

HIGH CAPACITY THERMOBALANCE ANODE REACTIVITY TESTING

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Abstract

As raw material quality changes and Potline Customer requirements become more onerous, anode reactivity has become an increasingly important quality measure. Conventional anode reactivity testing procedures require dedicated and expensive instruments that have relatively low sample throughputs. Smelters are often unable to test the reactivity of all the core samples they take due to reactivity test capacity limitations. This reduces the ability of plants to identify any changes in anode reactivity that may require countermeasures. A commercially available, multiple sample ThermoGravimetric Analyzer (TGA) has been successfully adapted to measure anode air reactivity. This paper describes the modifications made to the instrument and the standardization of a procedure for anode air reactivity testing. Results obtained from plant anode samples baked under different conditions are also discussed.

Introduction

Anode grade petroleum coke quality has changed significantly in the last 10 years and this trend is expected to continue [1,2]. These changes have included an increase in catalytic impurities such as Vanadium, which would be expected to increase the anode air reactivity. This does not appear to have had a widespread impact on anode performance to date, as in-cell airburn is controlled more by the degree of protection from air access afforded to anodes in the cell, than it is associated with anode quality [2,3]. Despite this, monitoring anode air reactivity can be important to detect changes in anode quality and signal the need for countermeasures. One of the factors that influences how quickly a change in anode quality can be detected is the number of samples tested. At present, this is limited by the relatively low throughput of conventional anode air reactivity testing equipment. This means that many plants are unable to test the air reactivity of all of the core samples they take; this represents a loss of data that can delay the identification of significant shifts in anode quality. The use of a high throughput air reactivity test could avoid this limitation.

Anode air reactivity testing has a number of complexities that make the development of a “technically ideal” test (i.e. a test that measures the intrinsic chemical reactivity of the anode carbon without mass transport effects, see Figure 1) for plant use somewhat difficult:

- The reaction rate is very dependent on temperature - as temperature increases, so does the reaction rate.
- The reaction between Carbon and air (Oxygen) is highly exothermic which makes temperature control of samples during testing very difficult.
- In addition to the intrinsic chemical reactivity of the anode carbon, the reaction rate is highly dependent on the rate of mass transport of air to, and through the sample (Figure 1). This means that the air flow conditions of a reactivity test

will significantly impact results unless the test is conducted at temperatures below 400°C; however reaction rates at these temperatures are too slow for practical reactivity testing.

These complexities mean that all air reactivity tests are somewhat of a compromise and they do not measure the real chemical reactivity of the anode carbon to air, e.g. the most common temperature range for air reactivity tests is 500 – 550°C [4]; which is in the Zone II/Zone III transition range of Figure 1 and hence mass transport (e.g. in-pore diffusion) and not chemical reactivity, is the dominant factor impacting the reaction rate in this temperature range.

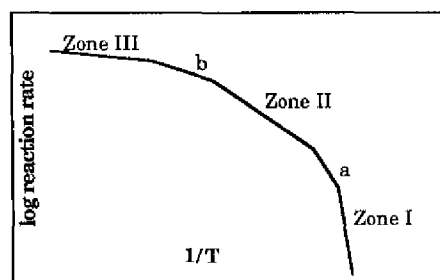


Figure 1: An schematic Arrhenius plot for the reaction between Carbon and Oxygen [from 3, P. 467], showing (log) reaction rate (Y axis) plotted against the inverse of reaction temperature (X axis – note that temperature increases to the left). In Zone I, reaction rate is controlled by the intrinsic chemical reactivity of the anode carbon. In Zone II, reaction rate is increasingly controlled by the diffusion of air through the anode pore structure, but intrinsic reactivity contributes at lower temperatures in the zone (i.e. in transition zone a). In Zone III, reaction rate is so fast that all oxygen is consumed immediately it reaches the anode surface, so the reaction rate is largely controlled by how fast the air reaches the anode and the anode geometry, with little contribution from other anode properties. Zone a (Transition from Zone I to II) occurs at about 400°C [4] and Zone b (Transition from Zone II to III) has been variously reported at around 500°C [3] and 800°C [4]. (See [3] for further discussion of anode air reactivity/mass transport.)

Since the development of a technically ideal test is not realistic for plant applications, the focus can be directed to tests that, while not technically ideal, still produce data that is practically significant, i.e. the results make sense from what we know about anode reactivity and the way anodes are consumed in cells. However, the development of a practically significant test is not straightforward - different parts of a single anode in a cell is exposed to temperatures >800°C and <400°C for long periods of its cell life, and air (mass) transport conditions within a cell can vary from still (i.e. good protection from air by anode cover), to a strong draft past the hot carbon surface. All of this leads to the question of what conditions can be used for a high throughput, practically

significant plant anode reactivity test. In this work to develop such a test, the conditions were selected on the basis that they gave results that differentiated between samples in a way that met expectations based on theory and experience. The following discusses the testwork undertaken in the development of a high throughput plant anode air reactivity test, and in the verification that the test generates results that are practically significant.

Experimental

Initial testing was performed to determine the viability of a high throughput anode reactivity test method using the Leco TGA 701 ThermoGravimetric Analyzer. The same instrument has been proposed for testing the Volatile Matter content of green cokes by others [5]. Modifications were made to the sample holders to improve contact between the samples and gas. A parametric analysis was undertaken to determine the influence of equipment parameters on test results, the outcome of this work was used to develop a robust routine test procedure. This procedure was then used to test the air reactivity of a range of plant manufactured anodes in the TGA apparatus. The samples were chosen to represent a wide range of baking conditions while minimizing differences in catalytic impurities. Details are now provided on each of these steps.

Equipment

The Leco TGA701 Thermo Gravimetric Analyzer (Figure 2) uses a rotating carousel design that allows a maximum of 19 samples to be tested simultaneously (Figures 3 and 4). Test parameters were computer controlled using software provided with the equipment. The internal balance of the TGA had a resolution of 0.0001g and was initially configured for a sample weight up to 5g. However, the equipment was altered to allow for samples up to 30g to allow larger anode samples to be tested.



Figure 2: TGA701 with desktop computer interface.



Figure 3: TGA with open lid and empty sample carousel.



Figure 4: TGA carousel loaded with ceramic crucibles.

The standard crucibles provided with the TGA (Figure 4 and Number 1, Figure 5) are constructed of solid ceramic. These crucibles are not well suited for allowing the reactant gas within the TGA easy access to the sample surface. To improve gas contact with the sample, a number of prototype sample holders were developed and tested (Figure 5). The favoured sample holder (Number 7, Figure 5) was made from Nichrome mesh pressed into a shape similar to the original ceramic crucibles. This design allowed gas contact with all surfaces of the sample and retained any dust particles that fell from the samples during testing.

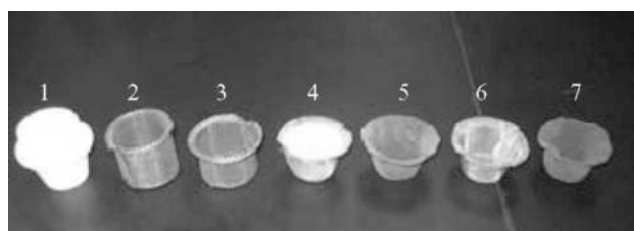


Figure 5: Development sequence for the sample holders. The final sample holders design (Holder 7) allowed for improved gas flow while capturing dust from the samples during testing.

At the temperatures used for anode reactivity testing, a Chromium Oxide layer formed on the surface of the Nichrome wire of the sample holders. To manage the weight change associated with this oxidation, the mesh sample holders were preheated at 950°C for 2 hours. Although small changes in the weight of mesh sample holders occurred with use; this rate of change was negligible compared to the weight loss of anode samples during testing.

The internal features of the TGA are shown in Figure 6. The ceramic carousel rests on the central support which rotates each sample crucible over the balance pedestal at a cycle time of 80 – 240 seconds, depending on the number of samples. To take the weight measurement, the support lowers the carousel, leaving the crucible on the balance pedestal. The weight of the sample is logged to give a record of weight loss versus time. The temperature and heat up rate are programmed before the test run. The temperature is controlled with dual thermocouples, one thermocouple inside the ring of samples and the other outside to better measure the temperature at the sample. Gas is introduced into the test chamber at two locations on each side. The TGA has the capability to introduce various gases during the same test run; however, dry purified air was used throughout this study.

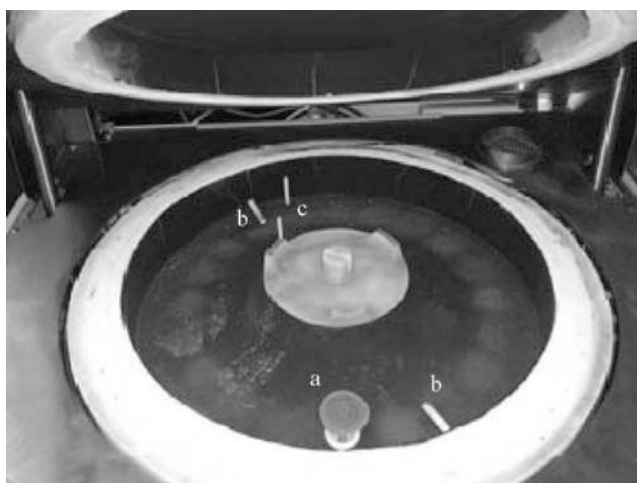


Figure 6: TGA test chamber with carousel removed. Components include: (a) Ceramic balance pedestal; (b) Gas inlet ports; (c) Dual thermocouples.

Test development and Parameter Evaluation

Initial testing was undertaken to determine the viability of a high throughput air reactivity test using a TGA. Five plant baked anode samples were chosen with varying air reactivities as determined previously by single sample thermobalance testing according to ASTM D6559. TGA samples for this study were 25mm high by 25mm diameter cylinders, with multiple samples cored from larger core samples using a water cooled coring drill and cut to length with a diamond saw. Samples were tested in the TGA, heated from ambient temperature to 650°C as dry purified air was introduced at 7.5 l/min; the air reactivity results measured at 550°C are shown in Figure 7, and the good agreement with the results from ASTM D6559 provided initial support for the proposal that a high throughput method could reliably indicate

differences in air reactivity. Given the issues with air reactivity testing discussed previously, the degree of repeatability as indicated by the narrow range bars for four of the five points in Figure 7 was considered to be very good.

Other air reactivity tests, such as ASTM D6559, use an initial nitrogen purge to avoid unwanted oxidation while the sample is heated to the desired temperature. However, in the TGA701, weight loss was experienced even with a high Nitrogen purge flowrate of 10l/min, indicating an imperfect chamber seal. Rather than use nitrogen to unsuccessfully purge during the temperature heat-up cycle, purified air was used for the entire procedure.

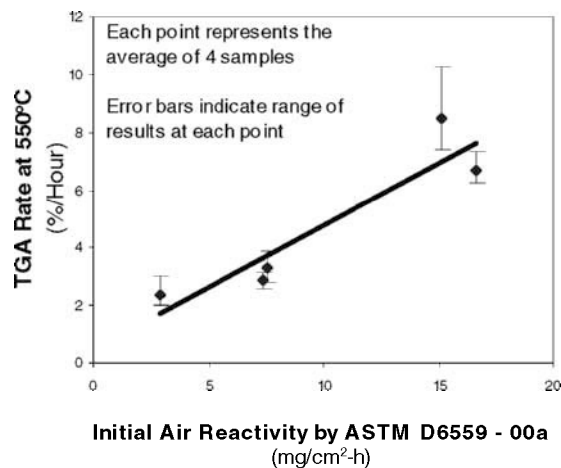


Figure 7: Results of initial TGA testing, showing that there was good agreement with previously determined results using ASTM D6559. This indicated the new high throughput equipment had potential to characterize anode air reactivity.

Prior to undertaking further plant anode testing, a parametric study was conducted to build a thorough understanding of the test equipment and ensure a robust experimental procedure. A large laboratory “all coke” anode was manufactured for use in the analysis to avoid the variation inherent in plant anodes from factors such as anode butts. Selecting parameters that maximized test repeatability was a key focus, and this was quantified using the normalized reactivity range (r_N) (Equation 1) at each point. A small reactivity range between duplicate samples was desired.

$$r_N = \frac{R_{Air,Max} - R_{Air,Min}}{R_{Air,Average}} \quad (1)$$

The parameters tested included temperature heat up rate, air flow rate, and sample position on the carousel. The influence of these parameters on sample air reactivity rate at 550°C is shown in Figures 8 – 16. Soak Time represents the period for which the sample was held at 550°C.

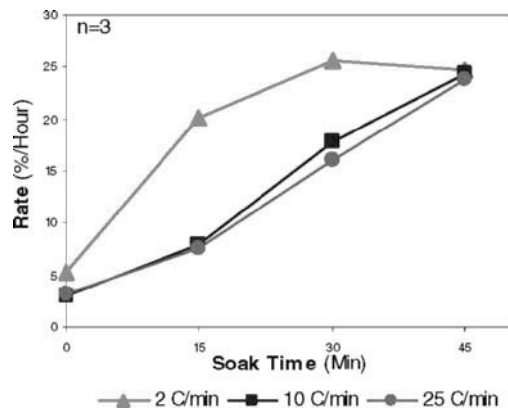


Figure 8: Impact of heat up rate on anode air reaction rate. The reaction rate at 10°C/min and 25°C/min lagged behind 2°C/min, likely due to the time for the testing chamber temperature to equilibrate.

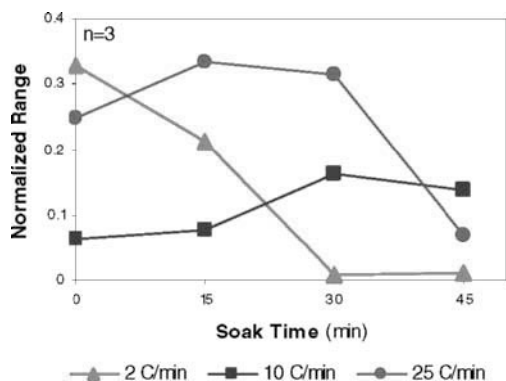


Figure 9: Normalized reactivity range (from Equation 1) for the heat up rates tested. A heat up rate of 10°C/min resulted in the smallest reactivity range and greatest consistency; the slow temperature ramp rate demonstrated no advantage in repeatability.

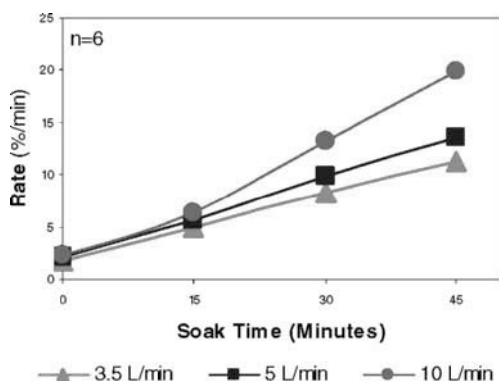


Figure 10: Impact of air flow rate on anode air reaction rate. The highest flow rate of 10l/min corresponded to the highest air reactivity rate, likely due to improved mass transport of air to the reaction surface on the samples.

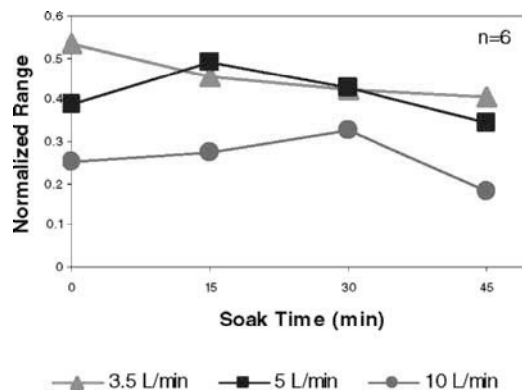


Figure 11: Normalized reactivity range at the tested air flow rates. A flow rate of 10 l/min provided the smallest normalized reactivity range (i.e. lowest variation in measured reactivity between the 6 repeat samples) and greatest consistency between the tests at different soak times.

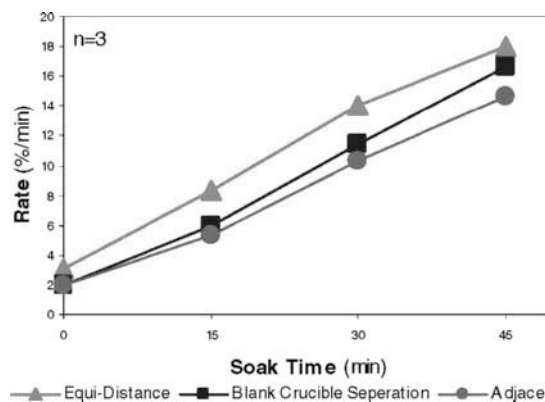


Figure 12: Impact of relative sample holder placement in the carousel. The “Equi-distance” sample arrangement (Figure 13) used evenly spaced samples around the carousel. The “Blank Crucible” separation configuration (Figure 14) used empty ceramic sample holders between samples. In the “Adjacent” configuration (Figure 15), samples were placed in consecutive positions. The results show that the highest reaction rate was with samples spaced Equi-distance on the carousel.



Figure 13: “Equi-Distance” sample placement represented by the dark, nichrome crucibles.

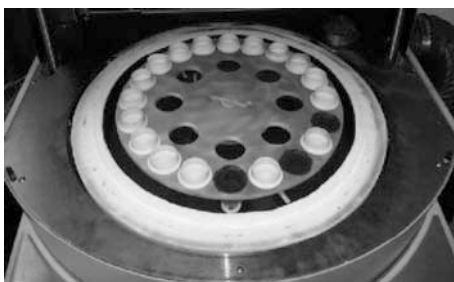


Figure 14: "Blank Crucible Separation" sample placement



Figure 15: "Adjacent" sample placement

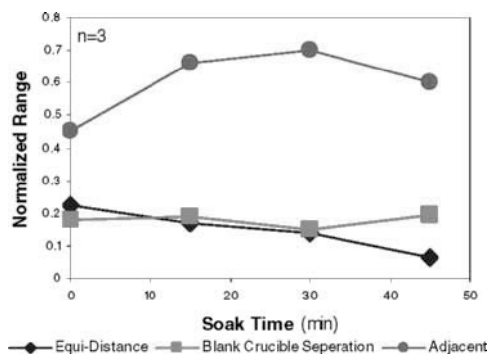


Figure 16: Normalized reactivity range for the sample holder locations tested. The range for adjacent samples was large, likely because samples placed next to each other interacted by, for example, radiative heat transfer giving sample temperature instabilities. The Blank Crucible Separation was selected as the preferred sample placement. Although this decreased the sample throughput from 19 to 10 per run, this is still significantly higher than other methods. Figure 17 demonstrates the sample arrangement for up to 10 samples.



Figure 17: Blank Crucible Separation used for the routine testing procedures. Samples are placed in the dark nichrome crucibles.

On the basis of the parametric testing, the following settings (Table I) were selected for routine anode airburn testing with the TGA:

Table I: Summary of testing parameters

Parameter	Setting
Heat up Rate	10°C/min
Soak Temperature	550 °C
Flow Rate	10l/min
Sample Location	Empty Crucible Between Samples

Testing of Plant Samples with varied baking temperatures

Twenty two plant anode samples were selected for testing to represent a range of final baking temperatures as indicated by carbon crystallite size (L_c). An effort was made to limit variation in catalytic impurity concentrations during sample selection.

The samples were prepared as previously discussed and tested using the parameters outlined in Table I. It was found that trimming the ends off the larger cores before the 25mm cores were taken significantly improved test result repeatability. Therefore, only internal samples from the larger core are included in the results. Dry, purified air was introduced at 10l/min during the temperature heat-up and throughout the soak period.

The weight loss profiles for two of the twenty two plant anodes during the entire bake cycle are shown in Figure 18. Sample 1 is characteristic of a high air reactivity, and Sample 2 is characteristic of a low air reactivity

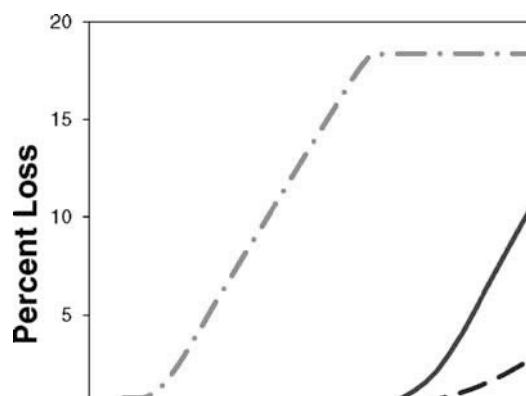


Figure 18: Anode weight loss profile for two anodes. Sample 1 has a higher air reactivity than sample 2.

Several metrics were considered to quantify the air reactivity. It was determined that the air reactivity rate after a soak period of 15 minutes at 550°C, described in Equation 2 below, provided the best resolution between samples:

$$R_{Air,15}(\%/hr) = -\frac{(W_{15} - W_{Previous})/W_I}{t_{15} - t_{Previous}} \times 100 \quad (2)$$

where W_{15} is the weight after 15 minutes at 550°C, $W_{Previous}$ is the weight at the previous measurement, W_I is the initial sample weight, t_{15} is the time of measurement W_{15} (hr) and $t_{Previous}$ is the

time of the measurement $W_{Previous}$ (hr) . Figure 19 shows the air reactivity rate for the same anode samples depicted in Figure 18. The vertical line represents the 15 minute soak period point where the reactivity measurement was taken.

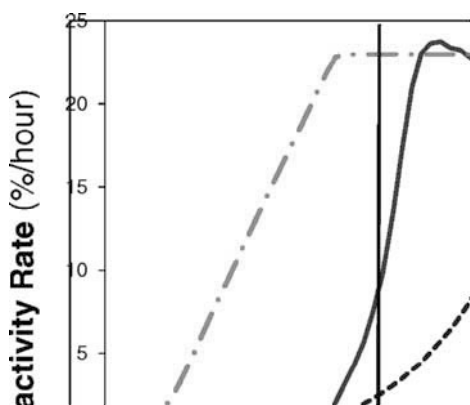


Figure 19: Air reactivity rates for samples plotted in Figure 18. The air reactivity rate after a 15 minute soak period, indicated by the vertical line, demonstrated a large measured difference between the two samples and provided high repeatability between duplicate samples.

The TGA air reactivity results of the twenty two samples are plotted against sample L_c in Figure 20 below. Duplicates were used for each sample, and the range of the two results shown with error bars. As can be seen from these bars, repeatability was generally excellent for plant anodes.

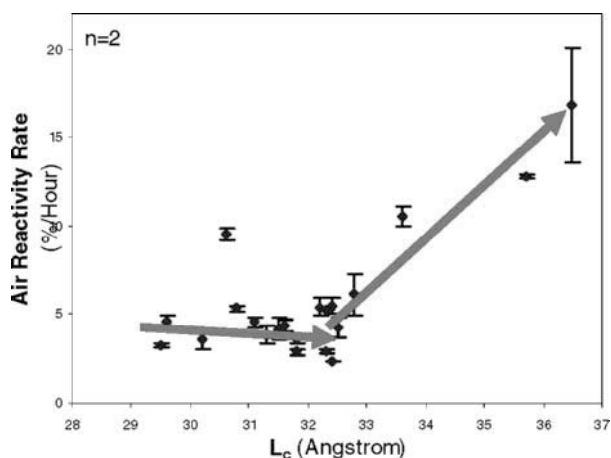


Figure 20: Impact of bake temperature on air reactivity rate. carbon crystallite size, L_c , was used as an indicator or bake temperature. A high L_c corresponding to a high bake temperature.

Results are generally as expected, with a slight decrease in air reactivity rate with increasing baking temperatures (i.e. increasing L_c) due to increased crystalline ordering, but then an increase in air reactivity rate as thermal desulphurisation becomes significant. This increases the (micro) porosity of the anode carbon, which increases the air accessible surface area and hence the air reaction rate. This trend is consistent with the observations of others, for example Coste and Schneider [6] and those results shown in Figure 21, with Air Activity Loss plotted against the final bake temperature.

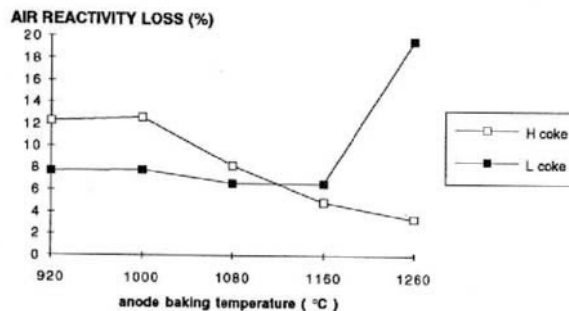


Figure 21: Effect of final baking temperature on air reactivity [from 6, Page 586]. Anode/coke H represents a low Sulfur anode (approximately 1.1% Sulfur in coke) and Anode/coke L represents a higher Sulfur anode (approximately 2.7% Sulfur in coke). The desulphurization of Anode/coke L at a final bake temperature greater than 1160°C resulted in an increase in air reactivity loss, i.e. increased air reactivity. Desulphurization was not observed for Anode/coke H. For the twenty two anodes in this study, the baked anode Sulfur content was greater than 2% and, as expected, showed the similar trend as Anode/coke L with respect to baking conditions.

Conclusion

Despite limitations in the proposed test method, such as the lack of individual sample temperature control and only general control of gas flow to samples, the method described in this paper appears to give a reliable and relevant indication of anode air reactivity. The key benefit of this method is the increased throughput, capable of testing 10 samples in 1.5 hours as compared to 1 sample in 3 hours when using other established tests such as ASTM D6559. Given the generally limited predictive ability of anode air reactivity tests due to compromises in test design, variable airburn conditions for anodes in the cell, and the dominant influence of plant anode cover on airburn rate, the increased throughput of the suggested test justifies the deviation from theoretical ideal test conditions. It is believed that this test can be used by Smelters to reduce the detection time for changes in anode quality related to air reactivity by significantly increasing the number of samples that can be tested compared with currently used tests. Although other, more theoretically correct test methods may exist, the positive implications of a practical, high throughput test has the potential to be just as valuable, or even more so, than these low throughput methods.

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