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USE OF SHOT COKE AS AN ANODE RAW MATERIAL

Les Edwards[1], Franz Vogt[1], Mike Robinette[1], Ric Love[2], Anthony Ross[2], Marilou McClung[2], RJ Roush[2], William Morgan[3]
[1]Rain CII Carbon LLC, 2627 Chestnut Ridge Rd, Kingwood, TX, 77345, USA
[2]Century Aluminum of West Virginia, Route 2 South, PO Box 98, Ravenswood, WV, 26164, USA
[3]Century Aluminum of Kentucky, 1627 State Route 271 N, PO Box 500, Hawesville, KY, 42348, USA

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Abstract

With the aluminum industry's rapidly growing demand for anode grade petroleum coke, supplies have become very tight and the industry has started using cokes not considered suitable as little as five years ago. Shot coke is available in large volumes and is currently used for fuel and TiO_2 applications. Rain CII Carbon and Century Aluminum started a project in 2004 to explore the use of shot coke and other isotropic cokes for anode production. The project was intended to address anode grade coke shortages being felt by the industry today. This paper summarizes the laboratory and plant test work completed and makes a strong case for routine incorporation of these cokes into anode blends. Depending on how it is used, shot coke can improve properties such as anode density and it offers a lower cost calcined coke in today's world of escalating raw material costs.

Introduction

In 2007, approximately 38 million tons of primary aluminum were produced worldwide [1] requiring about 14.6 million tons of calcined coke [2]. In 2012, aluminum production is forecast to rise to about 55 million tons. Correspondingly, calcined coke demand for aluminum production will jump to 21 million tons per year (tpy) by 2012. This additional 6.4 million tpy of calcined anode coke will require an extra 8.3 million tpy of green petroleum coke.

The increasing demand for "anode-grade" green coke for the aluminum industry and the declining quality of the green coke produced by oil refineries has been the subject of papers and presentations dating from 2001 [3,4,5]. These and many recent industry articles chronicle the increasingly difficult task of sourcing suitable anode grade green cokes at reasonable prices. While ample quantities of green petroleum coke will be available, much of this green coke will be higher in metal impurities, higher in sulfur and will have a structure different to the sponge cokes preferred by anode producers.

Fuel grade cokes with highly isotropic structures continue to be the predominant green cokes produced by the refining industry. Millions of tons of these cokes are burned directly for power generation and cement production. Shot coke is a form of isotropic coke and such cokes are readily available for a lower cost than sponge coke. In 2003, Rain CII Carbon (then CII Carbon) entered into a partnership with Century Aluminum to investigate the potential of using isotropic cokes like shot coke in carbon anodes.

Isotropic Coke and Shot Coke

Isotropic cokes are cokes with a fine grained texture which exhibit similar properties in all directions. Anisotropic cokes on the other hand, have a coarse texture with a layered structure and the properties change with orientation. The extreme example of anisotropic coke is needle coke which has a needle or ribbon-like structure. Delayed sponge coke used for making anodes has a heterogeneous structure with a mixture of coarse and fine textures.

Shot coke [6] is a form of isotropic coke with a unique structure. It has a fine texture with uniform properties, and the particles tend to be spherical in shape and more uniform in size. The structure can also be layered like an onion. Typical examples of the four structures mentioned above are shown in the photo-micrographs of Figure 1.

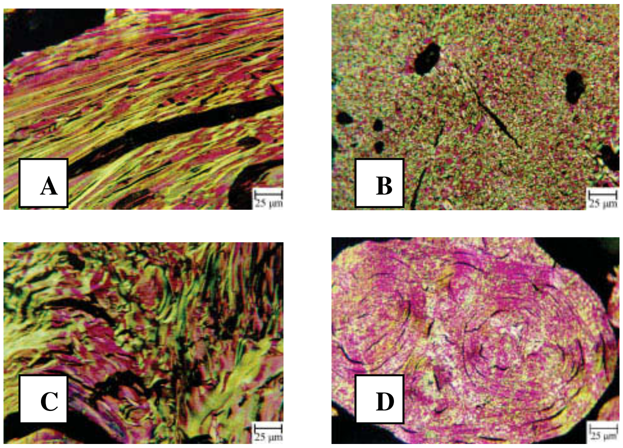


Figure 1: Coke structures with polarized light microscopy A) needle coke, B) isotopic coke, C) sponge coke D) shot coke.

The factors that affect coke quality and structure from a given refinery have been reviewed previously [7]. Crude oil quality is the single largest determinant of structure in a coke; it fixes the quality of the feed to the coker. A highly aromatic coker feedstock yields needle coke. A highly asphaltenic coker feedstock produces shot coke. In between are other heavy hydrocarbons which, in the proper proportion with aromatics and asphaltenes, produce the sponge cokes historically most desirable for anode grade coke.

The aluminum industry has avoided using highly isotropic cokes, particularly shot cokes, because they have high coefficients of thermal expansion (CTE) and low open porosity. Anodes made with these materials are more susceptible to thermal shock cracking during the rapid heat-up in aluminum electrolysis cells. They can also suffer from lower mechanical strength and dusting problems during cell operation. Shot cokes typically have low levels of open macro-porosity for pitch penetration. This reduces the ability of pitch to interlock and bond the structure together during carbonization. Some of these problems are well documented in smelter tests with a highly isotopic coke [8].

Laboratory Experiments

Rain CII Carbon and Century Aluminum started work on this project in early 2004. All initial work was done on a laboratory scale. In the first set of experiments, baseline laboratory anodes were prepared with the sponge coke used routinely at the Century Ravenswood smelter. Anodes with additions ranging from 12.5% to 85% of two different isotropic cokes were then prepared and tested. One of these was a well formed shot coke and the other was sponge coke with a highly isotropic structure. The cokes were blended uniformly across all size fractions. Selected property data for the three different cokes are shown in Table 1.

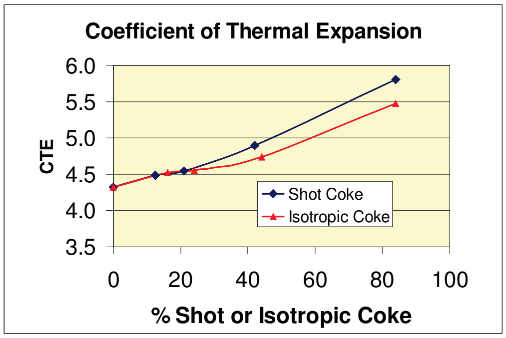
Table 1: Coke Property Data

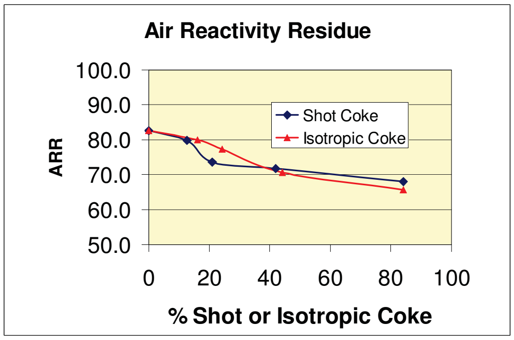
Coke Type	S (%)	Ni (ppm)	V (ppm)	Hg App. Density g/cc	VBD (g/cc)	Real Den. g/cc
Regular	2.6	160	230	1.76	0.80	2.07
Shot	4.5	320	670	1.80	1.10	2.04
Isotropic	4.5	320	700	1.73	0.80	2.06

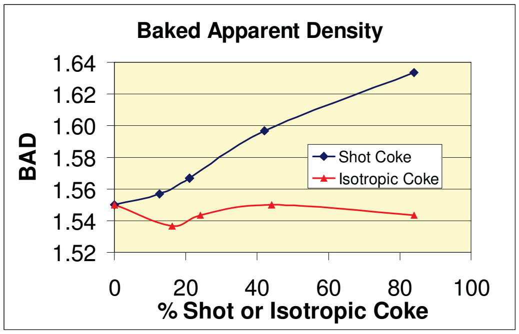
Key findings from the first set of experiments were:

- Anode air reactivities deteriorated as the percentage of isotropic coke and shot coke increased. CO_2 reactivities improved a little.
- Anode CTE's increased as the percentage of isotropic and shot coke increased.
- Anode density increased as the percentage of shot coke increased. No density improvement was seen with the isotropic coke.
- With up to 50% isotropic coke and shot coke, most other anode properties looked normal.

Graphs for CTE, air reactivity and density are shown below. Data points at 0% shot coke represent the baseline anodes.







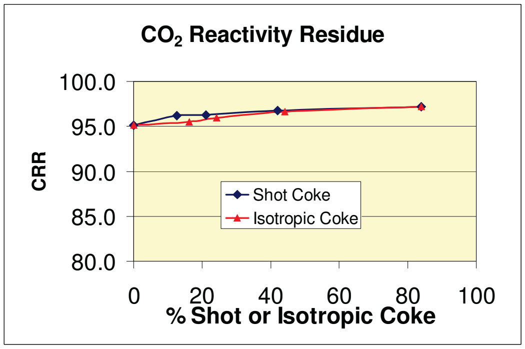


Figure 2: Selected results from early tests.

In the next set of laboratory experiments, the shot coke and isotropic coke were selectively added to different parts of the aggregate (i.e., coarse and fines fraction). There was a strong expectation that it would be advantageous to grind the shot or isotropic coke and concentrate it in the fines fraction to minimize the negative effects on CTE.

Fifteen different anode recipes were tested at different pitch levels to produce a total of 180 different anodes. Results were averaged and grouped together where possible to determine general trends. A summary of key results is given below followed by some comparative graphs for key properties.

- Isotropic coke added to the fine and coarse fractions from 25-75% had little effect on baked anode density.
- Shot coke added to the fines fraction had no effect on anode density but when added to the coarse fraction, the density increased significantly.
- Isotropic coke and shot coke additions to the fines fraction caused a progressive deterioration in anode air reactivity. Anode CTE and other mechanical properties were unaffected.
- Air reactivity deteriorated only slightly when isotropic coke and shot coke were added to the coarse fraction.
- Anode CTE increased almost linearly as isotropic coke and shot coke were added to the coarse fraction. Anode strength also decreased.
- Anode CO_2 reactivities were good for all formulations tested with isotropic coke and shot coke.

Figure 2 shows the baked anode density results for the 15 different anode recipes tested. The last 3 bars show a significantly higher baked density and these were generated from anodes with shot coke added to the coarse fraction at the 40% and 75% level. This increase in density is a direct consequence of the higher apparent and vibrated bulk density of the coke. An addition of 40% shot coke to the coarse fraction equated to an addition of 20% shot coke overall.

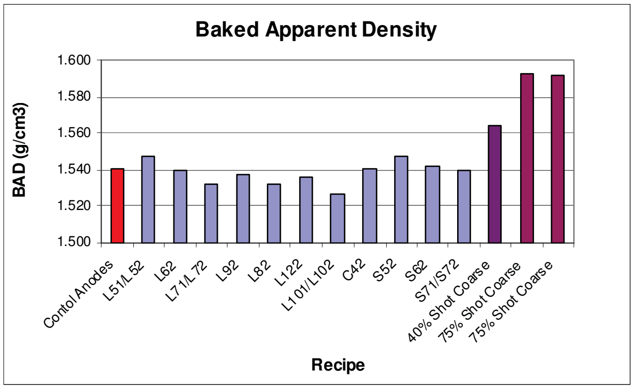


Figure 2: Baked anode density of different lab anode recipes.

Figure 3 shows the effect on CTE of adding shot coke to the fines (ball mill) fraction compared to the coarse fraction. When added to the fines fraction only, shot coke additions have very little effect on CTE but when added to the coarse fraction, the CTE increases linearly. Figure 4 shows the results for air reactivity with isotropic coke additions.

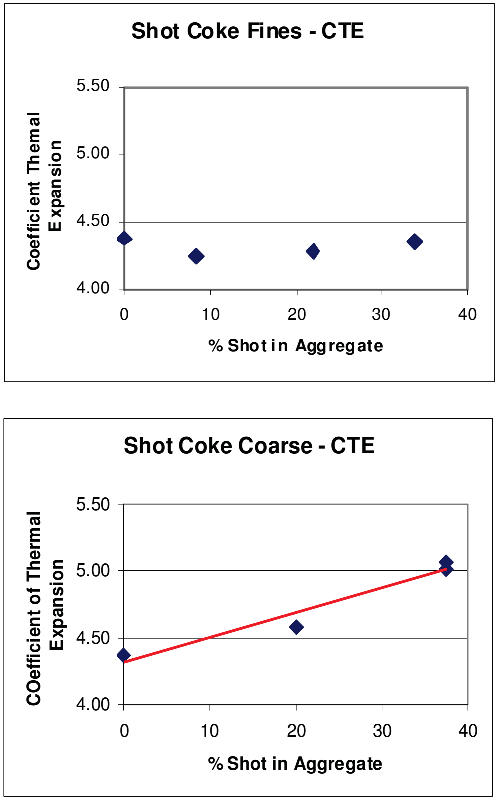


Figure 3: Effect on CTE of adding shot coke to the fines and coarse fraction.

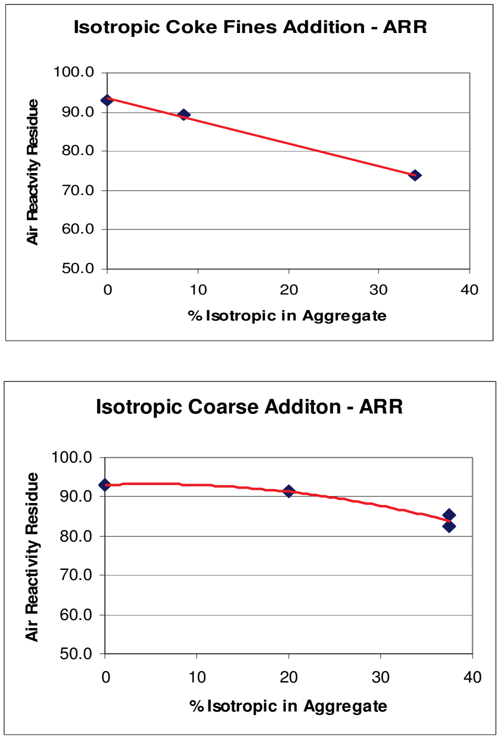


Figure 4: Effect on air reactivity residue of adding isotropic coke to the fines and coarse fraction.

The results from the second series of laboratory tests showed that anode properties with shot and isotropic coke additions are dependent on how the coke is added. Anode CTE does not increase when shot coke is added to the fines fraction but anode air reactivity deteriorates. When shot coke is added to the coarse fraction, the CTE increases significantly but anode air reactivity is not as significantly affected.

Following the above lab tests, Rain CII and Century decided to proceed with small scale plant tests of anodes produced with 20% shot coke in parallel to continued laboratory testing. An addition rate of 20% was selected on the basis of smelter SO_2 permit limits. With a 20% shot coke addition, anode sulfur levels could be maintained below the smelter SO_2 limit. The increase in anode density possible with the addition of shot coke is attractive if it can be done without a significant negative effect on anode performance. The biggest performance concern was thermal shock cracking due to high CTE of anode produced with shot coke. Thermal shock cracking problems are scale dependent and it was felt that the quickest way to evaluate this was to make full scale anodes.

Plant Trials

Disaster Check Trials at Ravenswood: The bulk of the plant test work has been done at the Century Ravenswood smelter in West Virginia. Ravenswood produces ~170,000 tons of primary aluminum using Kaiser P57 type cells operating at 93kA. Anode sizes are small compared to modern day cells but anode current densities are on the high side at 1 amp/cm^2. Thermal shock problems are typically worse with larger anodes and high current densities. In terms of anode production, Ravenswood uses batch mixers and a hydraulic press.

In 2005, a small number of anodes (~100) containing 20% shot coke added to the coarse fraction were produced. The aim was to make sure they could be baked, rodded and set in cells without major problems. The trial was intended as a “disaster check.” The first fifty anodes were over-pitched and had to be scrapped after baking. Shot coke has a lower pitch demand due to lower macro-porosity. The pitch content was reduced and the remaining anodes were baked without problems. No cracking or other problems occurred when the anodes were tested in the potlines.

After this disaster test, additional laboratory work was undertaken to optimize the aggregate recipe. More specifically, the fines content and fines Blaine Index of a recipe containing 20% shot coke in the coarse fraction was optimized. Additional plant testing was then done to optimize the pitch content.

Plant Trial 1 Ravenswood: With an optimized recipe, a larger scale trial involving 710 anodes was undertaken from April-June 2006. The anodes were tested in four closely monitored cells and this allowed three full anode cycles with the shot coke anodes.

Baked anode densities were 0.03 g/cc higher (1.60 for the shot coke anodes) and the optimum pitch level was 1% point lower than regular plant anodes. Both of these results were positive. With the pitch level optimized, baked anode scrap rates were no different from regular anodes and anode production presented no problems.

During the potroom trial, the following cell parameters were monitored: cell voltage, cell noise, anode effect frequency, number of separations (early change-outs) and butt weights. No differences were noted in cell performance and the butt weights of the shot anodes were slightly higher on average. Carbon consumption (kg C/kg metal) was similar. From an operational perspective, the plant workers did not notice any difference when using shot coke anodes compared to regular anodes and there were no thermal shock cracking problems.

Plant Trial 2 Ravenswood: Once the above trial was completed, a larger, more statistically valid trial was planned in mid-2007. The aim was to test shot coke anodes in a group of 14 cells for comparison against a group of 14 control cells. This required production of 2500 anodes and allowed operation of the cells with shot coke anodes for five full anode rotations.

The green anodes were produced with a 30% fines level (3400 Blaine Index), 18% butts, 32% coarse fraction (-4,+20 mesh) and 20% shot coke. The shot coke was added only to the aggregate coarse fraction. Regular anode butts were used to make all the anodes and no attempt was made to separate out butts containing shot coke for the second and third generation anodes.

Anode property data are shown in Table 2 including chemical analysis results. Pitch levels were 1% lower for the shot containing anodes and baked anode densities were ~0.02g/cc higher for the shot anodes (1.588 versus 1.565 g/cc). The vanadium level of the shot coke anodes was higher due to the higher vanadium level in the coke. Air permeabilities were a little higher in the shot anodes and air reactivity residues were slightly lower but still within the range of typical plant anodes.

Table 2: Anode Properties

Property	Control Anodes	Shot Anodes
Pitch Level (%)	15.8	14.8
Green Density (g/cc)	1.647	1.668
Baked Density (g/cc)	1.565	1.588
Electrical Resistivity (uΩ.m)	62.4	58.2
Air Permeability (nPm)	1.3	1.9
Air Reactivity Residue (%)	81.4	77.0
CO_2 Reactivity Residue (%)	85.6	93.0
Vanadium (ppm)	190	300
Nickel (ppm)	170	210
Sulfur (%)	1.82	2.15

The shot coke anodes were used in cells 1-14 and the performance was compared to the control cells 15-28. In addition to this comparison, the performance of cells 1-14 with regular anodes in the four month period prior to the test was examined. None of the performance comparisons showed any statistically significant differences except the vanadium content of the metal. This was higher in the shot coke cells as expected due to the higher vanadium content of the shot coke anodes. A summary of performance results for cells 1-14 before and after the test is shown in Table 3.

Table 3: Cell Performance Results

	Cells 1-14 Regular Anodes	Cells 1-14 w/ Shot Anodes
Cell voltage (V)	4.58	4.59
Noise (V)	0.030	0.029
Time on noise control (hrs)	3.1	3.0
Anode Effect Frequency	0.24	0.30
Metal Prod (kg/pot/day)	703	702
# Separation (burnoffs)	56	64
Butt Weights	Control	+4 kg
Iron (%)	0.18	0.14
Vanadium (%)	0.0070	0.0076
Nickel (%)	0.0015	0.0015

No problems with anode cracking or unscheduled changes were noted with the shot anode cells and no additional airburn was observed. According to plant operations personnel, the anodes were indistinguishable from regular anodes and the cells operated similarly. The slightly higher butt weights of the shot coke anodes were in line with the higher baked anode density and anode weights.

It should be mentioned that producing anodes with recycled butts containing shot coke was not attempted. Separating butts containing shot coke so they could be recycled into second and higher generation anodes would have significantly increased the complexity of a trial. This will be part of a larger trial now planned.

Plant Trial 3 Hawesville: Testing was expanded to the Century Hawesville smelter to explore the risk of thermal shock cracking with larger anodes. Hawesville operates Kaiser P69 designed cells and produces 245,000 tons/year of primary aluminum. Line currents are 165-175 kA and the Hawesville anodes are roughly three times the weight of the Ravenswood anodes.

Approximately 100 anodes containing 20% shot in the coarse fraction coke were produced in early 2008. Hawesville uses batch mixers like Ravenswood, but a vibroformer instead of a press. The aggregate recipe was a little different to that used at Ravenswood with 18% butts, 28% coarse, 20% shot, and 34% fines. A similar reduction in pitch level was noted by Hawesville with the shot coke anodes (13.7% vs 14.6% for regular anodes).

Hawesville achieved almost the same improvement in baked anode density as Ravenswood, despite the different recipe and forming technology. A full comparison of properties is shown in Table 4 below. CTE's are a little higher for the shot anodes as expected and air permeabilities are also a little higher. Other properties are very similar.

Table 4: Hawesville Anode Property Data

Property	Regular Anodes	Shot Anodes
Baked Density (g/cc)	1.575	1.596
Electrical Resistivity (uΩ.m)	54.3	52.8
Air Permeability (nPm)	0.79	1.43
CTE (10^{-6} K)	4.43	4.87
Thermal Conductivity (WmK)	3.66	3.74
Compressive Strength (MPa)	49.4	51.9
Flexural Strength (MPa)	8.3	8.9
Air Reactivity Residue (%)	82.3	79.9
CO_2 Reactivity Residue (%)	91.1	92.8

Anodes were set in two closely monitored cells at Hawesville through two full anode rotations. No problems were seen with anode cracking. In an effort to thermally stress anodes more severely, a number of shot containing anodes were set in "hot" cells with a high superheat. No problems were observed with cracking in these cells either. It is worth noting at this point that neither Ravenswood nor Hawesville uses slotted anodes. Slots can be beneficial in reducing thermal shock cracking by providing stress relief during anode expansion.

Discussion

The results presented in this paper show that shot coke and other isotropic cokes can be carefully blended with regular anode grade sponge coke and used successfully in anode applications. Adding 10% or 20% shot coke to an anode blend will not result in a sudden and catastrophic failure of an anode in a way that many people in the industry fear. Judicious use of shot coke can actually be advantageous for improving anode density.

Although not tested in this work, anodes made with 100% shot coke would be unlikely to perform well in an electrolysis cell. They would have poor mechanical strength due to inadequate pitch penetration and would likely suffer from thermal shock cracking problems due to high thermal expansion coefficients. It is not clear how much benefit slots would provide, but they would help reduce the risk of thermal shock cracking. Poor pitch penetration and high reactivity would lead to significant airburn and dusting problems in a cell.

Many smelters have specifications today which preclude the use of shot coke at any level. These specifications were set many years ago for two major reasons 1) a strong fear that use of shot would lead to major anode performance problems and 2) the ready availability of good quality anode grade sponge cokes. The results of the work presented in this paper challenges the first paradigm and offers a solution to the problems the industry faces with the future availability of high quality anode grade sponge cokes.

The performance of anodes with shot coke additions depends on how the shot coke is added. When shot coke is added uniformly to all aggregate size fractions, the following can be expected: Anode CTE will increase, pitch demand will decrease a little, anode density will increase and anode reactivities will deteriorate. The extent of the impact will depend on how much shot coke is added – the higher the addition rate, the greater the impact.

If shot coke is added only to the ball mill feed and aggregate fines fraction, anode CTE will not increase significantly, density and pitch demand will not change greatly, but anode air reactivity will deteriorate significantly.

When shot coke is concentrated in the coarse fraction, anode CTE will increase almost linearly with the amount of shot coke added, pitch demand will decrease, anode density will increase significantly and anode reactivities will not change significantly. The above concepts are described in more detail in a joint Rain CII Carbon/Century Aluminum patent on the use of shot coke in anodes [7].

The above means that shot coke can be used in a variety of ways and the smelter technology may dictate the best way to use it. The simplest way to use shot coke is to blend it uniformly with the coke used at a smelter. The impact will vary depending on the amount used – very little impact at 5%, some impact at 10% and a greater impact at higher levels.

If a smelter is looking to increase anode density, shot coke additions can be very helpful, especially when added to the coarse fraction. The CTE will increase but in this work, no evidence of thermal shock cracking problems was found at the 20% level. Laboratory tests suggest that higher proportions of shot coke could be used successfully. With the widespread use of slotted anodes today, the risks of thermal shock cracking will be lower than they have been in the past. Cracking is size dependent however, and a smelter using large anodes operating at high current density will be more sensitive to this problem than a smelter operating with smaller anodes.

The amount of shot coke and isotropic coke that can be added to a coke blend and anode recipe will ultimately be dictated by smelter purity constraints. Many isotropic cokes and shot cokes are higher in sulfur and metals than traditional anode grade cokes; sulfur levels in particular will dictate how much can be added to a blend. Virtually all smelters have SO_2 permit limits and in the absence of SO_2 scrubbing, these must be met.

As the gap between the supply of anode grade sponge coke and demand from the aluminum industry grows, shot coke additions offer a viable and cost saving opportunity for the industry. Shot coke should not be feared as part of the problem but rather, viewed as part of the solution for the future.

Conclusions

1. Acceptable quality pre-baked anodes can be made with a blend of sponge and very isotropic coke, including shot coke.
2. The specifics of how isotropic coke and shot coke are added to the aggregate distribution (coarse versus fines) determines the key anode properties of density, CTE and reactivity.
3. For maximizing the density of an anode, shot coke additions to the coarse fraction will provide a significant benefit. Anode CTE will increase but reactivities will not be significantly affected.
4. The impact on anode CTE can be minimized by adding isotropic coke and shot coke to the fines fraction. This will however, result in increased air reactivity. For modern cells with well covered anodes, this may not be a significant issue.
5. When very isotropic cokes are added uniformly to all size fractions, most anode properties are impacted in some way in direct proportion to the levels added.
6. Smelter tests with pre-baked anodes produced with 20% shot coke in the aggregate resulted in improved anode density and butt weight, no increase in net carbon consumption, no cell performance problems, but a calculable increase in vanadium in the metal.

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