Use of Thermally Desulfurized Shaft CPC for Anode Production

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Abstract

Thermal desulfurization (TDS) of petroleum coke during calcination is a well-known phenomenon which results in a significant decrease in bulk density. In 2011, Rain Carbon began experimenting with TDS in a shaft calciner and some results were unexpected, particularly an increase in real density. This paper reports on the results of extensive work to explore the fundamental differences between TDS in shaft calciners and rotary kilns. Pilot anode studies have been completed to explore the potential of using TDS coke from shaft calciners in anode production. The attraction is both commercial and environmental. High sulfur (S) cokes are readily available and cheaper than low S cokes and removing SO_2 during calcination is more efficient than removing SO_2 from potroom flue-gas streams to meet emission limits.

Keywords

Petroleum coke • Anodes • Shaft calcining • Sulfur • Desulfurization

Introduction

Thermal desulfurization (TDS) of petroleum coke is a well-studied phenomenon and two papers from 2007 and 2008 [1, 2] provide a detailed review including problems TDS creates during calcining and anode baking. A recent paper by Xiao et al. [3], provides an excellent overview of the structural changes occurring during TDS. The paper uses molecular modelling to show changes occurring for sulfur (S), nitrogen and oxygen containing molecules. An important conclusion is that these functional groups exist along the periphery of the coke structure making their removal easy during calcination.

Table 1 shows the results of a TDS trial in a rotary kiln with green petroleum coke (GPC) containing 4.6% S. The S loss under normal calcining conditions is 9–14% and it is important to note that this is not caused by TDS [1]. At higher calcining temperatures, the S loss increases to 30 and 47% due to TDS. This is accompanied by a drop in vibrated bulk density (VBD), real density (RD) and particle strength (shown as crush strength). Lc results are included to show the relative level of calcination (higher Lc = higher temperature).

The decrease in VBD (ASTM D4292, 30 × 50 mesh) and RD of calcined petroleum coke (CPC) resulting from TDS has previously been attributed to an increase in micro-porosity [4]. The best analytical method to characterize this is high pressure mercury (Hg) intrusion porosimetry. The pore size distribution curves of TDS coke show the appearance of a peak in the 0.01–0.10 µm pore size range that increases significantly as the level of TDS

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increases. An example is included later in the paper to show this.

Attempts to use TDS CPC from a rotary kiln to produce anodes have been unsuccessful. In a recent publication [5], a coke heated to 1500 °C with TDS was added to the ball mill fines (BMF) fraction of an anode recipe. The study concluded that it was not viable due to the significant drop in baked anode density (~0.04 g/cc) and deterioration of other anode properties.

The interest in TDS of coke is both an economic and environmental one. High S cokes are well known to sell at a significant discount to low S cokes due to their more plentiful supply [6]. Their use increases SO_2 emissions however, which must be reduced via scrubbing to meet permitted emission limits. In principal, it is more efficient/economic to remove SO_2 during coke calcining than aluminum production. SO_2 concentrations are much higher and flue gas volumes much lower compared to the high volume flows and low SO_2 concentrations from smelter (potline) exhaust gas streams.

In 2011, Rain Carbon began experimenting with TDS in a shaft calciner to investigate any potential benefits. Some unexpectedly high RD results led to extensive work over the 2011–2016 period. In August 2015, a shaft calcining company in China reported that it was constructing a high temperature shaft calciner specifically for TDS of coke.

The objective of this paper is to review the fundamental differences between TDS in a rotary kiln and shaft calciner and to report on the results of pilot anode testing. The paper will discuss the potential of using TDS to reduce smelting raw material costs and to deal with future SO_2 emissions issues.

2011 Shaft Calciner TDS Trial

The differences between rotary kiln and shaft calciners have been described previously [7]. Rain Carbon operated a small 20 kt/yr shaft calciner in China from 2009–2015. In 2011, a trial was carried out with two high volatile matter (VM), fine particle size GPC's. One was a very low S coke (0.4%) with ~13% VM and the other was a very high S coke (~6%) with 12.5% VM.

During the four-day trial, the low and high S cokes were fed to a separate group of four shafts each and a 50/50 blend was fed to another set of four shafts. The trials were run without recycle coke and in combination with the relatively high VM content, the operating temperatures were 30–50 °C higher than normal. Some key results are shown in Table 2.

The S level of the high S GPC decreased from 6 to 3% in the CPC indicating significant TDS (50% S loss). The S level of the low S coke appeared to increase slightly but this was likely due to contamination from the higher S blend used prior to the trial. The most significant finding was the high RD of the sample with extensive TDS. The VBD results were also of interest. When these high VM cokes are calcined in a rotary kiln, the VBD's are significantly lower (~0.83–0.86 g/cc) and the trial confirmed the VBD benefits of using a shaft calciner.

The VBD's for the high S sample and the blend were a little lower than the low S coke by itself but still very good relative to the rotary kiln TDS results in Table 1. When a Hg apparent density (AD) test was run however, the results were dramatically different. The Hg AD result was substantially lower for the high S coke and the blend. Very few labs have the capability to run the Hg AD test due to its hazardous nature but it can still provide useful information. Values below 1.70 g/cc are considered undesirable for anode applications.

Figure 1 shows Hg porosimetry results (up to 380 MPa) for the three cokes. The pore size distribution plots show the characteristic TDS peak at 0.01–0.10 µm for the high S coke and the 50/50 blend.

Relative to the rotary kiln results in Table 1, the shaft CPC with a TDS level of 50% has a much higher RD. This is despite a similar level of micro-porosity as measured by Hg porosimetry. This means that the decrease in RD from TDS in a rotary kiln cannot be due to the increase in micro-porosity.

Table 1 Results from rotary kiln TDS trial

Sample	S (%)	S loss (%)	VBD (g/cc)	RD (g/cc)	Crush St. (kg)	Lc (A)
Normal	4.0	13	0.862	2.078	3.4	29.5
Moderate TDS	3.2	30	0.775	2.029	3.3	39.3
Aggressive TDS	2.4	47	0.733	2.041	1.1	42.1

Table 2 2011 shaft calciner trial results

Sample	GPC S (%)	CPC S (%)	VBD (g/cc)	RD (g/cc)	Hg AD (g/cc)	Lc (A)
Low S	0.5	0.7	0.917	2.114	1.79	34.5
High S	6.0	3.0	0.885	2.110	1.67	36.9
Blend	3.2	2.1	0.881	2.112	1.72	35.3

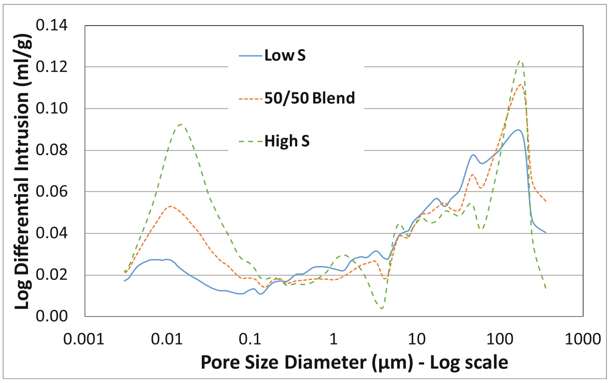


Fig. 1 Mercury porosimetry graphs

Thermal Dilatometry Testing

A key set of experiments to understand the above was thermal dilatometry testing. Large, single pieces (~50 mm) of a low and high S GPC (0.5 and 5.5% S) were calcined in a lab furnace to 1100 °C to remove the VM. The pieces were cut with a thin-bladed diamond saw to produce rectangular samples 20 × 10 × 10 mm. The work was difficult due to the brittle nature of the CPC and it took multiple attempts to get two samples of each coke for testing.

A dilatometer measures the thermal expansion of samples and an instrument capable of operation at 1500 °C with an inert atmosphere and variable heating rates was used. The coke samples were heated at fast (50 °C/min) and slow (1 °C/min) heating rates to simulate the difference between a rotary kiln and shaft calciner. The results (Fig. 2), showed a fundamental difference between TDS in a shaft calciner and rotary kiln.

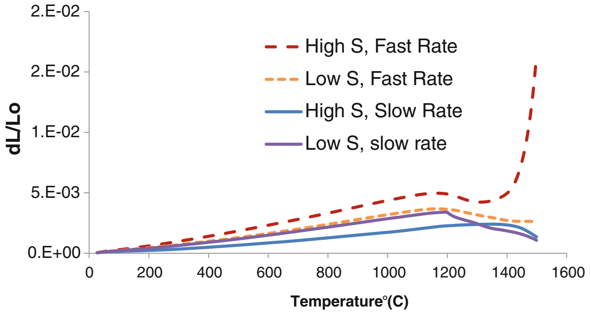


Fig. 2 Thermal expansion of high and low S coke samples

The thermal expansion profile for the high S coke heated at a fast rate is very different from the three other results. A large, irreversible expansion starts at around 1400 °C and continues until the measurement is stopped at 1500 °C. No such expansion occurs for the high S coke sample heated at the slow rate or for either of the low S coke samples. The large expansion is caused by the sudden loss of S from the coke. This phenomenon is well-known to graphite electrode producers and is referred to as "puffing". Numerous papers have been published on the subject [8] and puffing inhibitors like iron oxide are often added to reduce the disruptive and damaging effect of puffing during graphitization.

The above results show clearly that TDS of high S GPC in a rotary kiln results in puffing which contributes to a reduction in both RD and VBD. Puffing only occurs at high heating rates whereas TDS occurs at all heating rates and is independent of the calcining technology. The lack of puffing in a shaft calciner explains why the VBD drop is lower. TDS still occurs however, and has a damaging impact on the final coke structure.

SEM and 3D X-Ray Nano-Tomography

Three samples of a high S (5.1%) GPC were calcined to different temperatures at the same fast heating rate of a rotary kiln. The S level of the CPC samples was 4.5, 2.5 and 0.85%. The 0.85% S level was achieved by increasing the soak time from 15 min to 1 h. Table 3 shows selected properties to highlight the VBD decrease, the initial RD decrease and the BET surface area increase. The surface areas were measured with nitrogen adsorption on samples milled to a Dv 50 particle size of ~25 µm.

The three samples were analyzed first by high resolution scanning electron microscopy (SEM) and significant differences were observed. The non-TDS sample calcined at 1250 °C with 4.5% S was largely featureless at high resolution except inside pores and cracks. Both samples with TDS showed a very different structure with clear evidence of layering and ordering. Figure 3 shows high resolution SEM images of the 4.5 and 0.85% coke samples. The 0.85% S sample shows a high level of porosity between domains of a well-formed plate-like and ordered carbon microstructure.

The samples with 4.5 and 0.85% S were then examined using a nanoscale, 3D X-Ray microscope (ZEISS Xradia 810 Ultra). Details of the system theory and use can be

Table 3 Results of TDS trial with high S CPC

Sample	S (%)	VBD (g/cc)	RD (g/cc)	Lc (A)	BET SA (m^2/g)
1250 °C	4.49	0.943	2.077	29.5	5.5
1500 °C (15 min)	2.45	0.800	2.040	41.3	9.0
1500 °C (1 h)	0.85	0.769	2.100	44.5	13.3

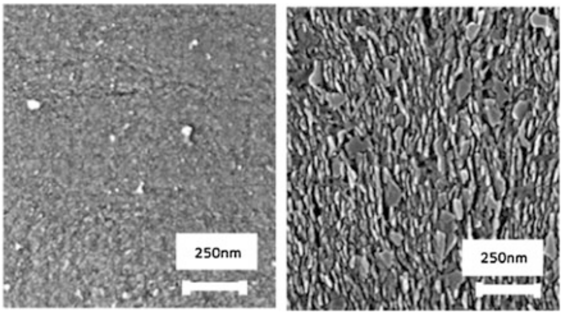


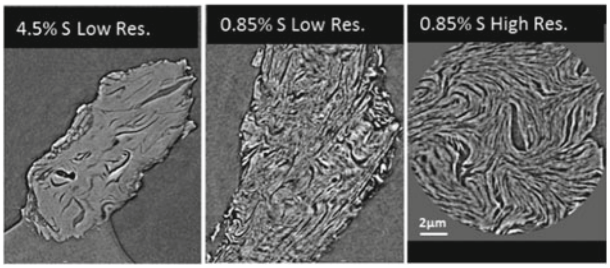
Fig. 3 High res. SEM images of 4.5 and 0.85% S sample

found elsewhere [9]. The microscope captures images of the sample at high magnification while rotating in an X-Ray beam. Specimens were prepared by selecting a single coke particle (~50 μm size) and attaching to the tip of a pin with epoxy. Scan times ranged from 16–34 h depending on the x-ray transmission and imaging mode.

The 3D images generated by the imaging software are best viewed via video simulation but Fig. 4 shows some representative 2D images. A low resolution image is included for the ~50 μm, 4.5% S particle (Fig. 4a) and low and high resolution images (Fig. 4b, c) are included for the ~60 μm, 0.85% S particle.

The difference between the two samples is dramatic. The 0.85% S coke shows a very layered structure and a high level of porosity. Whilst the level of TDS in the 0.85% S sample is very high, the images give a good indication of what happens to the coke structure when S is lost and why the particle strength decreases and the surface area increases significantly.

The increase in RD at 1500 °C with the one-hour soak time is likely due to the rupture of closed porosity and pore coalescence which makes the porosity accessible during the helium pycnometry RD test. This gives a good indication of what is likely happening at the much slower heating rates in a shaft calciner and why the RD shows no decrease with TDS. The S has more time to outgas and generates porosity which is connected to the outer surface of particles ground to <75 μm for the RD test. At faster heating rates, closed pores are created which contribute to puffing of the coke structure. These closed pores result in a lower RD.



4a 4b 4c

Fig. 4 **a–c** X-ray 3D nano-tomography images

The increase in Lc of the 1500 °C samples supports the transition to a more ordered structure. The S is likely to be playing a significant role via the mechanism of sulfur-enhanced graphitization described previously [10]. All of this shows that the coke microstructure is significantly changed through TDS and it cannot be considered as something which just increases porosity and decreases VBD.

Pilot Anode Studies

Numerous pilot anode studies have been completed since 2011 on coke which has been TDS in a shaft calciner and rotary kiln. A brief overview of some key results is presented in the following section.

Example 1

In this first example, a regular blend of high and low S cokes was TDS in a rotary kiln with the results shown in Table 4. Only the high S cokes in the blend (65% of total) underwent TDS and that is why the RD does not appear to decrease too much. The first sample is labelled “Normal” and the samples with 26 and 46% sulfur loss are labelled as TDS 1 and TDS 2.

Pilot anodes (150 mm Ø and 200 mm high) were produced in Rain Carbon’s pilot anode facility [11] using a coke blend containing 30% of the TDS 1 and TDS 2 cokes. The balance of the blend was a regular rotary kiln coke labeled BL = “Baseline” coke. To simplify the testing, none of the TDS coke was added to the BMF fraction. Baked anode scrap was added at a level of 20% to all anodes to simulate the butts addition in an anode plant. Results for selected pilot anode properties are shown in Table 5.

The results highlight the significant negative impact of adding TDS coke from a rotary kiln to an anode. Despite a modest addition of only 30% of this coke to a regular CPC blend, a significant reduction in anode density, strength, elasticity and an increase in the specific electrical resistivity were measured.

Example 2

In this next example, the high S shaft CPC with 50% TDS in Table 2 was blended at a ratio of 50/50 with a regular rotary kiln, low S coke. The sample is labelled 50TDS/50LS. Another sample was generated with a blend containing 50% of the same low S coke and 50% of a regular rotary kiln, high sulfur (HS) coke with no TDS (labelled 50HS/50LS).

Table 4 CPC results for normal and TDS CPC

	CPC sulfur (%)	Sulfur loss (%)	VBD (g/cc)	RD (g/cc)
Normal calc.	3.53	13.0	0.886	2.064
TDS 1	2.95	20.7	0.862	2.052
TDS 2	2.19	45.9	0.806	2.055

Table 5 Pilot anode properties for rotary kiln blends

Anode properties	BL	BL + TDS1	BL + TDS2
Baked apparent density (g/cc)	1.61	1.58	1.55
Spec. elect. resist. (μΩm)	55	64.1	73.9
Compressive strength (MPa)	54	41	33
Elasticity modulus (GPa)	4.2	2.9	2
Air permeability (nPm)	0.39	0.39	0.61

Bench scale anodes were prepared at an external lab to determine the optimum pitch level and pilot anodes were produced at the optimum pitch level for property measurement. No butts fraction or baked scrap was added to the anodes and selected results are shown in Table 6.

Both sets of anode densities were very low and air permeabilities were high due to a paste mixing problem at the lab. On a relative basis however, the deterioration in anode properties with the addition of TDS shaft CPC was not as dramatic as in a rotary kiln. This highlights the advantage of using a shaft calciner to TDS coke versus a rotary kiln due to the absence of puffing.

Looking at the other results in Table 6, the negative impact on anode strength and elasticity modulus when TDS coke is used is clear. The CO_2 reactivity residue and dust levels were also adversely impacted but this is partly explained by the higher calcium level (the S levels were similar at ~2.7%). The silicon (Si) level is also much higher and this will be discussed later under the refractory wear section.

The above work was repeated later at Rain Carbon's pilot anode lab but the coke with 50% TDS was added at a rate of 35% in a blend with BL rotary kiln coke. The TDS coke was added to the blend in three different ways:

1. Split uniformly across all aggregate fractions
2. Added to the BMF fraction and coke fines fraction only
3. Added only to the coarser coke fractions

20% baked anode scrap was added to all recipes. The baked anode densities were much better in this study ranging from 1.58 to 1.60 g/cc versus 1.61 g/cc for the 100% BL coke anodes. Adding the TDS coke to the BMF fraction had a very negative effect on electrical resistivity and mechanical properties like flexural strength however and increased the optimum pitch level by ~2%. When the TDS coke was added to the coarse fractions only, the mechanical properties and electrical resistivity were quite similar to the BL anodes and the only negative result was a lower baked anode density of 1.59 g/cc at an optimum pitch level 0.5% higher.

Example 3

In this next more comprehensive study, pilot anodes were produced at Rain Carbon's lab with coke TDS to a level of ~40% (40% S loss). For comparative purposes, the study includes reference anodes made with 100%, normal shaft CPC (no TDS) and anodes made with 100% normal rotary kiln CPC. All anodes were made with the addition of 20% baked anode scrap. The following labels are used in the graphs to identify the coke blends:

- BL Rotary: Baseline, 100% rotary kiln calcined coke.
- BL Shaft: Baseline, 100% shaft calcined coke.
- TDS Shaft/NCS Fines: TDS shaft coke used in all the coarse fractions and Normal Calcined Shaft coke (baseline shaft) used in the BMF fraction.
- TDS Shaft: TDS shaft in all fractions including BMF.

Selected results are presented in Fig. 5. The pilot anodes were produced at different pitch levels to determine the optimum.

The first point to make is that the baked anode densities for anodes made with 100% rotary kiln CPC (BL Rotary) are within the normal industry range. At the optimum pitch level of 14%, the baked density is 1.617 g/cc. The low air permeabilities for all the anodes in this study (<1 nPm) gives confidence that the anode paste was well mixed and well formed. As expected, the anodes made with 100% shaft CPC (BL Shaft) showed a higher baked anode density (1.647 g/cc) and a lower optimum pitch level (13% vs. 14%) relative to the BL rotary blend.

Anodes made with TDS shaft coke in all parts of the aggregate recipe (except baked scrap) showed significantly inferior results to the other anodes. The only property that looks reasonable is the baked anode density where the results were similar to the BL rotary kiln coke. The compressive strength, flexural strength and elasticity modulus are poor and the slope of the specific electrical resistivity curve is very steep and increases rapidly at lower pitch levels.

It is clear from this study that it would not be possible to make anodes with 100% of a coke that has undergone a moderate level of TDS (40% S loss) in a shaft calciner.

The most interesting results from the study were those generated using TDS shaft coke only in the coarser part of

Table 6 Pilot anode properties for TDS and non-TDS blend

Property	50TDS/50LS	50HS/50LS
Pitch level (%)	17.5	16.5
Baked anode density (g/cc)	1.447	1.464
Air permeability (nPm)	4.3	3.7
Spec. elect. resist. (μΩm)	63.5	63.0
Compressive strength (Mpa)	32	39
Elasticity modulus (GPa)	3.5	4.3
CO_2 reactivity residue (%)	88.7	95.2
CO_2 reactivity dust (%)	3.5	0.2
Calcium (ppm)	274	101
Silicon (ppm)	437	171

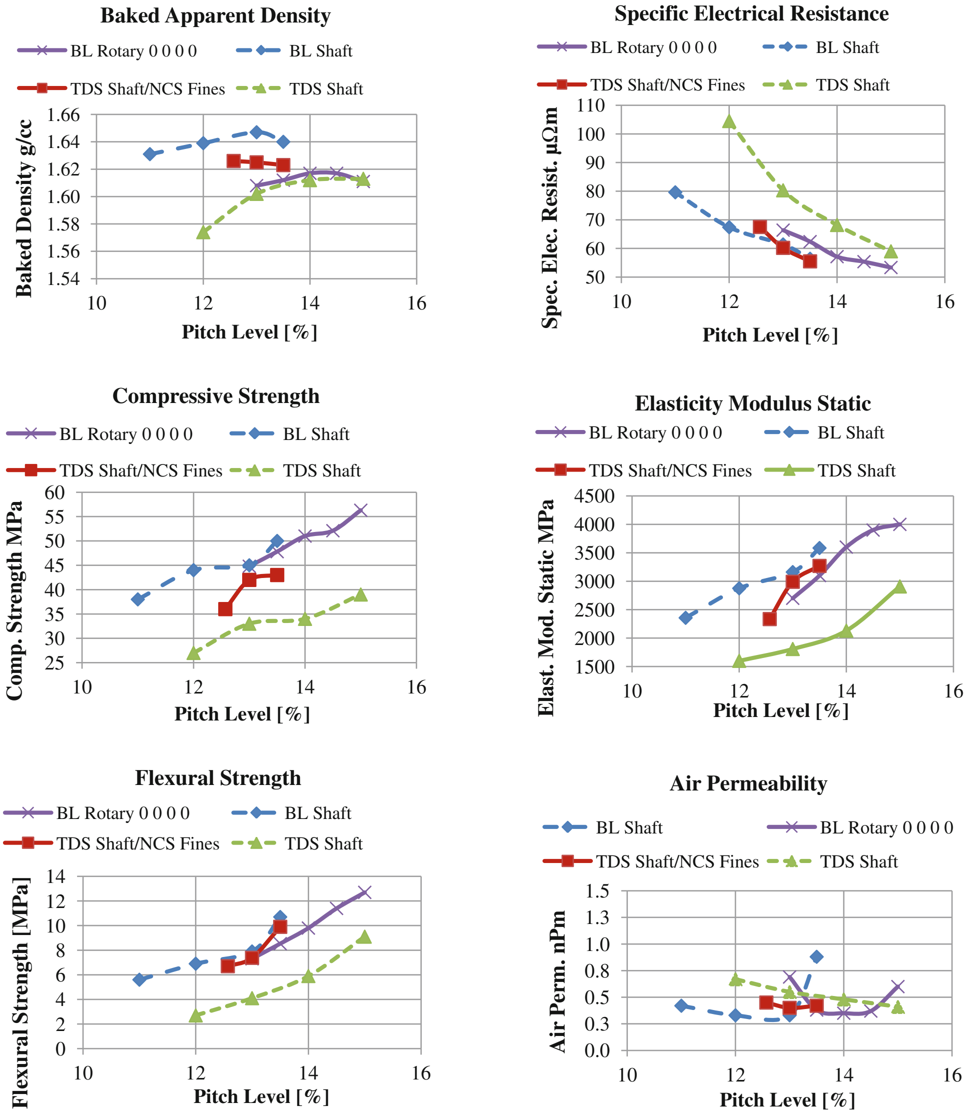


Fig. 5 Pilot anode properties at different pitch levels

the aggregate recipe. With a ball mill fines content of 26%, that means the anodes contained 54% of the TDS shaft coke. These anodes still showed better baked anode densities than the anodes made with 100% rotary kiln coke and the optimum pitch level of 14% was similar. The anode mechanical properties were also similar to the BL rotary and shaft anodes with the exception of the compressive strength which was a little lower.

Example 4

In this last example, a very high S coke (8.5%) was calcined in a lab furnace at the same heating rate as a shaft calciner. The aim was to see if a low cost, high S coke could be aggressively TDS and still used as a minor blend component. The S was driven down to a level of 3.4% representing a S loss of ~60%. Three sets of anodes were prepared as shown below and key results are shown in Fig. 6.

- BL = baseline anodes with 100% normal, rotary kiln CPC
- BL + TDS Fines = Baseline CPC with TDS coke milled and added to fines fraction (26% of the recipe)
- BL + TDS Coarse = Baseline CPC + 26% TDS CPC added to coarse fractions of aggregate.

The above results are very poor in terms of anode quality. Adding only 26% of this aggressively TDS CPC to either the BMF fraction or the coarser part of the aggregate recipe has a very negative effect on anode properties. Adding the TDS coke to the coarse fractions is marginally better, especially for specific electrical resistivity. In combination with the results from Examples 1–4, these results suggest that the amount of TDS that can be tolerated from a shaft calciner decreases rapidly at levels above ~40% sulfur loss.

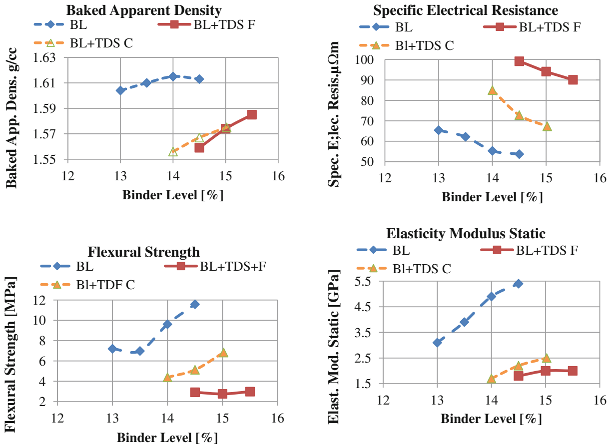


Fig. 6 Pilot anode results for shaft CPC with 60% S loss

Jet Milling Trials

It has been suggested that grinding CPC to a fine enough particle size will eliminate the TDS micro-porosity problem. Work was done in this area using a jet mill to grind coke that had been TDS to a level of 50%. The CPC was ground to a size of 90% <22 µm. This ultrafine coke was then added to the BMF fraction of a regular anode recipe and a modified recipe which used roughly half the amount of fines to compensate for the much higher surface area.

For brevity, the results will not be included in this paper but they were poor. In fact, Rain Carbon recorded its highest ever electrical resistivity with one of the anode batches made using the TDS ultrafine coke (135 µΩm). Anodes made with jet milled fines from non-TDS coke showed very comparable results to BL anodes. This work showed clearly that there is no way to grind-out the micro-porosity because it is too fine to be penetrated by the CTP binder.

Refractory Wear Problem

One problem with TDS in a shaft calciner is accelerated refractory wear. The inner shaft walls are built with high silica (~95% SiO_2) bricks. These bricks are cost effective and readily available in China. At temperatures between 1200 and 1300 °C however, the partial pressure of SiO (a product of C reacting with SiO_2) increases and causes refractory wear. In the presence of sulfur bearing gases like H_2S and S_8, SiO_2 reacts to form SiS. The equilibrium partial pressure of SiS is an order of magnitude higher than SiO which creates a second, more significant refractory wear mechanism.

From 1200–1300 °C, the activity of SiO increases by a factor of five and the partial pressure of SiS increases about threefold. This will cause a rapid deterioration of the refractory lining and most shaft calciner operators are aware of this problem. It can reduce the refractory life from an average of 8–10 years to <2 years. This problem also causes Si contamination of the CPC product. This is why the Si level is so high in Table 6 for the TDS anode blend. The projected Si level was 160 ppm versus an actual level of >400 ppm.

The above will significantly limit the ability of shaft calciners to TDS coke. The solution is to change the type of refractory brick but this will increase the cost. At least one shaft calciner is testing this idea based on a patent [12] which discloses the use of refractory materials like ZrO_2, magnesite etc. The patent claims stable operation at 1350–1500 °C and targets a sulfur reduction level of 42–72%. The challenge will be production of a usable product for the reasons outlined in this paper and the high RD of the product (>2.10 g/cc) which is undesirable for anode production.

H_2S Generation

One final potential problem with aggressive TDS is generation of H_2S gas. Rain Carbon experienced a problem with H_2S emissions at one point when running high S cokes. The problem was evident when draft levels were low during discharge of the CPC. In the reducing atmosphere inside the coke bed, H_2S generated from TDS should travel up through the coke bed and into the flue walls where it will mix with oxygen and combust to form SO_2. Under low draft conditions, some of the H_2S stays with the product and is very noticeable by its odor during product discharge.

At one stage, the above problem was compounded by water leaks from the cooling water jackets. Water which leaks into the coke bed will generate steam and then hydrogen gas via the reaction:

$$H_2O + C \rightarrow CO + H_2$$

The hydrogen gas can potentially accelerate the TDS of coke which will exacerbate the H_2S emission problem by reacting with elemental S gaseous species to the point where it can be both a significant operator safety risk as well as a community odor problem. A patent was filed in 2009 [13] claiming the use of a shaft calciner in this way but the patent was never examined.

Although the presence of hydrogen gas has the potential to lower the TDS temperature [14], detailed studies funded by Rain Carbon at an external research lab (Kingston Process Metallurgy Inc.) were not successful in demonstrating any meaningful benefits [15].

Discussion and Conclusions

The results from this study highlight a fundamental difference between TDS in a shaft calciner and rotary kiln. In a rotary kiln, the high heating rates and rapid S loss lead to an irreversible volume expansion and “puffing” of the coke structure which causes a significant reduction in bulk density. The creation of micro-porosity in coke during TDS cannot be avoided in a shaft calciner or rotary kiln and permanently damages the CPC. As the S loss increases, the damage increases to the point where it negatively effects the strength, porosity and microstructure of the CPC.

It is difficult to say exactly what level of TDS can be tolerated when making an anode but pilot anode testing suggests the S loss needs to be <40% and a lower level will always be better. The study also shows that it is not possible to make an anode with 100% of a coke that has been TDS to a level of 40% or more. It can only be used as a blend component at levels of 50% or lower. It is also better to keep TDS coke out of the BMF fraction.

Although the above may sound like a major constraint, this study has shown that it should be possible for the industry to use coke that has undergone moderate TDS (15–35%) in a shaft calciner if it is blended with other normally calcined cokes. In a world where GPC S levels are expected to continue increasing on average, this approach can bring value for the industry. CPC and GPC may appear to be readily available in 2016 but this situation could change very quickly once global aluminum production resumes its inevitable expansion to meet growing product demand.

Many smelters have learned to deal with higher trace metal impurities in CPC like vanadium and nickel and the tolerance depends to a large extent on the metal product mix of the smelter. S represents a more challenging problem because the global pressure to reduce SO_2 emissions is increasing. From this perspective, it is more economic to remove S from coke and scrub SO_2 at the calciner than it is to scrub SO_2 from the low concentration, high flue gas volumes found in a smelter.

TDS in a shaft calciner is not without its problems however, and most shaft calciners will not pursue this given the significant negative impact on refractory life. It would never be economic to rebuild a shaft calciner every 2 years and most calciners are looking for ways to increase refractory life. Rebuilding a shaft calciner with different refractory bricks to mitigate this problem is an option but it will increase the capital cost significantly.

The other practical limitation of TDS in a shaft calciner is the H_2S emissions problem. This would not be a problem in a new shaft calciner with good draft levels but it can become more problematic as the furnace ages (and lining cracks develop) and/or when flue walls become partially blocked with unburned VM and draft levels drop. H_2S is a very toxic gas and care needs to be taken if detected.

The H_2S problem may also not be confined to the calciner. Rain Carbon’s lab has reported an H_2S odor when opening sample buckets containing TDS CPC. Crushing and milling of the samples has also led to the detection of H_2S. The human nose can detect very low concentrations with its characteristic rotten egg gas smell. It is not clear what creates this additional H_2S problem other than entrapment of minute levels of H_2S inside pores in the CPC. This could be become an issue for a carbon plant but larger scale trials are needed to make this determination.

One final point to make with TDS is that traditional bulk density test methods do a poor job of detecting its presence. A coke which has undergone TDS may appear to look okay on the basis of ASTM 30 × 50 or 20 × 35 VBD tests but a Hg AD test can show quite a different result. One definitive way to check for evidence of TDS is to run a Hg porosimetry test. A peak in the 0.01–0.10 µm pore size range as shown in Fig. 1 acts as a fingerprint for TDS and can be used to determine whether a coke has undergone TDS.

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