

MINIMIZING IMPACT OF LOW SULFUR COKE ON ANODE QUALITY

Angelique Adams¹, Roy Cahill¹, Yves Belzile², Katie Cantin², and Michel Gendron²

¹Alcoa Inc.; 300 N. Hall Road; Alcoa, TN, 37701, US

²Alcoa Inc.; 1 Boulevard des Sources; Deschambault, Quebec, G0A 1S0, Canada

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Abstract

Approximately 95% of the SO₂ emissions generated by a smelter can be attributed to sulfur found in the incoming petroleum coke used in anode production. Efforts to reduce smelter SO₂ emissions and increasingly demanding environmental permit requirements have resulted in a number of plants shifting to lower sulfur coke. Lower sulfur concentrations in the anode have been demonstrated by others to negatively impact anode quality and potentially Potroom performance by increasing the anode carboxy reactivity. In the following paper, we explore various methods to minimize this impact. These include, types of low sulfur cokes to be used in the coke blend, alterations in aggregate granulometry, and improved baking practices. The results from these studies are presented.

Introduction

It has been shown that the anode reaction with CO₂ can be a major contributor to carbon dust in electrolytic cells [1]. Carbon dust at elevated quantities will increase pot temperature and ultimately reduce current efficiency and metal production. It is for these reasons that understanding the carbon plant factors that can contribute to dust generation is critical. Many publications (e.g. Müftüoğlu and Øye [2]) have shown that anode CO₂ reactivity increases with increasing sodium concentrations. The authors of this paper have also witnessed this phenomenon on various occasions within the Alcoa smelting operations.

It is also known, however that the catalytic behavior of sodium is counteracted by the presence of sulfur [3]. Hume et al. [3] has shown that the reaction of sodium with sulfur inhibits the catalytic behavior of the sodium and reduces the tendency of the Sodium to migrate during the baking process. Higher sulfur cokes and anodes will, therefore have lower carboxy reactivities and less potential for dusting. This has been reported in the literature [3,4], and observed in plant operations (see Figure 1).

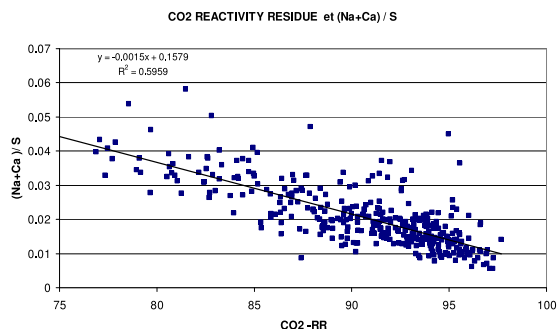


Figure 1. Dependence on CO₂ Reactivity Residue on Na, Ca, and S. Relationship was found to be (Na+Ca)/S (ppm/%).

In this case, the CO₂ Reactivity Residue (CRR) was found to be inversely proportional to Na and Ca levels and proportional to sulfur content. Comparison of anode sulfur level to CO₂ reactivity dust (CRD), Figure 2, shows an exponential trend with lower sulfur anodes having higher dusting.

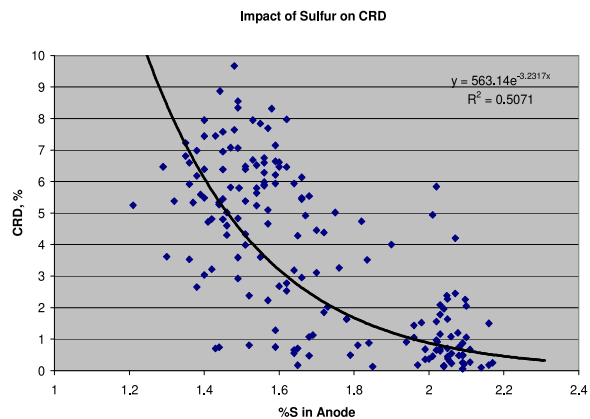


Figure 2. Impact of sulfur in carbon anode on CO₂ reactivity dust.

When faced with more stringent environmental legislation or goals, the first step to reduce SO₂ emissions is to decrease the sulfur content in coke. Having established the negative impact of lower sulfur concentrations on anode quality with respect to CRR and CRD, it becomes quite challenging for carbon plants to balance Potroom requirements with environmental concerns. The options available to carbon plants to minimize this negative impact will now be explored.

Experimental

Anode Baking Study

Two green anodes from a single plant but made utilizing different cokes were supplied to the AJ Edmonds Laboratory in Mead, Washington. Six 5.5" diameter cores were taken from each anode and cut into three samples each. The top and bottom of the original cores were discarded. Samples were baked in a laboratory baking furnace using a programmable temperature controller. From 125-700°C, the heating rate was 10°C/hr. After reaching 700°C, the heating rate was increased to 80°C/hr until the final temperature was reached (either 1150 or 1200°C). The soak time at temperature was either 8 or 16hrs.

For each baking scenario, three specimens from each green anode type were removed from the same coring position and were packed in a single layer in the baking furnace. The maximum temperatures for the furnace and sample thermocouples for each scenario were 1200 and 1150°C (furnace) and 1187 and 1137°C (sample), respectively. The baking scenarios can be found in Table I.

Table I. Baking Scenarios Utilized for Each Anode Coke Type

Bake #	Peak furnace Temperature (°C)	Soak Time (Hr)
1	1200	16
2	1150	16
3	1200	8
4	1150	8

Granulometry Optimization

Two samples of high sulfur cokes (HS-A and HS-B) and four samples of low sulfur coke (LS-A, LS-B, LS-C, and LS-D) were shipped to AJ Edmonds for laboratory anode manufacturing. A listing of the coke properties of interest for this study can be found in Table II.

Table II. Coke Properties for Individual Cokes Used

Coke	HS-A	HS-B	LS-A	LS-B	LS-C	LS-D
S, %	2.88	2.63	1.79	1.1	0.68	1.28
Na, ppm	12	60	70	120	30	50
Ca, ppm	35	140	190	140	20	130
V, ppm	270	300	110	100	230	140
Ni, ppm	100	160	190	80	210	80

A standard granulometry curve was used in all testing. The aggregate fractions targeted an actual distribution of 23% butts, 32% Coarse, 20% Intermediates, and 25% fines fraction. Butts for the test were supplied by the Alcoa Deschambault smelter in Canada. The cokes were sized appropriately and blended in the scenarios presented in Table III. The aggregate and solid pitch were placed in separate ovens at 220 and 198°C, respectively, for 2 hours prior to being introduced to the hot oil heated sigma blade mixers. The materials were mixed for 30 minutes with stops every 10 min to scrape down the walls and paddles. At the end of the 30 min mixing cycle, the paste temperature was 170±2°C. For each blend, a 5 level pitch optimization test was conducted.

Table III. Granulometry Blend Scenarios

% HS-A	% LS-A	Comment
60	40	Straight blend
60	40	Straight blend
60	40	Fines fraction consist of 100% low sulfur coke
60	40	Fines fraction consists of 100% high sulfur coke

Paste samples were removed from the mixer and cooled slightly prior to anode formation. The laboratory anodes were pressed at a sample pressure of 4800 psi, mold temperature of 130°C, and pressure hold time of 120 seconds. Three anodes were obtained per batch or pitch level.

The formed specimens were then loaded into the laboratory-scale baking furnace with sample “A” loaded in the bottom layer, sample “B” in the middle, and sample “C” in the top layer. The heating profile was the same as described previously with the target peak furnace temperature of 1200°C and a soak time of 16hr. The final specimens were cored and anode properties

determined. For CO₂ reactivity, a modified ASTM procedure with test duration of 13.5 hr versus the typical 7 hr was utilized.

Low Sulfur Coke Evaluations

Utilizing the procedures described above, various low sulfur cokes were blended with a high sulfur coke (HS-B) using the standard aggregate blending technique or straight blending. The butts used for these tests were supplied by the Mt Holly Smelter located in South Carolina, USA. Table IV provides the blending scenarios used for the tests. For these tests, anode target sulfur levels were 1.2, 1.4, 1.6, and 1.8 wt%. Sodium fluoride was also added to the paste mixes of a separate batch of 1.8% S targeted blends (scenarios 14-17) to increase Na content by 400ppm.

Table IV. Coke Blend Scenarios to Meet Specific Sulfur Targets in Total Coke Blend

Scenario	Sulfur target – blend description
1	1.2%S – HS-B 8.92%, LS-B 91.08%
2	1.4%S – HS-B 21.66%, LS-B 78.34%
3	1.6%S – HS-B 34.39%, LS-B 65.61%
4	1.8%S – HS-B 47.13%, LS-B 52.87%
5	1.2%S – HS-B 26.59%, LS-C 73.41%
6	1.4%S – HS-B 36.86%, LS-C 63.14%
7	1.6%S – HS-B 47.13%, LS-C 52.87%
8	1.8%S – HS-B 57.39%, LS-C 42.61%
9	1.2%S – HS-B 0.00%, LS-D 100.00%
10	1.4%S – HS-B 8.89%, LS-D 91.11%
11	1.6%S – HS-B 23.70%, LS-D 76.30%
12	1.8%S – HS-B 38.52%, LS-D 61.48%
13	1.8%S – HS-B 0.00%, LS-A 100.00%
14	1.8%S – HS-B 47.13%, LS-B 52.87% + 500ppm Na
15	1.8%S – HS-B 57.39%, LS-C 42.61% + 500ppm Na
16	1.8%S – HS-B 38.52%, LS-D 61.48% + 500ppm Na
17	1.8%S – HS-B 0.00%, LS-A 100.00% + 500ppm Na

Results

Anode Baking Study

The design of this experiment was to examine the impact of final finishing temperature and soak time on anode carboxy reactivity. Both Dreyer [5] and Fisher [6] have shown that carboxy reactivity decreases with increasing finishing temperatures. Fisher noted, however, that for high sulfur anodes, bake temperatures below thermal desulphurization are needed. Once desulphurization begins to take place at a significant rate, the carboxy reactivity of the anode begins to increase. The CO₂ reactivity total loss and dust loss (CO₂TL and CO₂DL, respectively) results from our tests are shown in Figures 3 and 4. The magnitude of the statistical effect of anode type, peak finishing temperature, and soak time on the CO₂TL and CO₂DL is shown in Figure 5.

T-ratio tests showed that for both CO₂ total and dust loss, anode type had a very significant influence (t-ratio greater than 4 in both cases). Anode soak time showed a significant influence on CO₂DL (t-ratio between 3 and 4). Surprisingly, peak temperature did not exhibit a significant influence on either total loss or dust loss (t-ratio less than 2 in both cases).

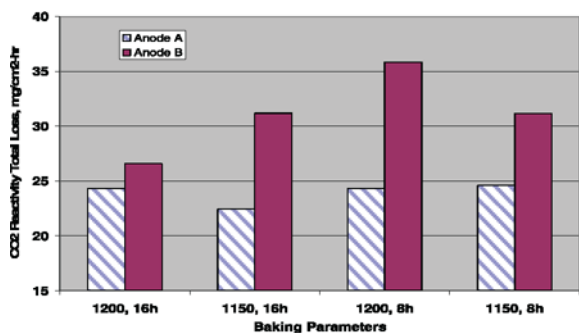


Figure 3. CO₂ reactivity total loss data for the baking parameters examined.

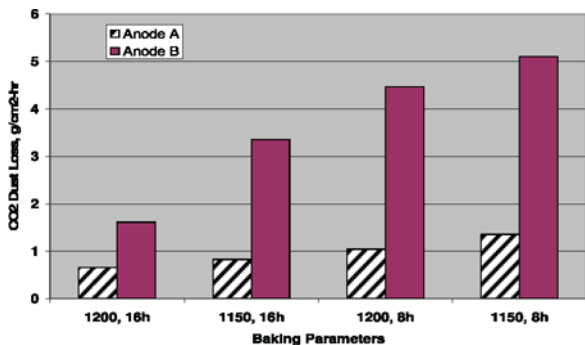


Figure 4. CO₂ reactivity dust loss for the baking parameters examined.

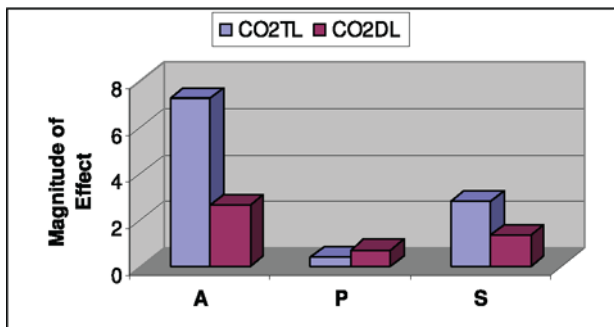


Figure 5. Impact of main effects: A – anode type, P – peak temperature, and S – soak time on CO₂TL and CO₂DL.

As anode type had the greatest influence on both CO₂TL and CO₂DL, it is necessary to explore the differences between the two types in more detail. The average properties for the baked specimens for each baking run are provided in Table V. As can be seen, Anode B had a slightly lower sulfur content and higher sodium content. Both of these could be contributing to the higher carboxy reactivity and dust levels.

However, a third reason for the different behaviour of the anode types could be from the cokes utilized to make the anodes. Both cokes were from a single supplier, but made from a blend of different green cokes at the calciners. The coke blend used to produce Anode A contained a lower percentage of low sulfur coke compared to the coke blend used to produce Anode B. The impact of using smaller quantities of low sulfur coke in a blend, while maintaining the equivalent total sulfur content, is explored later in this paper.

Table V. Baked anode properties for the anodes used in the bake testing

Peak Temp (°C)	Anode A		Anode B	
	1150	1200	1150	1200
Soak time (hr)	16	16	8	8
Ca ppm	191	174	173	176
Fe ppm	837	541	538	527
Na ppm	367	304	309	294
Ni ppm	110	107	107	108
S %	1.58	1.56	1.58	1.6
Si ppm	143	148	207	144
V ppm	172	173	172	174

Granulometry Optimization – Laboratory Testing

Laboratory anodes were made by blending 60% of a high sulfur coke (HS-A) with 40% of a low sulfur coke (LS-A) in three methods: 1) straight blending where each fraction contains 60/40 of the two cokes, 2) fines fraction contains 100% of high sulfur coke, and 3) fines fraction contains 100% of low sulfur coke.

The tests were designed to evaluate the hypothesis that the coke formed by pyrolysis of pitch is the most susceptible to reaction with CO₂. Most of the pitch is used to coat the finer coke particles, hence it can be inferred that the fine coke particles will have more intimate contact with the pitch coke. If this is true, by having the high sulfur coke in the fines fraction and in closer proximity to the pitch coke, the probability of sodium migrating into the pitch coke to increase its reactivity should be reduced.

CO₂TL and CO₂DL data obtained from the tests were evaluated using JMP software and the results are presented in Figures 6 and 7. Using high sulfur coke in the fines fraction showed a statistically significant reduction in CO₂TL compared to using the standard aggregate blend. Using low sulfur coke in the fines fraction caused a statistically significant increase in CO₂TL compared to using the standard aggregate blend. For dust generation, no statistical difference was observed between the standard blends and placement of high sulfur coke in the fines fraction. However, using low sulfur coke in the fines fraction showed an increase in dust generation rates.

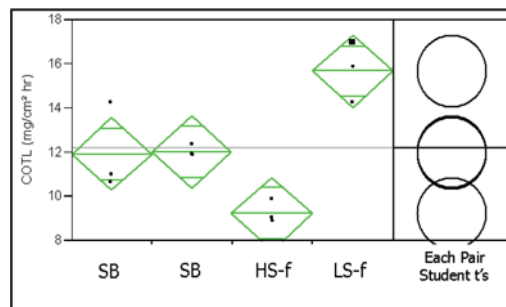


Figure 6. Impact on CO₂ TL of using high and low sulfur cokes in the fines fraction

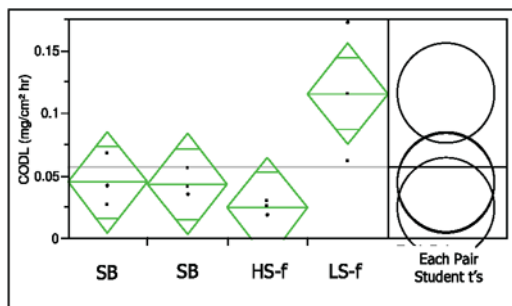


Figure 7. Impact on CO₂ TL of using high and low sulfur cokes in the fines fraction.

Granulometry Optimization – Plant Trial

The favorable results of the laboratory tests prompted trialing within the Alcoa Deschambault Smelter [7]. At the time of the trial, the aggregate blend percentages were 60% low sulfur coke (LS-A) and 40% high sulfur coke (HS-A). The test was conducted in duplicate. During the test, a ball mill feed tank was emptied and the high sulfur coke material was directed to this tank. The ball mill product during the runs was segregated into specified fines tanks and these were used for anode production during the tests. The fines fraction still contained a mixture of coke from the addition of process dust and natural fines content found in the low sulfur coke. However, the fines fraction was predominantly high sulfur coke.

The impact on anode CO₂ reactivity residue and dust from changing the composition of the fines is shown in Figures 8 and 9. As can be seen, a desirable increase in CRR of between 2 and 4% was observed when the high sulfur coke was directed to the ball mill. In contrast to the laboratory data that did not show a significant effect on CO₂ dust of having the high sulfur coke directed to the fines fraction/ball mill feed, the plant data showed a decrease in dust of 1-2%. The discrepancy could be caused by having a higher percentage of low sulfur coke in the blend for the plant trials or just differences between the ASTM test procedure and the R&D Carbon test procedure.

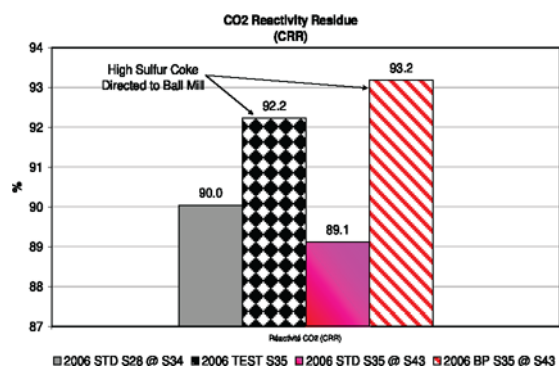


Figure 8. CO₂ Reactivity Residue results from plant trials of directing high S coke to the Ball Mill.

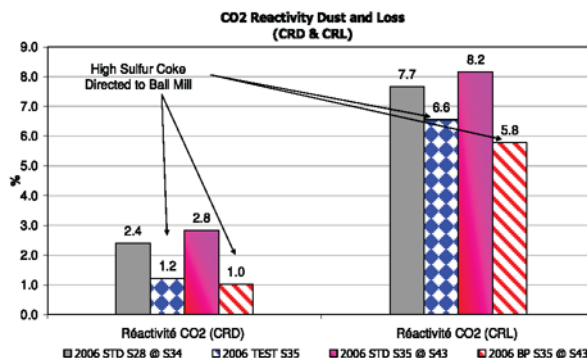


Figure 9. CO₂ Reactivity Dust and Total Loss results from plant trials of directing high S coke to the Ball Mill.

While positive anode results with respect to carboxy reactivity were obtained in the anode core properties, the most important factor is performance in the reduction cells. During the time of testing, a number of cells were experiencing higher levels of dust than desired; this was evident in the dust auditing surveys. It was therefore decided to trial the anodes with the modified recipe in the cells with dusting issues. Audit results are shown in Figure 10. The audit is based on three metrics: Code 1 represents the % of cells with >1 inch of carbon dust around the tap hole; Code 2 represents the % of cells with 1/2 to 1 inch of carbon dust around the tap hole; and Couverture is the % of cells with dark anode cover visible when opening the doors. As can be seen in Figure 10, an improvement in the audit scores was observed after the modified granulometry anodes were placed in the reduction cells.

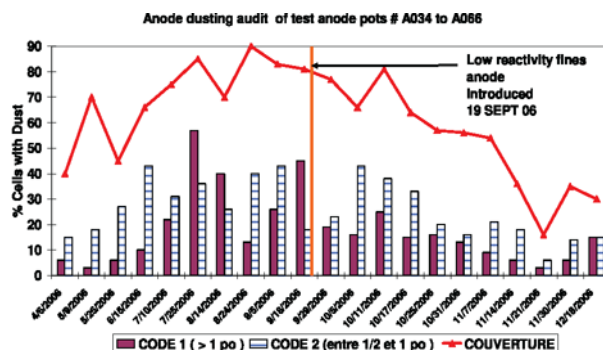


Figure 10. Dust auditing scores for the cells containing modified granulometry anodes.

The results from both the laboratory and plant tests support the hypothesis stated at the beginning of this section. By segregating the low sulfur coke to the coarse fraction in the anode aggregate and subsequently increasing the high sulfur coke used in the fines fraction, the likelihood that the sulphur can inhibit the effect of sodium has increased, thus reducing the overall anode CO₂ reactivity. However, this decrease in anode carboxy reactivity could be at the expense of lower anode densities depending on the types of cokes used in the blends. For instance, if blending a low sulfur coke with low vibrated bulk density with a high sulfur coke with high vibrated bulk density, placing the higher density material into the ball mill circuit has the potential to decrease anode density. The decision to sacrifice anode density for improved carboxy reactivity is a financial decision to be made by each plant.

Low Sulfur Coke Evaluations

It has now been shown that anode CO₂ reactivity can be improved by two means: (1) increasing the anode soak time within the bake furnace and (2) when using a blend of cokes, targeting the high sulfur coke to the ball mill feed. While important findings, these results don't help smelters select low sulfur cokes that minimize carboxy reactivity. To provide insight on this, laboratory anode tests were conducted with 4 different low sulfur cokes: LS-A through D (Table II). These were blended with the high sulfur coke HS-B to target final anode sulfur levels of 1.2, 1.4, 1.6, and 1.8%. The actual anode sulfur concentrations and the resulting CO₂TL data are presented in Figure 11. In the case of LS-A, only one anode sulfur target was possible due to the sulfur level of the coke, and this sample used 100% LS-A for the coke portion of the anode aggregate. As shown in the figure, the 4 different LS/HS coke blends reacted at different levels - a general trend was observed of lower anode sulfur levels resulting in higher reactivities, but it is apparent from the data that the type of low sulfur coke also has an effect.

Multivariable linear regression analysis was performed with anode sulfur content, % sulfur coke used in the blend, and sodium as variables. Surprisingly, the factor that had the highest influence on CO₂TL was the percent of sulfur in the cokes used in the blend. This analysis was carried out with and without the single LS-A point. The results presented in Figure 12 exclude this data point. The LS-A coke is a blend of several green cokes and contains higher calcium levels than the other cokes examined.

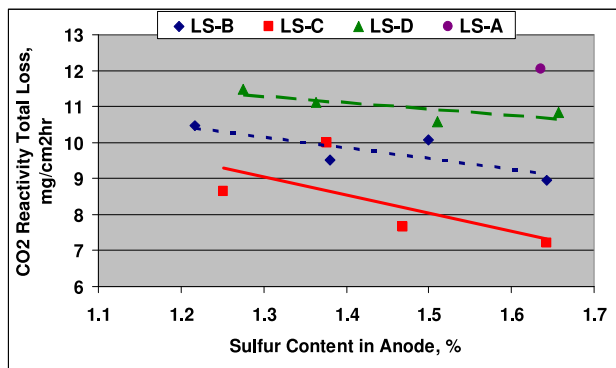


Figure 11. CO₂TL versus total anode sulfur level.

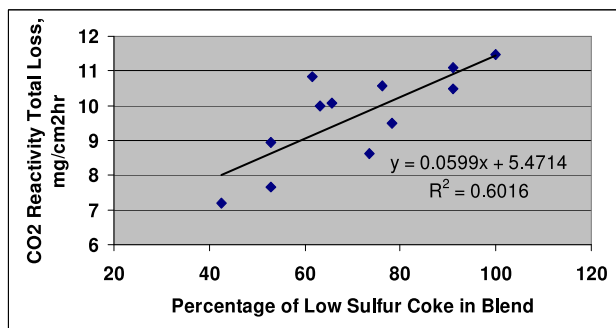


Figure 12. Dependence of CO₂TL on the percent low sulfur coke used in the aggregate blend.

The dependency of CO₂ reactivity on the proportion of low sulfur coke in the blends used helps to explain the differences in the reactivity behaviour of the coke blends in Figure 11. LS-B coke

contains the lowest concentration of sulfur. Therefore, at each targeted anode sulfur level, LS-B samples will contain less low sulfur coke than all other samples. As these are straight blends with all aggregate fractions containing the same proportion of low and high sulfur cokes, the likelihood of the sodium in the anode being able to interact with the sulfur in the anode should increase with the greater number of coke particles with a higher sulfur concentration in the anodes.

Similar results were observed for CO₂DL tests as shown in Figures 13 and 14. Multivariable linear regression again found the highest correlation between CO₂DL and the proportion of low sulfur coke used in the blend. Little or no dependency was observed for sodium. However, this may be caused by the small spread in sodium concentrations for the specimens examined; the range of sodium concentrations used was only 50ppm.

To determine if a difference exists between low sulfur cokes and their susceptibility to sodium catalysis of the CO₂ reaction, a separate set of 1.8% S target samples was made. NaF was added to this set of samples to increase sodium concentration in the anode by 400ppm. Table VI contains the actual sodium concentrations of the spiked and unspiked samples.

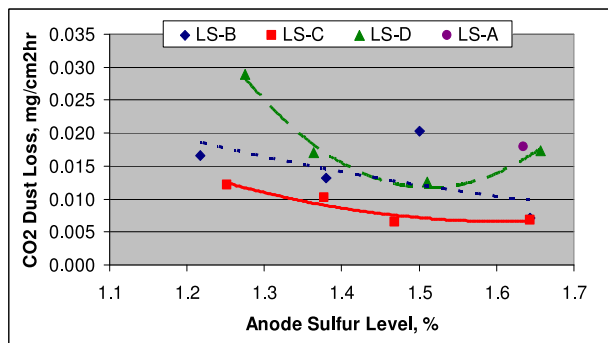


Figure 13. CO₂DL versus total anode sulfur level.

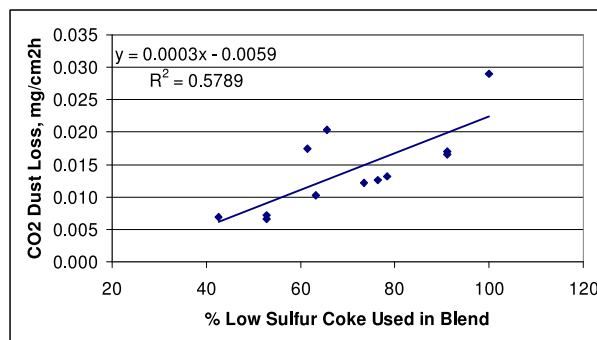


Figure 14. Dependence of CO₂DL on the percent low sulfur coke used in the aggregate blend.

Table VI. Sodium concentrations in the 1.8% sulfur targeted anodes, original and spiked with NaF.

Coke	Na Concentration, %		
	Baseline	Na Spiked	Difference
LS-A	0.0133	0.0509	0.0376
LS-B	0.0161	0.0564	0.0403
LS-C	0.0144	0.0547	0.0403
LS-D	0.0142	0.0539	0.0397

The impact of the increased sodium concentration on CO₂TL and CO₂DL is shown in Figures 15 and 16. In the case of CO₂TL, the relative change in reactivity is fairly constant for all cokes. This suggests that the low sulfur cokes tested all reacted in a similar way in response to the sodium spiking. However, the change in dust loss (CO₂DL) is different for each coke examined and the magnitude of the changes in CO₂DL from the increased sodium is 10-50 times greater than the changes observed from the low sulfur coke content in the baseline samples. This suggests that the impact of sodium on dust generation is greater than the impact low sulfur coke content in the blend. Examination of the relationship between CO₂DL and % low sulfur coke in the blend, Figure 17, shows that the content of low sulfur coke does have an impact on dust levels.

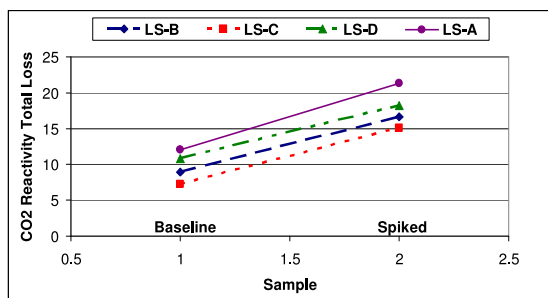


Figure 15. Impact of added sodium on CO₂TL.

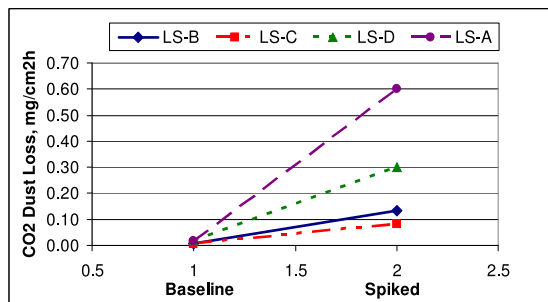


Figure 16. Impact of increased sodium on CO₂DL.

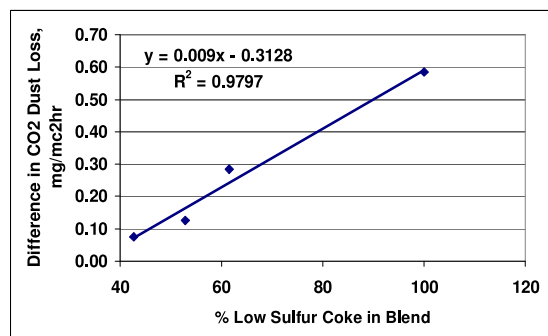


Figure 17. Change in CO₂DL for the baseline and Na spiked samples versus the % of low sulfur coke used in the blend.

Conclusions

Due to environmental regulations, aluminum plants are utilizing low sulfur coke as key lever in the strategy to reduce SO₂ emissions. A negative impact of that action is an increase in CO₂ reactivity of the anode. The results of this work show that the following actions can be taken in the carbon plant to minimize the negative impact:

- Increase anode baking soak time.
- Direct higher sulfur coke to the fines fraction.
- Minimize the proportion of low sulfur coke in the aggregate blend by selecting cokes with very low sulfur.

Acknowledgements

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