes, can dramatically impact air reactivity.

To further examine such reported findings, a study was initiated by Calciner Industries, Inc. in conjunction with Kaiser Aluminum & Chemical Corporation, Primary Products Division Technology Center in Mead, Washington, using a designed experiment approach to investigate and quantify the impact of both soak time and final baking temperature on the desulfurization and resultant quality of a particular anode type.

## Experimental

A regular green anode having a sulfur content of 2.3 % was taken from an operating smelter and cored as shown in Figure 1 to give 54 core samples that were 12.7 cm (5 inches) in diameter and 17.8 cm (7 inches) in length. Thirty-six of these cores were required for the subsequent test program and these were randomly selected from the population and assigned an identification number as shown in Table 1.

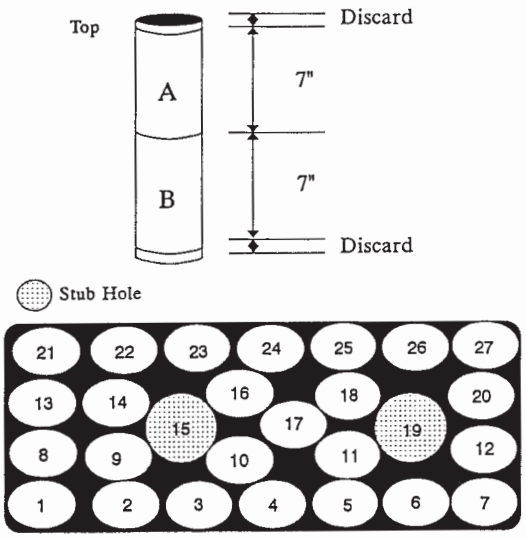



**Figure 1: Core sampling pattern within the anode**

**Table 1: Random assignment of anode cores to the test program**

| Anode Pos | A | B | Anode Pos | A | B |
|---|---|---|---|---|---|
| 1 | 3658 | 3655 | 15 | - | - |
| 2 | 3664 | 3661 | 16 | 3656 | 3659 |
| 3 | 3670 | 3667 | 17 | 3680 | 3683 |
| 4 | 3676 | 3673 | 18 | - | - |
| 5 | 3682 | 3679 | 19 | - | - |
| 6 | 3668 | 3671 | 20 | 3689 | - |
| 7 | - | - | 21 | 3654 | 3657 |
| 8 | 3684 | - | 22 | 3660 | 3663 |
| 9 | - | 3685 | 23 | 3666 | 3669 |
| 10 | 3662 | 3665 | 24 | 3672 | 3675 |
| 11 | 3674 | 3677 | 25 | 3678 | 3681 |
| 12 | - | 3686 | 26 | - | - |
| 13 | 3687 | - | 27 | - | - |
| 14 | 3688 | - | | | |

Commercially available software was used to help design the experiment and evaluate the data. This software requires that the variables under test be selected around "mean values." The mean value case is run in duplicate to establish the experimental error. The Taylor Expansion Equation is then used to model the desired responses as a function of these variables. By comparing actual observed values with calculated values from the model, the percent of variation explained by the model can be quantified along with the unexplained variation, taking into account the experimental error.

The test program is summarized in Table 2. The variables are final baking or "peak" temperature (1150, 1200 and 1250°C) and soak time (20, 50 and 80 hours). The mean value case, run in duplicate, is a bake at 1200°C for 50 hours. A standard bake at 1150 °C for 8 hours was run as a baseline. Three cores were baked at each of the ten test conditions and six cores baked for the baseline case. The heat-up rate for baking followed standard laboratory ramp rates up to the target temperature and then were held at that temperature for the target soak time.

**Table 2. Test program**

| BAKE # | PEAK TEMPERATURE(°C) | SOAK TIME(Hr) | SAMPLE # |
|---|---|---|---|
| 1 | 1250 | 20 | 3654,3655,3656 |
| 2 | 1200 | 50 | 3657,3658,3659 |
| 3 | 1200 | 50 | 3660,3661,3662 |
| 4 | 1200 | 20 | 3663,3664,3665 |
| 5 | 1200 | 80 | 3666,3667,3668 |
| 6 | 1250 | 50 | 3669,3670,3671 |
| 7 | 1150 | 80 | 3672,3673,3674 |
| 8 | 1250 | 80 | 3675,3676,3677 |
| 9 | 1150 | 20 | 3678,3679,3680 |
| 10 | 1150 | 50 | 3681,3682,3683 |
| 11 | 1150 | 8 | 3684,3685,3686, 3687,3688,3689 |

Samples were prepared and analyzed as shown in Figure 2 to give the desired responses (anode properties). The results of all of the analyses were averaged. The conditions for the model can be summarized as follows:

Variables and Levels

| | -1.0 | 0.0 | 1.0 |
|---|---|---|---|
| X1=Peak Temperature | 1150°C | 1200°C | 1250°C |
| X2=Soak Time | 20 hours | 50 hours | 80 hours |

Responses

Y1 = Sulfur (%)
Y2 = Weight Loss (%)
Y3 = Average Dimensional Change (%)
Y4 = Ash (%)
Y5 = Baked Density (g/cc)
Y6 = Thermal Conductivity (W/mK)
Y7 = Compressive Strength ($kg/cm^2$)
Y8 = Young's Modulus ($N/m^2 \times 10^8$)
Y9 = Flexural Strength ($kg/cm^2$)
Y10 = Electrical Resistivity ($\mu$ohm-m)
Y11 = Air Permeability (nPm)
Y12 = $CO_2$ Reactivity TL ($mg/cm^2hr$)
Y13 = Air Reactivity TL ($mg/cm^2hr$)

Taylor Expansion Equation

$$Yi = k_{-0} + k_{-1}[X1] + k_{-2}[X2] + k_{-3}[X1]^2 + k_{-4}[X2]^2 + k_{-5}[X1][X2]$$

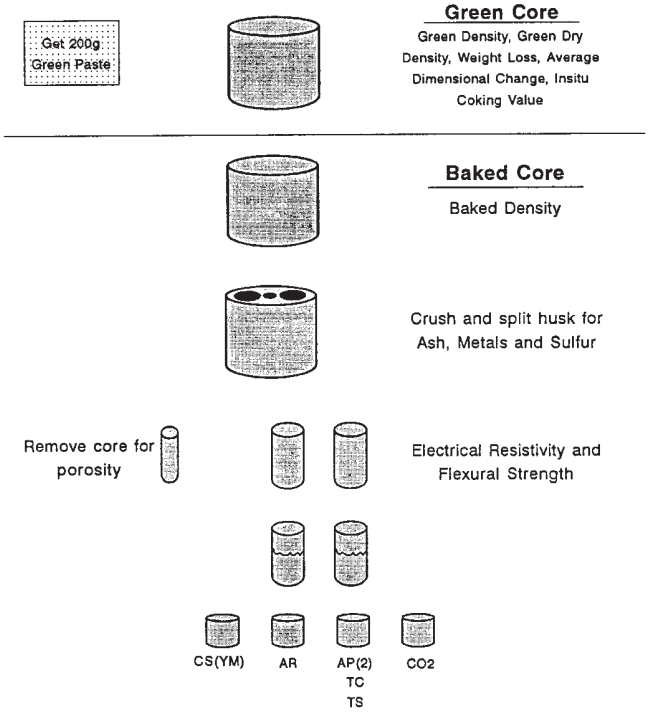



**Figure 2. Sample preparation showing properties analyzed.**

## Results

The software literature indicates that a significant level of confidence is achieved when the percent variation explained by the model is >70 %. A low confidence level can result from data that is unaffected by the variables tested, inhomogeneous samples and/or variation within the test which is large when compared to the variation within the samples.

For each of the anode properties under test, Table 3 gives the percent of variation explained by modeling the baking conditions, the percent due to experimental error and the percent unexplained by either the model or experimental error. Figures 3a, b, c, d, and e show graphical representations of the model for most of these anode properties.

Table 3. Summary of the percent of variation that is: explained by the model; due to experimental error; and unexplained by either the model or experimental error.

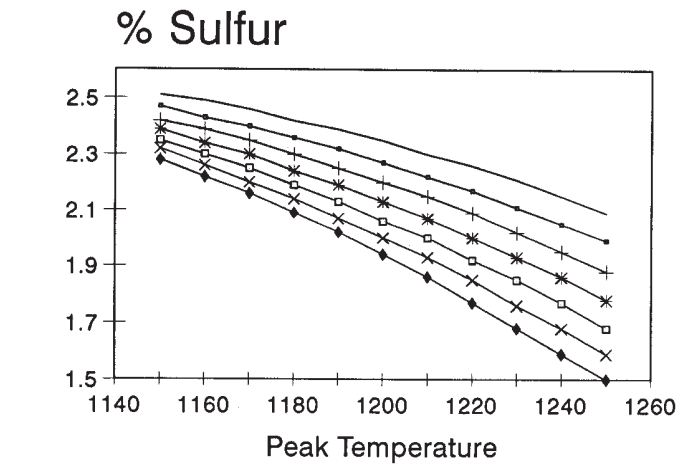
| PROPERTY | % Variation explained by Model | % Variation Due to Experimental Error | % Variation Unexplained |
|---|---|---|---|
| Sulfur | 97.22 | 0.81 | 1.97 |
| Ash | 56.98 | 0.82 | 42.20 |
| Weight Loss | 97.81 | 0.27 | 1.92 |
| Avg. Dimensional Change | 90.86 | 5.21 | 3.93 |
| Baked Density | 76.84 | 2.73 | 20.43 |
| Compressive Strength | 91.62 | 8.20 | 0.18 |
| Young's Modulus | 80.80 | 4.94 | 14.26 |
| Flexural Strength | 57.36 | 9.83 | 32.81 |
| Electrical Resistivity | 58.72 | 11.84 | 29.44 |
| Thermal Conductivity | 67.03 | 1.8 | 31.17 |
| Air Permeability | 90.90 | 3.01 | 6.09 |
| $CO_2$ Reactivity | 90.56 | 0.25 | 9.19 |
| Air Reactivity | 61.48 | 11.63 | 26.89 |

## Discussion

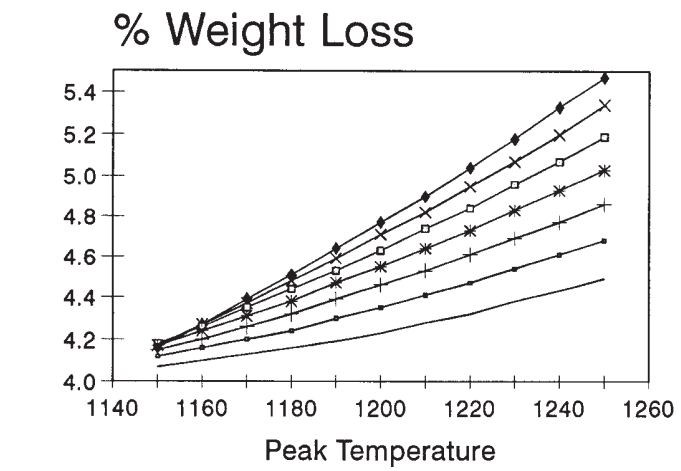
The anode properties measured in this study can be conveniently categorized into three areas for discussion purposes: impurities (sulfur, ash); physical properties (density, mechanical properties); and chemical properties ($CO_2$ and air reactivity).

## Impurities

Based on the high confidence level (97.72%) of the family of curves seen for sulfur (Figure 3a), it is clear that both peak temperature and soak time lead to desulfurization of this particular anode type. It can be seen that any increase in peak temperature or soak time results in additional sulfur loss indicating that some degree of desulfurization is always occurring over the range of values studied here. For example, if one considers the bake at 1150 °C for 20 hours, an increase in soak time to 80 hours or an increase in peak temperature to just above 1220 °C both result in a 0.25% (absolute) loss in sulfur. Of critical importance is the amount of porosity created by such sulfur loss. This has been determined by Hg




97.2% Explained by the Model




97.8% Explained by the Model

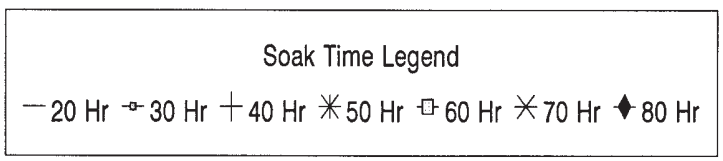
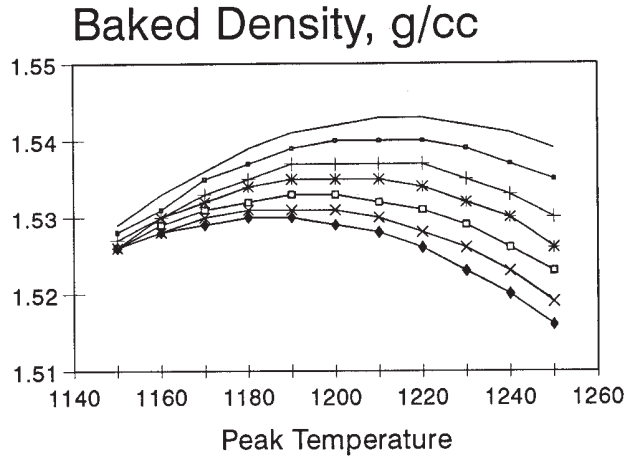
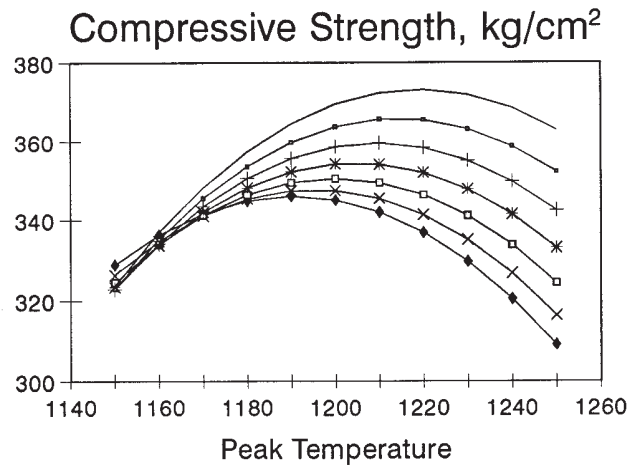



Figure 3a: Selected anode properties as a function of peak temperature and soak time.




76.8% Explained by the Model




91.6% Explained by the Model

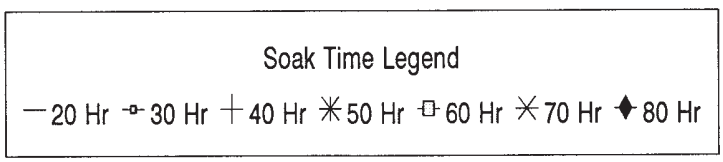
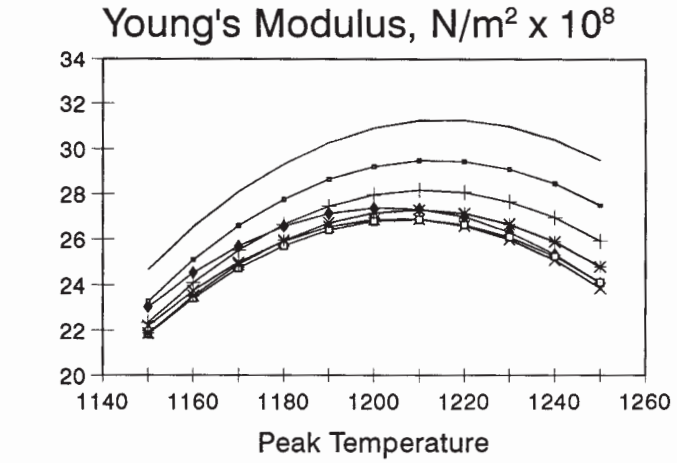
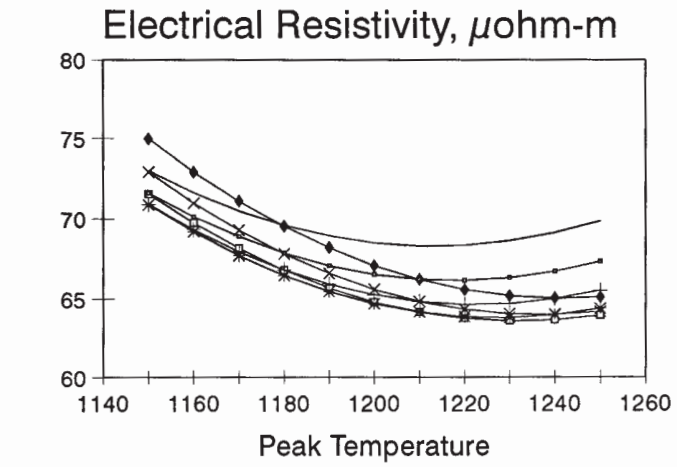



Figure 3b: Selected anode properties as a function of peak temperature and soak time.




80.8% Explained by the Model




58.7% Explained by the Model

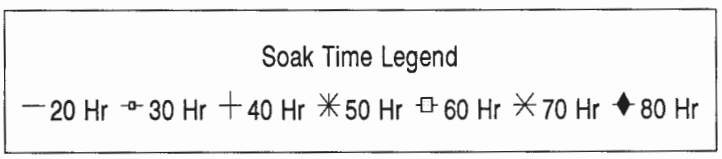
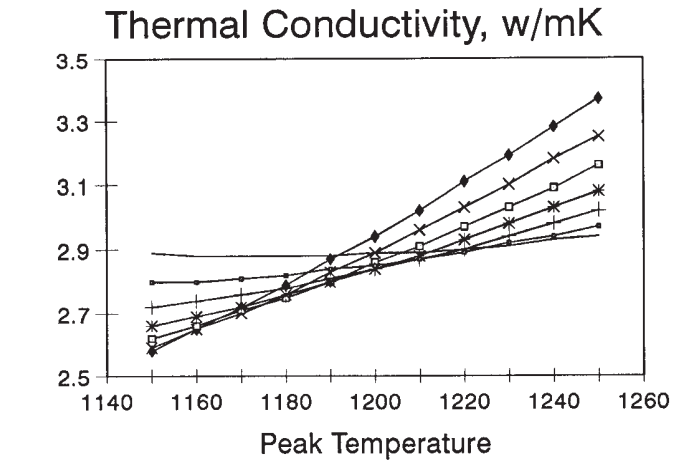
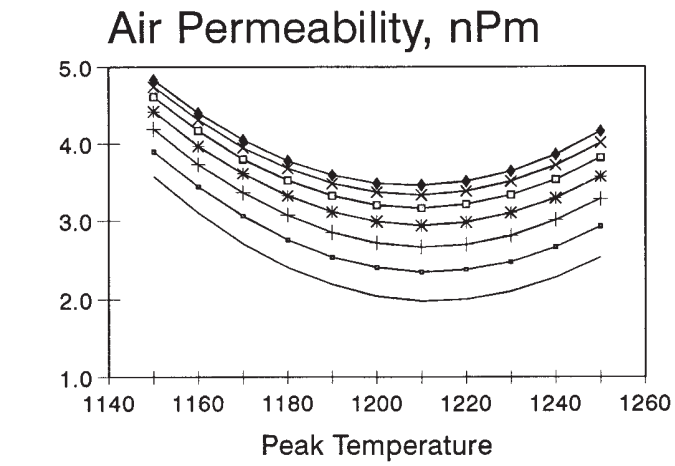



Figure 3c:Selected anode properties as a function of peak temperature and soak time.




67.0% Explained by the Model




90.9% Explained by the Model

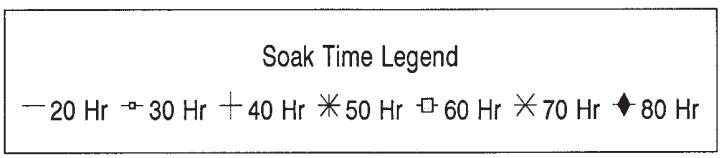
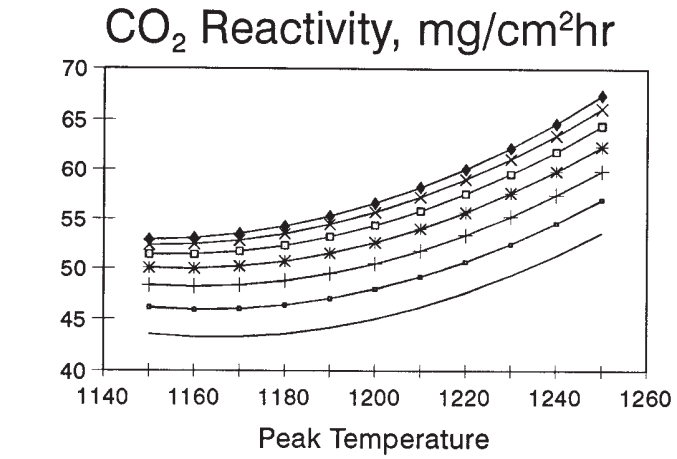
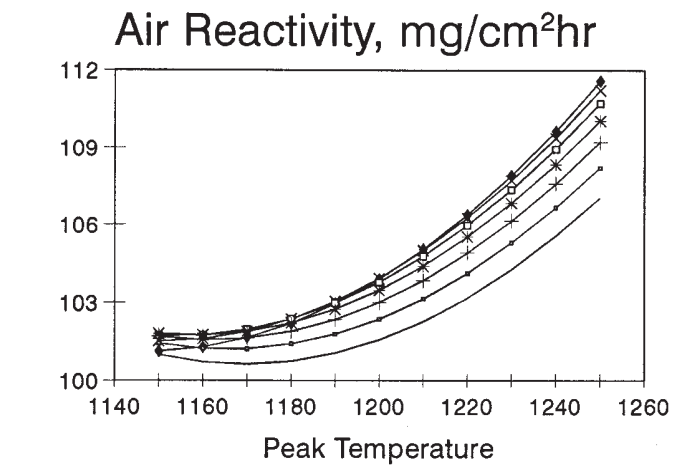



Figure 3d:Selected anode properties as a function of peak temperature and soak time.




90.6% Explained by the Model




61.5% Explained by the Model

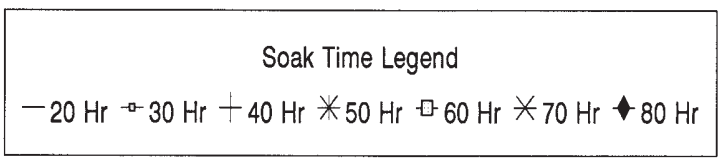



Figure 3e:Selected anode properties as a function of peak temperature and soak time.

porosimetry and is shown in Figure 4. The porosity resulting from the 0.25 % loss in sulfur when increasing soak time to 80 hours is much greater (161 $mm^3/g$) than that found when raising peak temperature to 1220°C (155 $mm^3/g$). Consequently, the way in which the sulfur is lost, and not the total loss, will affect the resulting porosity characteristics of an anode. As will be seen in the following discussion, this has significant implications for the anode properties.

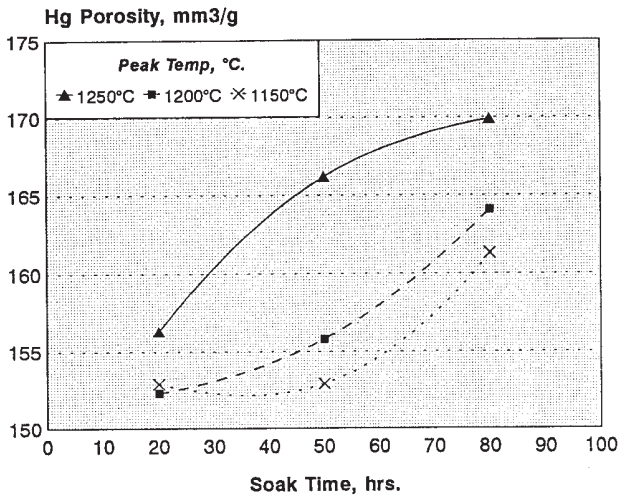



**Figure 4. Anode porosity, as determined by porosimetry, as a function of peak temperature and soak time.**

The low confidence level for ash (56.98 %) indicates that ash levels are unaffected by the baking conditions. Any volatile loss of inorganic matter, for example sodium as reported by Stokka[5], appears to be constant for a given anode type over the range of peak temperatures and soak times investigated.

Physical Properties

With the exception of flexural strength, electrical resistivity and thermal conductivity, all physical properties have been modeled with a high level of confidence. The apparent lack-of-fit for these three properties is attributed to transverse hairline cracks in the core samples which can significantly affect the measured value[6]. This is supported by the high percent of variation due to experimental error seen for flexural strength and electrical resistivity.

In general, the trends shown by each modeled property resemble those reported in the literature where peak temperature was varied at constant soak time[4, 7-10]. Baked density, compressive strength, Young's modulus, electrical resistivity, thermal conductivity and air permeability all show maxima/minima indicating an optimum peak temperature at a given soak time. This results from the competing phenomena of densification due to graphitization versus desulfurization-created porosity.

Heintz[11] has shown that heat treating graphitizing carbons, such as those found in an anode, leads to a progressive improvement in the degree of order and growth of the graphitic crystallites that make up the carbon structure. In an anode, subsequent densification of the material with a resulting decrease in porosity is characterized by improvements in baked apparent density and mechanical properties. However, as seen in this study for sulfur, the more extensive the heat treatment, the greater the sulfur loss until ultimately the impact of the resultant porosity counteracts and exceeds the benefits derived from structural development due to graphitization. A similar trade-off between structural and porous effects has been reported in a study on the effect of calcination temperature on calcined coke properties[12].

The families of curves for each physical property indicate that lower soak times lead to better anode properties irrespective of peak temperature. This can be attributed to the significant increase in porosity that has been observed with extended soak times due to the nature of the sulfur evolution (see Figure 4).

Chemical Properties

A high level of confidence is seen for the $CO_2$ reactivity model. The low level of confidence seen for the air reactivity model appears to be due to a large variation within the samples. This is evidenced by the high percent of variation due to experimental error. Nonetheless, the trends, showing an optimum baking temperature at a given soak time, are similar to those reported by Fischer et al.[4] with the porosity created by the loss of sulfur ultimately contributing to poorer reactivity behavior. This is due to an increase in the number of active sites available for the oxidant molecules to attack the carbon surface[13].

For both $CO_2$ and air reactivity lower soak times lead to better anode performance as was similarly observed for the physical properties.

Conclusions

1. This study has shown that desulfurization during baking is a function of both peak temperature and soak time. Sulfur loss occurs constantly during the heat treatment of carbon anodes and is not "triggered" at a certain critical temperature.

2. The families of curves generated for each anode property from the software typically show an optimum peak temperature for a given soak time.

3. The family of curves generated for each anode property from the software typically show that lower soak times lead to better performance at all peak temperatures.

4. As changes in peak temperature and/or soak time have a similar impact on both the physical and chemical properties of an anode, two strategies are suggested for the operation of a baking furnace:

   a. Where a pre-selected soak time has been chosen to ensure an even temperature distribution in the pits, an optimum peak temperature exists below which the full benefits of graphitization have not been reached and above which the detrimental effects of desulfurization begin to occur.

   b. Where a pre-selected peak temperature has been chosen to give the desirable anode properties, the soak time should be maintained at the shortest practical time to ensure a minimal degradation of anode properties arising from desulfurization while still allowing suitable time for pit temperature uniformity.

5. The absolute values of peak temperature and soak time giving optimum performance are uniquely dependent on the particular anode quality, raw material used, and the desired strategy for operating the baking furnace. For this reason this study has focused more on the observed trends rather than recommending precise operating conditions.

Epilogue

The smelter which experienced the high levels of desulfurization during baking has since reduced its target baking temperature to 1150°C. Efforts have also been made to improve the variation in baking temperature by modifications to the firing system. The result is now a variation of below $\pm$50°C. Anode quality is much improved with fewer "desulfurized anodes."

## REFERENCES


1. R. M. Garbarino and R. T. Tonti; "Desulfurization and its effect on calcined coke properties." Light Metals 1993, p. 517-520.

2. R. E. Gehlbach, L. I. Grindstaff and M. P. Whittaker; "Effect of calcination temperature on real density of high sulfur coke." Light Metals 1977.

3. E. E. Hardin, P. J. Ellis, C. L. Beilharz and L. McCoy; A comprehensive review of the effects of calcination at various temperatures on coke structure and properties Part II." Light Metals 1994, p. 571-581.

4. W. K. Fischer, F. Keller, R. Perruchoud and S. Oderbolz; "Baking parameters and the resulting anode quality." Light Metals 1993, p.683-689.

5. P. Stokka; "The effect of petroleum coke sulfur content on the loss of sodium during baking." Light Metals 1994, p. 695-699.

6. W. K. Fischer and R. C. Perruchoud; "Determining prebaked anode properties for aluminium production." Journal of Metals, Vol. 39, No. 11, p. 43-45, (1987).

7. A. Slagtern, K. Grjotheim, T. Foosnaes and T. Naterstad; "Thermal expansion of carbon materials calcined at various temperatures: structure, pore volume and content of impurities." Light Metals 1987, p. 449-458.

8. S. R. Brandtzaeg, O. Lid and J. Arntzen; "Anode quality related to operational parameters by baking. A comprehensive large scale test." Light Metals 1987, p. 597-602.

9. C. Dreyer; "Anode reactivity influence of the baking process." Light Metals 1989, p. 595-602.

10. D. L. Belitskus; "Effect of petroleum coke calcination temperature and anode baking temperature on anode properties." Light Metals 1991, p. 557-564.

11. E. A. Heintz; "Crystallite growth and ordering of cokes in the pre-graphitization temperature range." Proc. 5th London International Carbon and Graphite Conference, Society of Chemical Industry, Vol. II, p. 575-587, (1978).

12. W. K. Fischer and R. C. Perruchoud; "Influence of coke calcining parameters on petroleum coke quality." Light Metals 1985, p. 811-826.

13. P. L. Walker, F. Rusinko, L. G. Austin; "Gas reactions of carbon." Advances in Catalysis, Vol. 11, p. 133, (1959).