A COMPREHENSIVE REVIEW OF THE EFFECTS OF CALCINATION AT VARIOUS TEMPERATURES ON COKE STRUCTURE AND PROPERTIES

PART II

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Abstract

Laboratory calcinings were performed to determine the effects on coke structure and properties when calcined at different temperatures. The temperature range was from 1200°C to 1500°C with emphasis at temperatures in close proximity to what is considered typical of commercial calcining temperature. The five cokes selected represented a wide range of properties from low sulfur cokes at 0.78% to high sulfur cokes at 4.2% and from anisotropic to isotropic in structure. In the initial "Part I" paper which was presented at the 1993 AIME Light Metals, the focus was on the bulk density and those properties often associated with measurements used to quantify and control degree of calcining including real density, electrical resistivity, and the crystalline features Lc and d-spacing. This "Part II" paper will discuss various property relationships to temperature including mercury apparent density, porosity, nitrogen, hydrogen, sulfur and metals, coefficient of thermal expansion, Hardgrove Grindability, and air and carboxy reactivity.

Introduction

A laboratory calcining program was performed to determine the effects of calcining temperature on coke properties. Specifically, the purpose was to determine the effects on coke properties at calcining temperatures from 1200°C to 1500°C. This study is different from many studies which have been performed and published in that emphasis was placed on the coke property effects at temperatures in close proximity to what is considered typical for commercial calcining. This was achieved by employing 25°C increment calcinings between 1250°C and 1350°C which is often considered typical of the temperature range employed in commercial calcining of anode grade cokes. At the lower and higher temperatures, 50°C increment calcinings were performed.

The final scope of this study is now complete. "Part I" of this study was presented at the 1993 AIME Light Metals(1). Properties which were covered in this "Part I" paper included vibrated bulk density, real density, electrical resistivity, and the crystalline features Lc and d-spacing. This "Part II" paper will cover many other properties including mercury apparent density, porosity, nitrogen, hydrogen, sulfur and metals, coefficient of thermal expansion, Hardgrove Grindability, and air and carboxy reactivity.

It is recommended that the "Part I" paper be read initially so that a more complete picture of the study and results from this "Part II" paper can be grasped.

Experimental

Cokes Evaluated

A total of five raw cokes were selected representing a wide range of properties. All of the cokes selected for this study are presently used either as a single coke and/or as a blend component in producing calcined coke used in the aluminum industry for preparing anodes. Properties were provided in the "Part I" paper, but are shown again in Table I for each of the five cokes tested.

Calcination

Laboratory calcinations were performed according to Great Lakes Special Analytical Method No. 139C. In brief, a representative 500 gram, -3 mesh size, dried coke sample is calcined. This is heat treated at the desired calcining temperature for a 30 minute period. This laboratory calcining technique was described in more detail in the "Part I" paper.

A. Tomsett and J. Johnson (Eds.), *Essential Readings in Light Metals*

Table I

RAW COKE PROPERTIES					
Sample No.	TE-314	TE-315	TE-316	TE-317	TE-431
Coke Description	Gulf Coast	Mid-Western	Mid-Western	Off-Shore	Gulf Coast
Volatile Matter, %	11.4	9.0	10.5	11.3	9.6
Hardgrove Grindability Index	67.2	50.0	72.2	99	74.8
Hydrogen, %	3.8	3.7	3.8	4.0	3.7
Nitrogen, %	1.1	1.7	1.4	1.8	1.1
Ash, %	0.20	0.18	0.20	0.20	0.12
Sulfur, %	4.2	1.7	2.2	0.78	4.1
Silicon, %	0.016	0.005	0.010	0.010	0.004
Iron, %	0.041	0.039	0.030	0.012	0.011
Vanadium, %	0.020	0.024	0.025	0.0077	0.025
Nickel, %	0.0061	0.012	0.010	0.0042	0.0065
Calcium, %	0.002	0.008	0.005	0.013	0.008
Aluminum, %	0.005	0.004	0.004	0.001	<0.001
Sodium, %	0.0011	0.0048	0.0026	0.026	0.0057
Titanium, %	0.0006	<0.0002	0.0005	<0.0002	0.0002
Coefficient of Thermal Expansion x 10^{-7}/°C	13.7	14.1	10.0	18.1	8.2
Shot Content, %	0	0	0	0	0

Coke Properties

All properties were determined using Great Lakes analytical test methods. Many of these were adapted from ASTM methods. Brief descriptions of the test procedures were provided in the "Part I" paper of this study. However, the Great Lakes reactivity test method was not described and a brief description is a follows:

Reactivity - The air and carboxy (CO_2) reactivities are measured in the same equipment but vary with respect to temperature, atmosphere and flow rate of the gas producing the atmosphere. The test measures the rate of weight loss (mg/min) as taken from the slope of the weight loss curve after sufficient time to achieve linearity.

Reactivity samples are composed of crushed and uncrushed -10/+20 mesh (Tyler) coke. Particles are weighed into a 2 1/4″ diameter 80 mesh PT-10Rh flat bottom sample holder, designed to provide maximum contact of the reacting gas with the sample. The sample is then lowered into the preheated vertical furnace with a series of platinum wires and suspended from a balance. The furnace is lined with a 2 1/2″ diameter Inconel tube insert.

The initial atmosphere is nitrogen which is used during sample change and until the temperature is restabilized after hanging of the sample holder on the balance. Gases (air or CO_2) are introduced at the bottom of the long Inconel furnace tube insert. Furnace temperature is controlled with a chromel-alumel thermocouple extending from the bottom of the tube to just beneath the sample holder and is controlled to ±1°C. Following the test period, the reactive gas is turned off, nitrogen is introduced to the system and the recorder turned off. The sample is removed from the furnace at this time.

The dynamic reactivity rate (mg/min) is calculated graphically by determining the slope of the weight loss curve once linearity has been established, usually 30-45 minutes into the test. Average of duplicate values are reported. Specific parameters for air and carboxy reactivity tests are as follows:

Parameters	Air Reactivity	Carboxy Reactivity
Purge/Preheat Gas	100 l/h N_2	100 l/h N_2
Furnace Temp.	525°C (see note)	1000°C
Sample Type	10x20 mesh Tyler	10x20 mesh Tyler
Sample Quantity	2.00 grams	5.00 grams
Gas Flow Rate	100 l/h	50 l/h
Standard Test Time	60 minutes	60 minutes

Note: The air reactivity often exhibits considerable spread from coke to coke. Test temperatures are varied (typically between 490°C to 550°C) if the coke is determined by established guidelines not to be sufficiently reactive or too reactive with the reactivity value corrected to 525°C according to the Arrhenius rate equation.

Results and Discussion

Apparent Density and Porosity

The relationships of mercury apparent density (AD) and porosity to calcining temperature are depicted in Figures 1-5. The AD, like vibrated bulk density (VBD), is frequently used as a measurement to quantify coke density. It is directly related to VBD and both are inversely related to porosity. It has been reported that the best single coke variable correlating with anode density is the VBD followed closely by mercury AD(2). It also has been reported that when an equation was developed which included a coke bulk density measurement (such as -28/+48 mesh VBD) along with porosity (such as the porosity below 5 micron size in diameter), that this provided a much improved indicator(3). A bulk density measurement gives a good indication of overall coke porosity, but it is reported that pores below a certain micron diameter are not penetrated by pitch. Therefore, at equal coke bulk density, the anode density would increase as the amount of fine microporosity (say less than 5 - 15 micron diameter) decreases. For this reason many aluminum users are interested in both a coke bulk density measurement (such as VBD and/or AD) as well as the pore size distribution to best quantify predicted anode density.

Figure 1

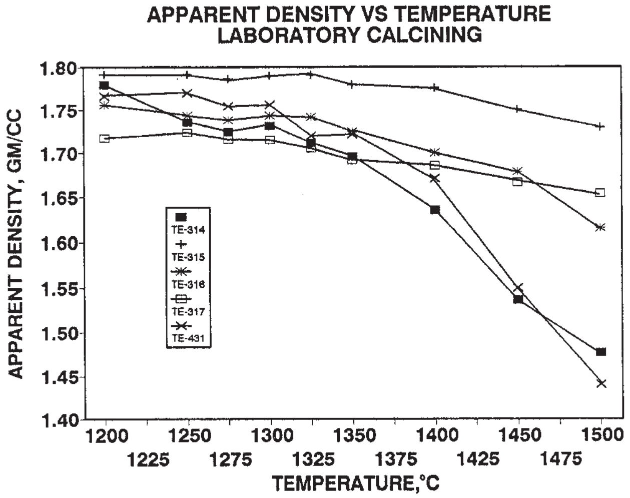


Figure 2

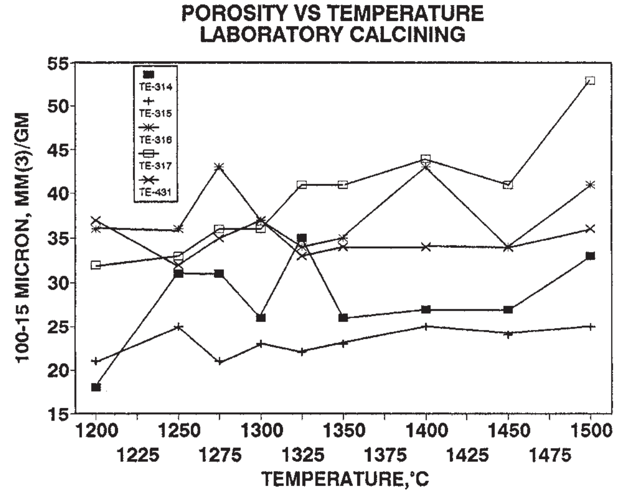
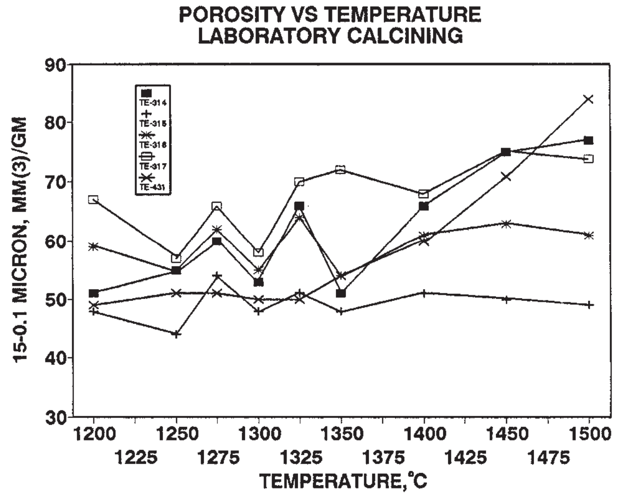
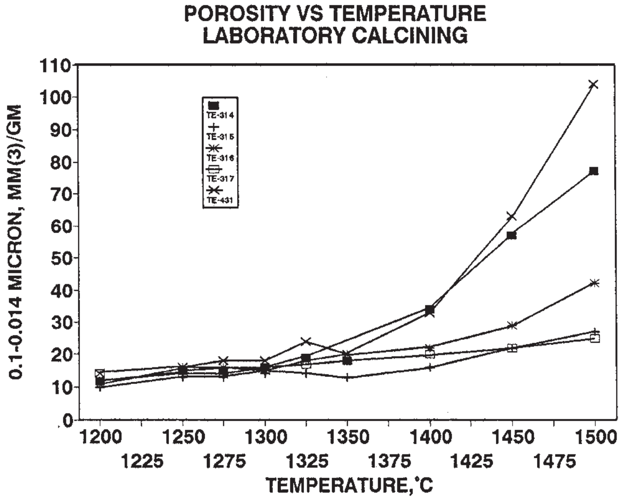


Figure 3



The AD and porosity data reveal at least two interesting points substantiating what was observed with the VBD relationships discussed in "Part I" paper. The first obvious thing to note is the sharp decrease in AD for the two high sulfur cokes, particularly noticeable beginning at above 1350°C. As pointed out in the "Part I" paper this is due to thermal desulfurization and is well documented in the literature[4,5]. The decrease in AD due to thermal desulfurization is substantiated by the increase in porosity for pore sizes between 15 and 0.1 micron in size (see Figure 3) and particularly for pores less than 0.1 micron in size (see Figure 4).

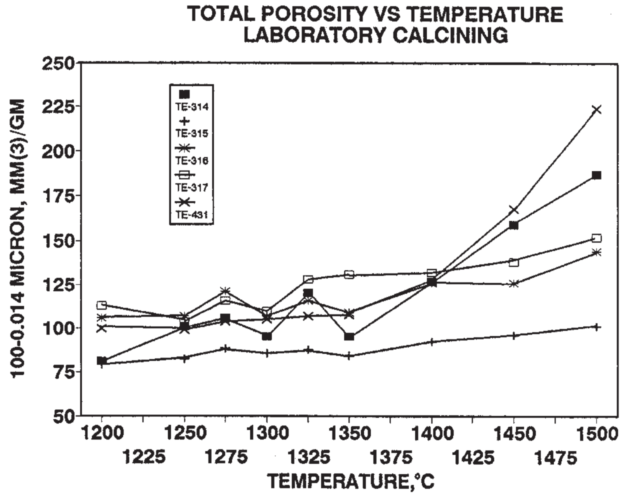
Figure 4



A second interesting point to note is that maximum AD was achieved between 1200 to 1300°C and that beginning at between 1300 and 1350°C, the AD decreases significantly for all five cokes. This is particularly interesting since none of the five cokes (even the two high sulfur cokes) show any measurable sulfur reduction in this temperature range. Thus the AD decrease is apparently not due to thermal desulfurization. This decrease in AD is substantiated by the small but steady increase in total measured porosity (see Figure 5) most readily apparent in the 0.1 - 0.014 micron range (see Figure 4). The AD decrease may be due in part to the rate of release of the volatile matter such as the gaseous components hydrogen and nitrogen.

This finding is important because it indicates that the final temperature selection in commercial calcining operations may be more significant than realized. There appears to be a temperature range which gives maximum coke density for both low and high sulfur cokes. The potential problem is that many commercial operations may be calcining above this critical temperature range where maximum coke bulk density is achieved and still be within what is considered "typical" calcining temperature by today's standards. This is especially true for real density specifications where many aluminum users are requiring higher and higher values and thus higher calcining temperature requirements.

Figure 5



Sulfur, Hydrogen, and Nitrogen Release

The sulfur, hydrogen, and nitrogen release curves for the five cokes at various calcining temperatures are depicted in Figures 6 - 8 respectively.

Sulfur (Figure 6) - The two high sulfur cokes (#TE-314 & 431, 4.2% and 4.1% sulfur in the raw coke) exhibit typical sulfur release curves(5) with initial evolution of sulfur commencing at above 1350°C and significant release above 1400°C. The percentages of sulfur reduction in the products between the 1200°C and the 1500°C calcinings for these two high sulfur cokes were 48% and 60% respectively. The lowest sulfur coke (#TE-317, 0.78% sulfur in the raw coke), shows no additional measurable sulfur release even in the product calcined at 1500°C. The next lowest sulfur coke (#TE-315, 1.7% sulfur in the raw coke) exhibited about a 0.1% sulfur loss between the 1200°C to 1500°C calcinings and the third lowest sulfur coke (#TE-316, 2.2% sulfur in the raw coke) exhibited about a 0.3% sulfur loss.

At calcinings performed between 1200 and 1350°C temperatures (more typical of commercial calcining temperatures where little if any thermal desulfurization is realized), the average percentage of sulfur reduction from the raw coke to that in the product ranged from about 5-10%. This is typical in commercial operations with a "general rule of thumb" being that the product sulfur will be from 8-15% lower than the raw feed sulfur level provided high temperature thermal desulfurization is prevented.

It is an interesting question(6,7) as to why some cokes tend to contain more thermally resistant sulfur than others. It is believed that the organo sulfur is bound up in various ways which explains the different rates of sulfur removal. Most of the sulfur given off at typical calcining temperatures is hydrogen sulfide and elemental sulfur which accounts for most of the 8-15% reduction in sulfur noted earlier. The sulfur bound to the aromatic ring structure, as opposed to the sulfur bound to the lateral chains or volatile matter, is more thermally resistant requiring higher temperatures to break down the sulfur bond. The way the sulfur is tied up in the coke is believed to be related to the type of coker feeds used in delayed coking. Crudes with low sulfur and low asphaltic materials and high aromatic pyrolysis residues usually give cokes having the greatest amount of thermally resistant sulfur while crudes with high sulfur content often contains large amounts of sulfur components which are thermally unstable(6).

Figure 6

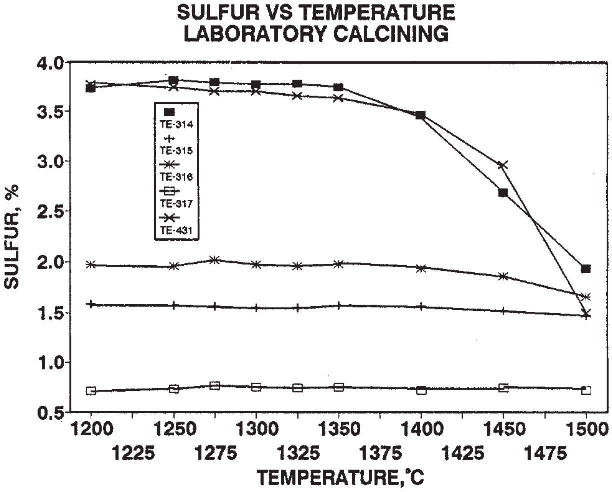
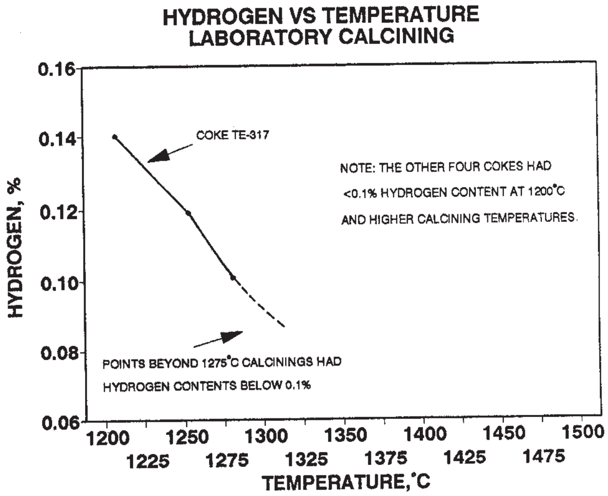


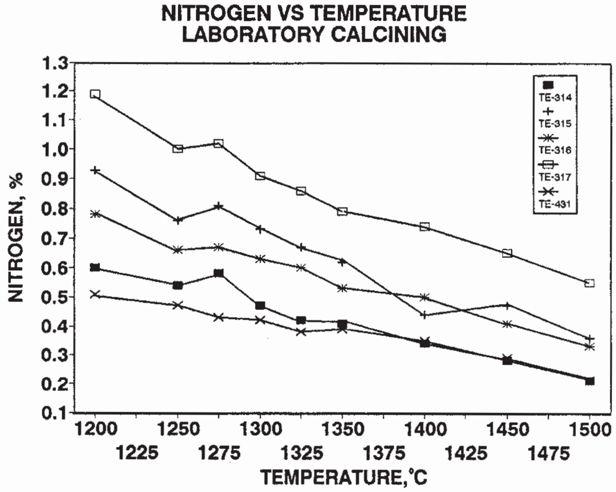
Figure 7



Hydrogen (Figure 7) - The data shows that for all but one coke (#TE-317), most all the hydrogen is released (to less than 0.1% level) after reaching 1200°C temperature. The off-shore coke had some residual hydrogen up to 1275°C calcining. Hydrogen in the form of water starts leaving between 100 and 200°C; around 500°C propane and propylene leave and hydrogen starts to leave; around 550°C ethane and ethylene leaves; and at 600°C methane leaves. Most all the hydrogen is indeed gone by 1000°C(6).

Nitrogen (Figure 8) - The nitrogen curves for the five cokes reveal that for the temperature range tested, the slopes of the curves remain parallel and exhibit a fairly constant rate of release. The highest nitrogen coke (#TE-317, 1.8% nitrogen in the raw) remained high in relation to the other cokes throughout the calcining test temperatures while the two lowest nitrogen cokes (#TE-314 and 431, both 1.1% nitrogen in the raw) remained the lowest. Although there is an insufficient number of data points it appears that the nitrogen level is inversely related to the sulfur content in the raw coke.

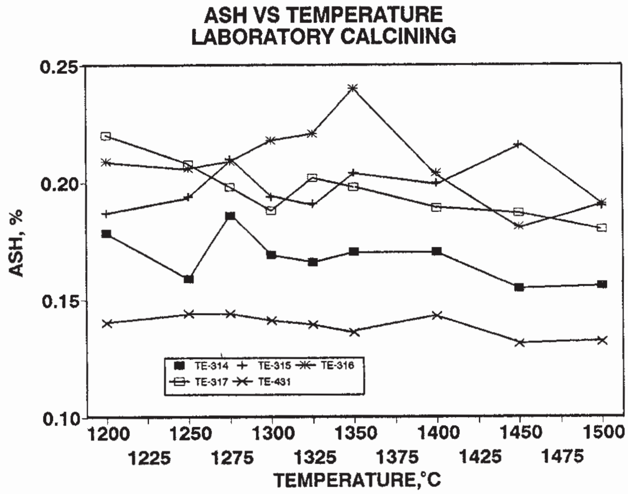
Figure 8



For certain non-anode applications of calcined coke, such as a carbon raiser, users desire as low a nitrogen content as possible. Thermal denitrification processes have been described(8) and would seem to be an attractive option. However as has already been pointed out, unlike thermal desulfurization (where the high sulfur cokes expels sulfur at a greatly increased rate at some critical temperature), this is not true with nitrogen which has a more uniform rate of release, even at the higher calcining temperatures.

Ash and Metals - The relationships of ash and the metals (aluminum, calcium, iron, nickel, silicon, sodium, titanium, and vanadium) to calcining temperatures are depicted in Figures 9-17. There appears to be some variation in ash and some of the measured elements from calcining temperature to calcining temperature but not necessarily exhibiting any specific trends. Of course this variation in part is due to coke sampling and test measurement errors. We also know that sampling and test errors are increased due to the fact that coke formation in the delayed coker drum, shows ash levels and thus elemental levels that vary significantly both top to bottom and side to side within the drum. The variability of certain metals is worse than others(9,10).

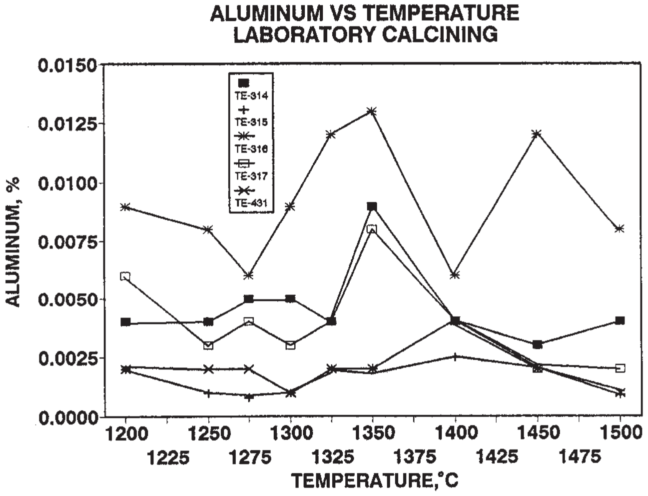
Figure 9



Of the elements measured calcium, nickel, and vanadium show little erratic variation from one calcining temperature to the next and remain fairly constant within the temperature range tested. It is generally true that nickel and vanadium are more uniformly distributed in the coke having less tendency to segregate in the coker drum during formation. Also there is little opportunity to pick these metals up from other, external sources such as during transportation and calcining. The titanium curve appears to exhibit considerable variation but actually the levels are typically below 15 ppm and, as such, the variation is not significant.

However, it should be noted that for the two high sulfur cokes, the nickel content actually shows an increase beginning at about 1350°C. This coincides with thermal desulfurization. The decrease in sulfur weight does not account for the increased nickel levels observed. Since one cannot make nickel, it is an interesting finding. Presvious studies(11) have shown that when measuring certain elements by x-ray fluorescence, it is necessary to correct the absorption enhancement effects associated with the variation of sulfur weight percent by determining a sulfur influence factor. Simply stated, the lower the sulfur the less the interference. Presently the Great Lakes procedure used here does not correct nickel for possible sulfur interferences, and further work will look into this effort. Certainly this could explain in part the nickel increase observed in the two high sulfur cokes as the sulfur level is significantly reduced at the higher temperatures.

Figure 10



The sodium also exhibits little variation and remains constant for all the cokes except the off-shore coke (#TE-317). The sodium for this coke does drop from a high of about 250 ppm to a low of about 150 ppm. This may explain in part the decrease noted in the ash level of this coke from about 0.22% ash to about 0.18% ash. There seems to be little change in the ash content with regards to calcining temperature for any of the other four cokes. It is possible that the sodium present in this off-shore coke may in part be present as free sodium (which vaporizes at <1000°C) on the coke surface. It may be from an external source such as the cutting water used during decoking.

Figure 11

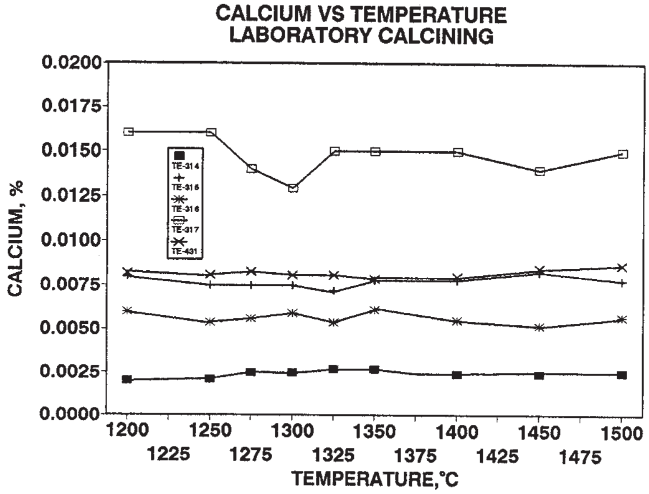
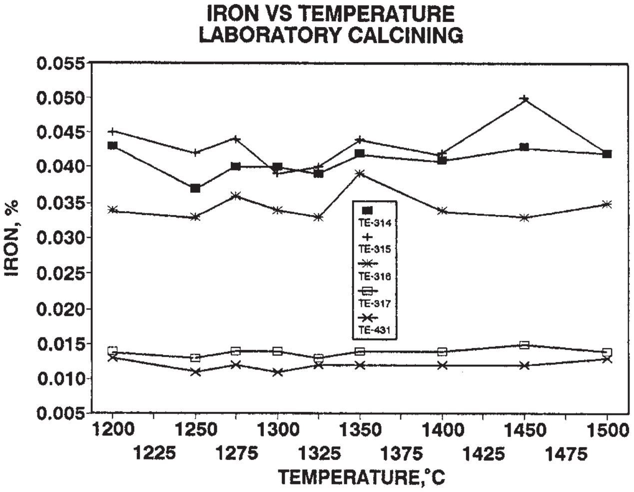
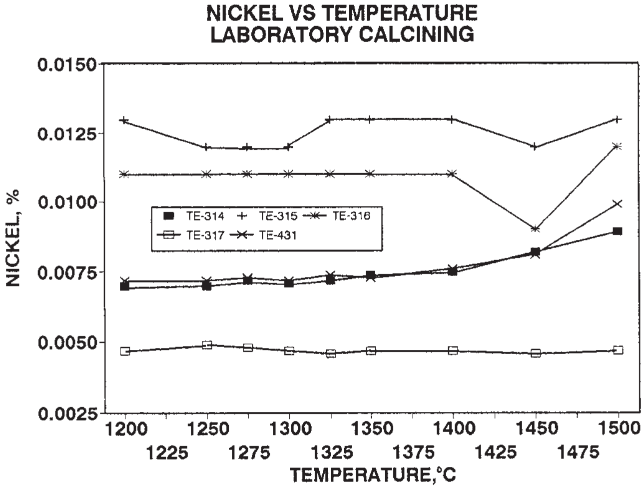


Figure 12



The ash spikes noted on coke #TE-316 at 1350°C and for coke #TE-315 at 1450°C are not explainable except that maybe part of the increased ash is due to the iron spike also observed at these temperatures. Although extreme caution was taken in preparing the individual calcining samples for each coke, iron is the most difficult element to analyze for in regard to both accuracy and repeatability. This is mainly due to the fact that iron is the worst element to segregate in the coker drum during formation and therefore is inherently non-uniformly distributed in the coke. This is compounded by the fact that iron is so common that it is easily picked up from many sources during handling and calcination. This makes it difficult to sample and to measure.

Figure 13



Aluminum varied considerably from one temperature to the next for the three highest aluminum cokes. This is not explainable at this time, but may in part be due to test method variation. Silicon has less variation from temperature to temperature but there appears to be a decrease in silicon with increasing temperature for all five cokes. It is especially noticeable for coke #TE-314. Since the boiling point of silicon or silicon carbide is in excess of 2000°C, this phenomenon is interesting. If the silicon is present as a low volatile compound such as silicon sulfide (which vaporizes at 1130°C), then certainly this observed decrease would be possible.

Figure 14

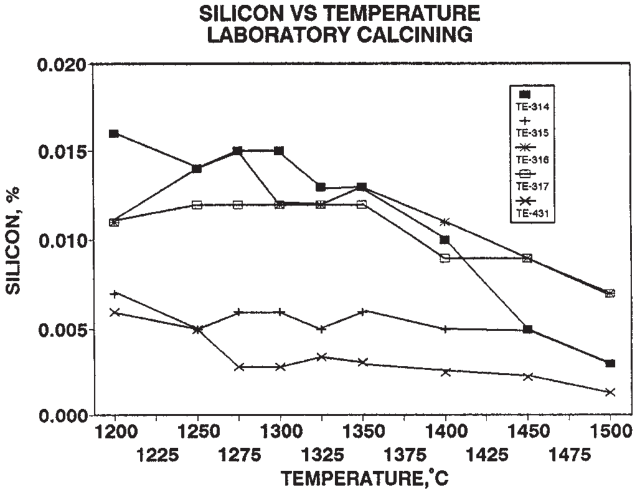
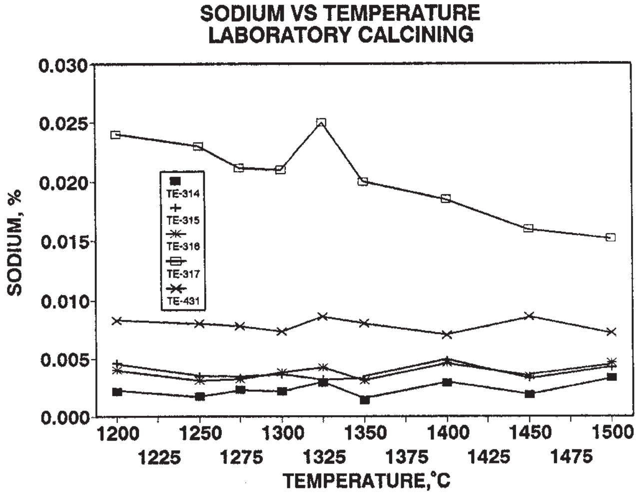


Figure 15



Coefficient of Thermal Expansion and Hardgrove Grindability Index - The relationships of coefficient of thermal expansion (CTE) and Hardgrove Grindability Index (HGI) to temperature are depicted in Figures 18 and 19. These two properties are not often used in characterizing raw anode grade cokes. CTE is used primarily to characterize needle cokes used in the making of electrodes for the steel industry. HGI is used mainly to quantify "calcined" coke grinding which is most important for aluminum producers in the preparation of their anode recipe. Only in recent years has the usefulness of these two properties in quantifying and understanding raw coke quality been discovered.

Figure 16

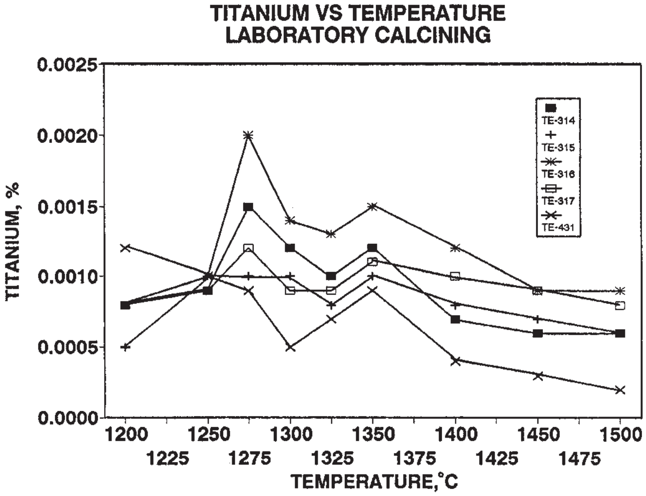
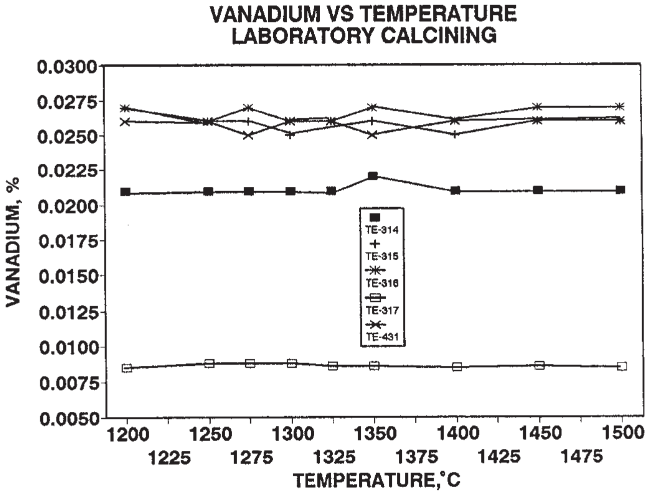


Figure 17



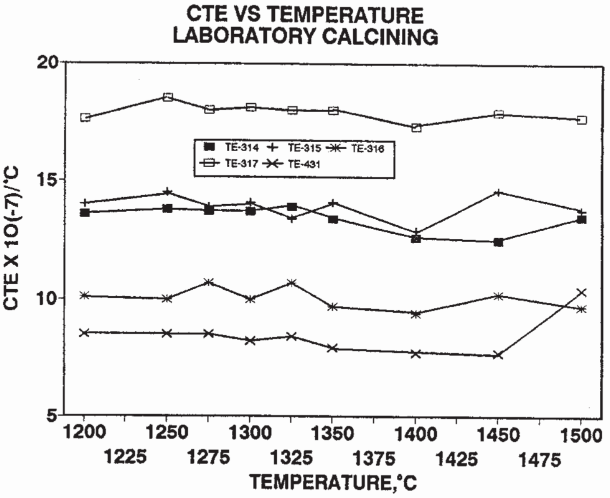
CTE and raw coke HGI are important because of their relationship to the bulk density of the coke upon calcining. CTE is directly related to bulk density (as the coke becomes more isotropic and all else is the same, the bulk density will increase). To provide an indication for the use of the CTE as generated by the Great Lakes test method, typical numbers are given below for various coke types:

Electrode Premium Needle cokes	2-5 CTE
Anode Grade Cokes	8-20 CTE
Shot Cokes	>20 CTE

HGI (which is directly related to volatile matter) is also directly related to bulk density. Great Lakes has found that HGI, not volatile matter content, is the single most reliable coke property for predicting coke bulk density. However HGI combined with CTE provides a much improved indicator.

As can be seen from the CTE relationship, calcining temperature has no significant impact on coke structure. An interesting point was noted however with the HGI relationship. The two high sulfur cokes show a definite HGI decrease beginning at about 1350°C. This is most likely attributed in some way to the impact by thermal desulfurization. Although insufficient data is available, it appears on the other hand that the HGI of the two lowest sulfur cokes show a slight increase. The coke at the middle sulfur level (#TE-316, 2.2% sulfur in the raw) shows a slight HGI increase up to the 1450°C calcining like the other two lowest sulfur cokes, but at the 1500°C calcining the HGI decreased. This ties into thermal desulfurization and resultant increase in the microporosity as was noted for the two highest sulfur cokes.

Figure 18



Although this data involves only five cokes, if one plots CTE vs HGI, realizing the slight effects of calcining temperature on HGI, there seems to be an inverse relationship. Of course this is true only when those points where severe desulfurization in the two high sulfur cokes are removed at the 1450°C and 1500°C calcinings (see Figure 20). It is known that as CTE increases, cokes show increased isotropic structure. This type of structure is associated with higher bulk density and less porosity resulting in a harder, denser coke more difficult to grind and thus a lower HGI[12].

Figure 19

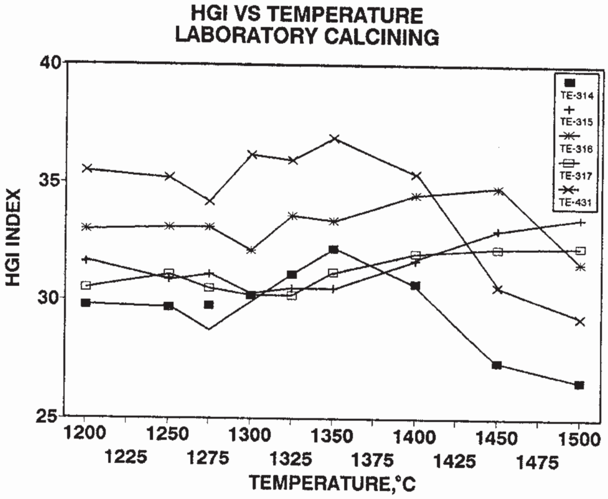
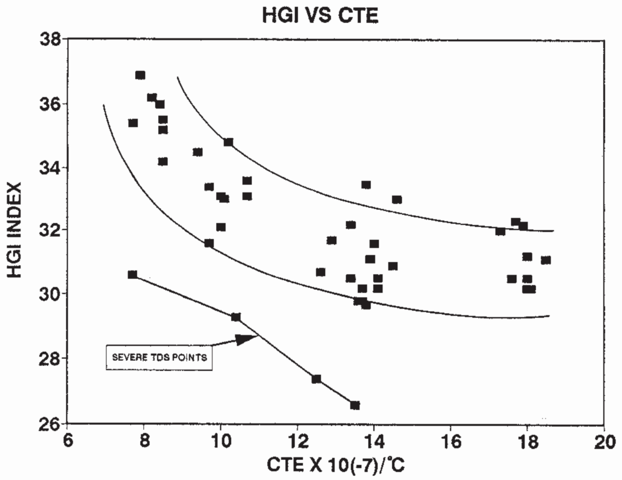


Figure 20



Results and Discussion

Air and Carboxy Reactivity - The relationships of air and carboxy reactivity are depicted in Figures 21 and 22.

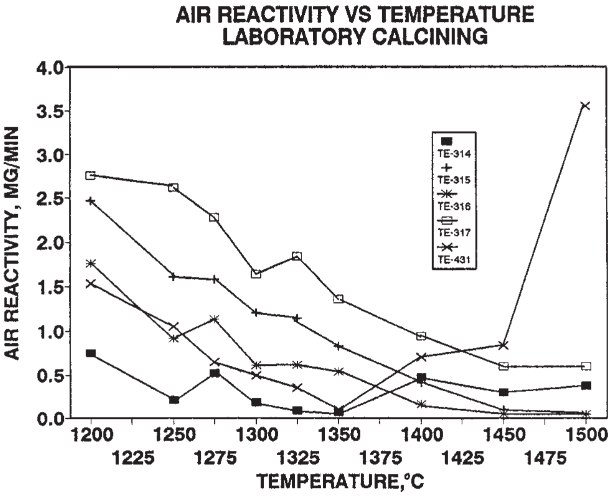
Air Reactivity - It is documented in the literature that air reactivity decreases with increasing calcining temperatures. Great Lakes has studied this thoroughly in commercial coke calciners and have indeed found that higher calcining temperature is an effective tool to decrease air reactivity. However, as the curves reveal it appears that of the five cokes, the two high sulfur cokes (#TE-314 & 431), especially evident for high sulfur coke #TE-431 exhibit a surprising finding. The air reactivity for these two cokes does decrease with increasing calcining temperatures, like the other three lower sulfur cokes, but surprisingly begins to increase at 1350°C.

It is obvious from prior discussions in this paper as well as the "Part I" paper, that thermal desulfurization commences for these two cokes at 1350°C with resultant generation of large quantities of microporosity (refer to Figure 4). It is believed that the increase in air reactivity is due to this increase in porosity. This is supported by work reported in 1985 by Fischer and Perruchoud(13).

This is extremely important when blending high sulfur cokes with low sulfur (sweet) cokes and calcining at higher than normal temperatures to reduce overall air reactivity. From these results if calcining temperatures are achieved which initiate even the early stages of thermal desulfurization for the high sulfur cokes, attempts to calcine at higher temperatures may be counter productive due to the presence of the high sulfur coke. Also it will result in lower overall bulk density and increased porosity (due to the thermal desulfurization) neither of which are positive for achieving good quality anode grade coke.

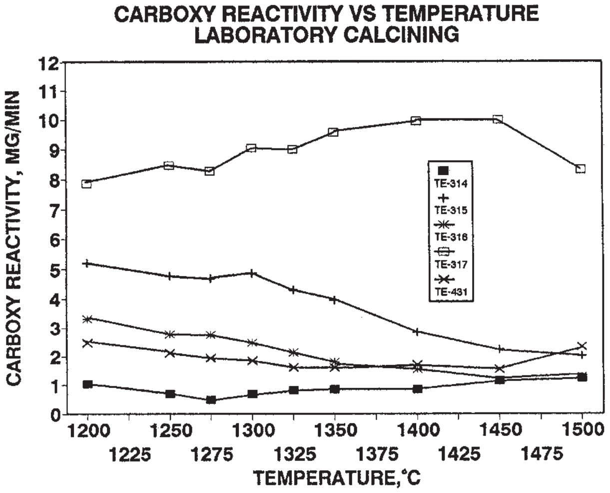
Carboxy Reactivity - Upon examination of the carboxy reactivity curves even more surprising results are observed. Like air reactivity, the two high sulfur cokes exhibited an increase in carboxy reactivity at about 1350°C. This trend had been previously observed and presented at the 1982 Light Metals(14) with additional findings at the 1985 Light Metals(15).

Figure 21



The second surprising point to note is that the lowest sulfur off-shore coke (#TE-314, 0.78% sulfur in the raw) actually increased with increasing temperatures at the onset. Unlike the high sulfur cokes, porosity cannot explain this since this coke shows no sulfur reduction and the least amount of porosity increase (this is true for any porosity range, even the microporosity range) of any of the five cokes. In unpublished studies conducted by Great Lakes in 1984, this surprising result was first noted with this same type of off-shore coke. Upon further investigation it appeared that increasing carboxy reactivity with increasing calcination temperature was related to low sulfur and high nitrogen and possibly a combination of the two. It was speculated that high nitrogen in coke may alter reactivity by tying up certain impurities which would catalyze oxidation and that increasing calcination temperatures may be progressively decomposing these compounds or complexes expelling nitrogen and concentrating the catalytic elements to enhance oxidation(14).

Figure 22



Summary and Conclusions

This program has verified much information which has been published in the literature and has revealed some new and interesting relationships between coke properties and calcining temperatures. It has served to remind us that it is imperative to understand and know the behavior of individual cokes at various calcining temperatures. It appears that for every general relationship between coke properties and temperatures there are cokes which are exceptions. This is true whether calcining involves low or high sulfur cokes and mixed coke blends. There are many individual conclusions which can be reached from this rather extensive study reported in both the "Part I" and "Part II" papers. Some general conclusions are summarized below. Remember these results are based on the five cokes selected, calcining in a laboratory calciner unit, and to temperatures ranging from 1200°C to 1500°C.

1. When calcining high sulfur cokes, it is imperative to avoid thermal desulfurization. When thermal desulfurization occurs, several coke properties are affected including the following:

   a. Bulk density (quantified as vibrated bulk density or mercury apparent density) is reduced.

   b. Porosity is increased (especially pores below 0.1 micron in size which are probably not penetrated by pitch in anode fabrication).

   c. Both air and carboxy reactivity is increased with increasing temperature once desulfurization has commenced (air reactivity especially can be greatly increased).

   d. The Hardgrove Grindability Index will decrease.

2. Maximum apparent density was achieved between 1200°C and 1300°C for all five cokes including the high and low sulfur cokes. Between 1300°C and 1350°C, apparent density decreased for all cokes tested. This decrease is not due to thermally induced microporosity generated from desulfurization.

3. The severity of thermal desulfurization (amount of sulfur removed and impact on coke apparent density and porosity) appears to be directly related to the sulfur content in the raw coke. High sulfur cokes are easily desulfurized commencing at relatively low temperatures. For this lab calcining study significant desulfurization in the high sulfur cokes began at just above 1350°C.

4. Typically all hydrogen (except for a few hundredths of a percent) was removed prior to the low 1200°C calcining except for the low sulfur off-shore coke.

5. The rate of nitrogen release was fairly constant and the release curves remained the same with the highest nitrogen coke remaining high in relation to the other cokes throughout the temperatures tested and the lowest nitrogen cokes remaining the lowest.

6. The ash was relatively unaffected with increasing calcining temperature. Of the individual elements measured, the levels were relatively unchanged from the low 1200°C to 1500°C calcinings with these noted exceptions:

   a. The nickel level increased for the high sulfur cokes once desulfurization commenced. This is of course not possible and is believed to be due in part to test method techniques in the x-ray unit.

   b. The sodium level for the off-shore coke (which also was highest in sodium level) decreased with increasing calcining temperature.

   c. The silicon level in all five cokes decreased with increasing temperature from that measured at the low 1200°C calcining. If the silicon is present as a low volatile point compound (such as silicon sulfide which vaporizes at 1130°C), then certainly this would be possible.

7. Coke structure as quantified by CTE measurement is not affected by temperature for the range studied.

8. The Hardgrove Grindability Index increased slightly with increased temperature, but actually decreased if and when thermal desulfurization commenced.

9. The air reactivity decreased with increased temperatures but increased when thermal desulfurization commenced.

10. The carboxy reactivity relationships are not so clear cut as air reactivity. Like air reactivity, the carboxy reactivity typically decreased with increased temperatures up until thermal desulfurization occurs and then it increased. However some cokes, with at least one of the common links being low sulfur and high nitrogen, actually increase with increasing temperature. This was true for the off-shore coke, with carboxy reactivity increasing with increasing temperature at the very onset of 1200°C calcining with no thermal desulfurization involved.

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