Thermal Desulfurization of Petroleum Coke for Anode Use

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Abstract

Thermal desulfurization (TDS) of petroleum coke during calcination is a well-known phenomenon which results in an increase in porosity and decrease in bulk density. Rain Carbon presented a paper recently which explored the potential of using a shaft calciner to TDS coke instead of a rotary kiln calciner. There are some significant benefits in using a shaft calciner due to the slower heat-up rate but the coke structure is still irreversibly changed when sulphur (S) is driven from the coke. This paper presents a review of the differences in TDS at different heating rates and includes high resolution scanning electron microscopy and helium ion microscopy images. The potential for TDS petroleum coke to allow a wider range of GPC raw materials to be used for anode production is discussed. At least one coke calcining company in China has attempted aggressive TDS on a production scale. High 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. There are significant practical limits to the level of TDS that can be tolerated however, both from a calciner's perspective and for anode quality/performance reasons.

Keywords: Petroleum Coke, Anodes, Shaft Calcining, Sulphur, Desulfurization.

1. Introduction

Thermal desulfurization (TDS) of petroleum coke is a well-studied phenomenon and a recent paper discussed the differences between TDS in a rotary kiln and a shaft calciner [1]. The heat-up rate in a rotary kiln calciner is much higher (~50°C/min) than a shaft calciner (~1°C/min) and this causes a phenomenon known as "puffing" when sulphur (S) is driven from the coke structure. As reported in [1], puffing causes an irreversible volume expansion which results in a decrease in the real density and bulk density of the coke structure. Puffing does not occur at the much slower heating rate in a shaft calciner and the real density of the coke does not decrease as the temperature increases and S is driven from the coke structure. The structure is however, irreversibly damaged from the loss of S though the creation of fine porosity which reduces the strength, modulus of elasticity and bulk and apparent density of the coke particles.

This paper will review the differences between TDS in a shaft calciner and rotary kiln and will show high resolution microscopy images of coke particles damaged by TDS. Extensive pilot anode testing has shown that it is not practical to use coke which has undergone aggressive TDS (>40% S loss) even when using a shaft calciner. It may be possible to use coke TDS to lower levels in a shaft calciner however as long as the percentage used in a blend is not too high.

2. Brief Review of Thermal Desulfurization

The majority of S in petcoke occurs in stable aromatic S compounds like benzothiophene and dibenzothiophene, Figure 1 [2]. Over the normal range of calcination temperatures (1200-1300 °C), these compounds are relatively stable and the S remains intimately bound within the carbon matrix. Petroleum coke typically loses 7-14% S during calcination and this is S lost from side chain thiol-type compounds and elemental S which has been condensed in pores during delayed coking. The S is driven out at lower temperatures (<1150°C) along with condensable tars from volatile matter, CH_4 and hydrogen gas.

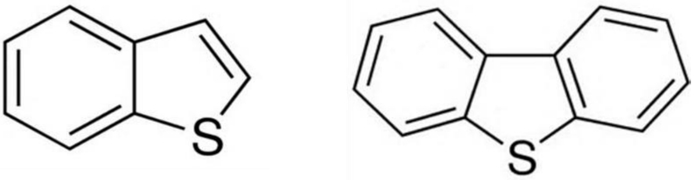


Figure 1. Benzothiophene and Dibenzothiphene

The process of TDS starts at higher temperatures and involves decomposition of the aromatic thiophenes in petcoke due to thermodynamic instability. The impact of TDS on coke properties has been well described in the past and two review papers in 2007 [3] and 2008 [4] explain the impact on coke and anode properties. Most past studies looked at TDS from cokes heated in a rotary kiln or at heat-up rates similar to those found in a rotary kiln calciner which are typically ~50°C/min or even higher in the tertiary air zone inside the kiln. One characteristic feature of TDS is a decrease in real density of the coke structure. Figure 2 shows the results of laboratory TDS studies on a wide range of green cokes ranging from a S level of 1.6% to 8.5%.

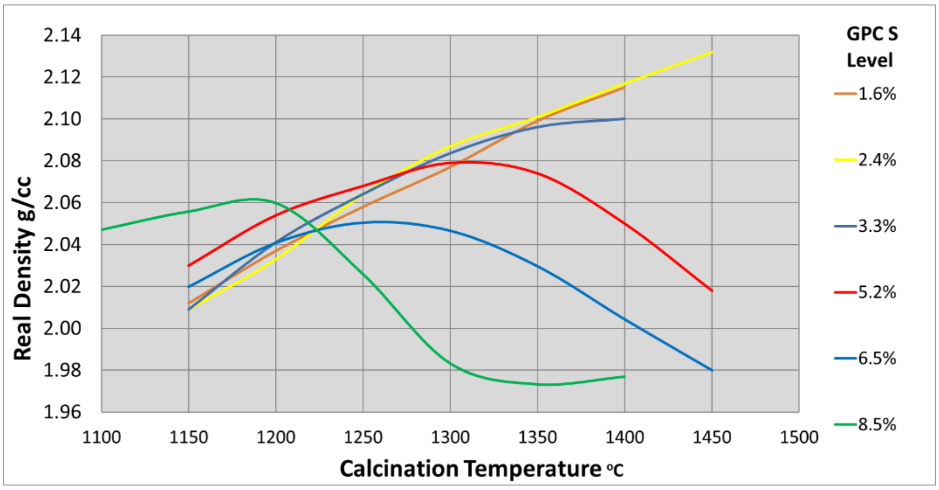


Figure 2. Real density vs temperature relationship for green cokes with different S levels

Cokes with S levels ranging from 0.3-4.0% show very little, if any TDS over the normal calcination range of 1200-1300 °C. As the coke S level increases, TDS becomes more pronounced and the rate of S loss and reduction in real density increases. The temperature at which TDS starts also becomes significantly lower and can start as low as 1200°C for very high S cokes like the 8.5% S coke shown in Figure 2.

Table 1 shows the results of a TDS trial in a rotary kiln with green petroleum coke (GPC) containing 4.6% S. The calcining temperature was increased in three stages from a normal level to a high level and then very high level. The Lc measurement is the best measure for degree of calcination and values above 35 Angstrom are considered very high. At the 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 or compressive strength).

Attempts to use TDS coke from a rotary kiln to produce anodes have been unsuccessful. Results are presented in the paper referenced earlier [1] and in another recent publication [5]. 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 removed or reduced via scrubbing to meet permitted emission limits. In principal, it is more efficient/economic to remove SO_2 during coke calcining than during aluminium 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.

Table 1. Results from Rotary Kiln TDS trial

Sample	S %	S Loss %	VBD g/cc	RD g/cc	Crush St. kg	Lc Å
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

In 2011, Rain Carbon began experimenting with TDS in a shaft calciner to investigate whether the slower heat-up rate would help reduce the negative effects of TDS. Initial results looked promising and a high S coke desulfurized to a level of 50% did not show the usual large drop in real density. This prompted an extensive body of work over the 2011-2016 period. Some key results from the 2017 paper [1] are presented here along with more recent high resolution microscopy results on cokes which have been TDS.

3. Results from Initial 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% S) with ~13% VM and the other was a very high S coke (~6% S) 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 ^{o}C higher than normal. Some key results are shown in Table 2.

Table 2. Shaft Calciner Trial Results

Sample	GPC S %	CPC S %	VBD g/cc	RD g/cc	Hg AD g/cc	Lc Å
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

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 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 CPC and the blend were a little lower than the low S CPC but still very good relative to comparable rotary kiln TDS results like those shown 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 CPC and the blend CPC. Very few labs have the capability to run the Hg AD test today due to its hazardous nature but it can still provide useful information. Values below 1.70 g/cc are considered undesirable for anode applications.

Samples of the 10x20 mesh (0.84 – 1.7mm) portions of the low and high S CPC used for the Hg apparent density tests were also sent out for a BET surface area analysis (nitrogen) and they showed a big difference. The low S coke with no TDS showed a very low surface area of 0.32 m^2/g whereas the high S, TDS sample showed a value of 11.6 m^2/g. This latter result was unexpectedly high for the relatively coarse particle size but the microscopy work presented later in this paper provides clues as to why the surface area was so much higher.

Figure 3 shows Hg porosimetry results (up to 380 MPa) for the three cokes. The pore size distribution plots show a TDS peak at 0.01-0.10 µm for the high S CPC and the 50/50 blend. This characteristic peak has been discussed in previous papers [8] and it makes mercury porosimetry particularly well suited to detecting TDS in cokes.

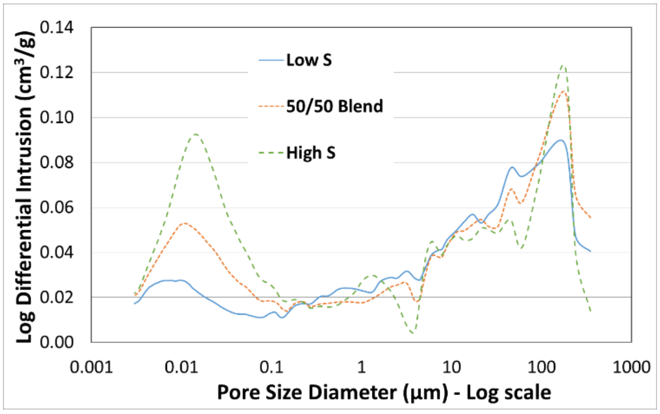


Figure 3. Mercury Porosimetry Graphs

Relative to a rotary kiln, 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.

4. Thermal Dilatometry Testing

The reason for the increase in real density in a shaft calciner was not understood initially but additional lab scale testing provided the answer. 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 20x10x10 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, Figure 4, showed a fundamental difference between TDS in a shaft calciner and rotary kiln.

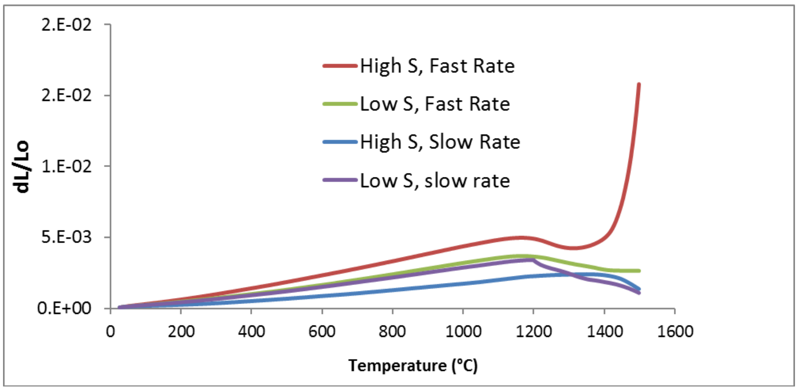


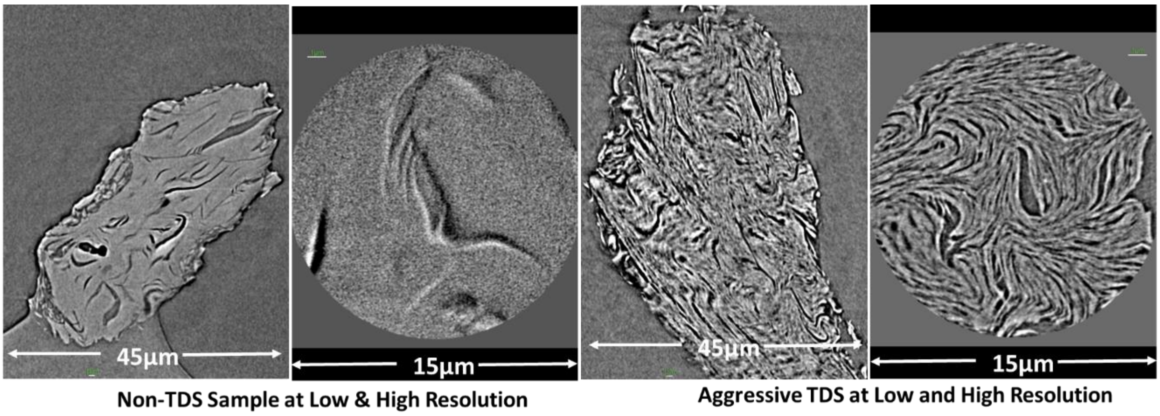
Figure 4. Thermal expansion of high and low S coke samples

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 ^{o}C and continues until the measurement is stopped at 1500 ^{o}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 [9] 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.

5. 3D X-Ray Nano-Tomography

High resolution X-Ray nano-tomography images were included in the earlier paper [1] and further details about the method can be found in that paper. Two high S green coke samples (5.1% S level) were calcined at very different levels – the first at a normal calcination temperature of 1250 ^{o}C resulting in a final S level of 4.5% (S loss 12%). This sample had no TDS. The other sample was calcined very aggressively at 1500 ^{o}C using a similar heating rate to a rotary kiln and underwent aggressive TDS with a final S level of 0.85% (85% S loss. 2D images are shown in Figure 5.



Non-TDS Sample at Low & High Resolution
Aggressive TDS at Low and High Resolution

Figure 5. Xray nano-tomography images of non-TDS and TDS coke samples

The difference between the two samples is dramatic. The 0.85% S coke shows a very layered structure with a high level of porosity. It is easy to understand why it would never be practical to use coke with such a damaged structure but the primary purpose of this work was to look at an extreme example of TDS and whether 3-D X-Ray nano-tomography would be a useful method for characterizing the structure. Short, 3D videos of each structure were re-created by combining the successive 2D slices and these proved to be very insightful.

6. SEM and Scanning Helium Ion Microscopy Work

In more recent microscopy work performed at the Oak Ridge National Laboratory [10], high S coke samples calcined in both a rotary kiln and a shaft calciner with a 13% S loss (ie no TDS) and a 50% S loss were examined using high resolution SEM and helium-ion microscopy (HIM). The aim of this work was to look at samples with a more modest level of TDS to better understand how the physical structure is changed by TDS. Figure 6 shows an SEM image of a rotary kiln particle which has undergone TDS. The first image is a low resolution shot and the second is taken at higher magnification. What is clear from the second image is a structure which shows the formation of microcracks caused by puffing and TDS. These cracks are quite large with a length up to 20 µm and width from <0.1µm to up to 2µm wide (see Figure 7).

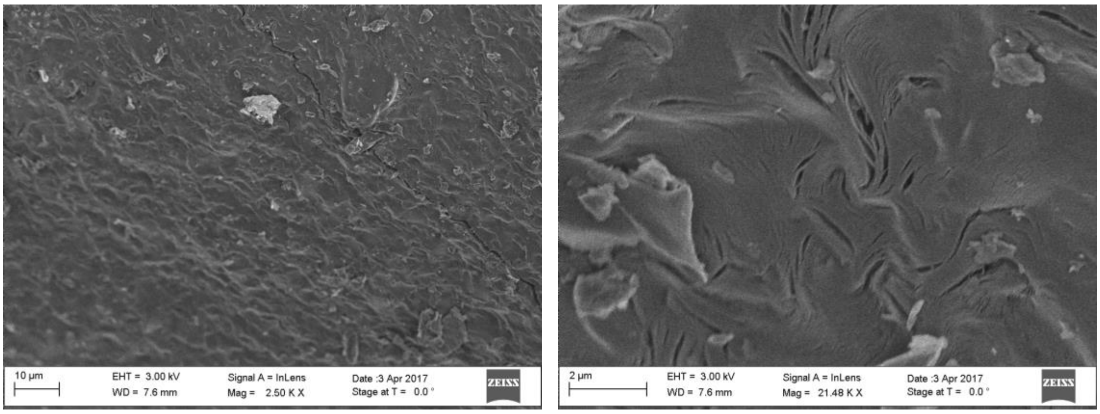


Figure 6. SEM images of TDS coke particle at low and higher resolution

Figure 7 shows a set of HIM images from a TDS coke particle which is just starting to show the damaging effects of TDS with the first appearance of significant microcracks in the coke structure. The HIM is capable of producing quite stunning images with a much higher depth-of-field resolution than an SEM. The second higher magnification image shows a detailed view image inside one of the micro-cracks. The cracks are quite large with a length up to 20 µm and width from <0.1µm to up to 2µm.

Figure 8 shows an additional series of HIM images from the shaft calcined coke particle with TDS. It is very easy to see the high level of ordering or parallel stacking of graphite-like layers in close proximity to the micro-cracking. In this image, the layers appear to have been pushed apart, possibly from the internal pressure generated from the release of S from deep within the coke structure during the TDS process.

The micro-cracks appear to penetrate quite deeply into the coke structure. The cumulative surface area provided by all these microcracks is significant and accounts for the increase in surface area mentioned earlier for 10x20 mesh samples. It also shows why the mercury apparent density decreases since these cracks will be present throughout the structure and will not be accessible by mercury at lower pressures. Likewise for pitch penetration – these cracks are too small for pitch penetration during anode production.

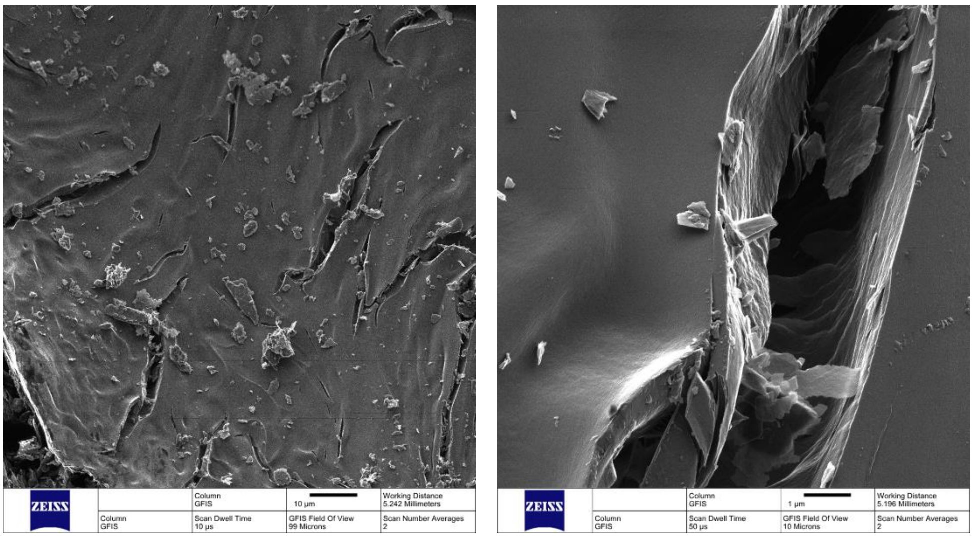


Figure 7. HIM images of coke particle damaged by TDS

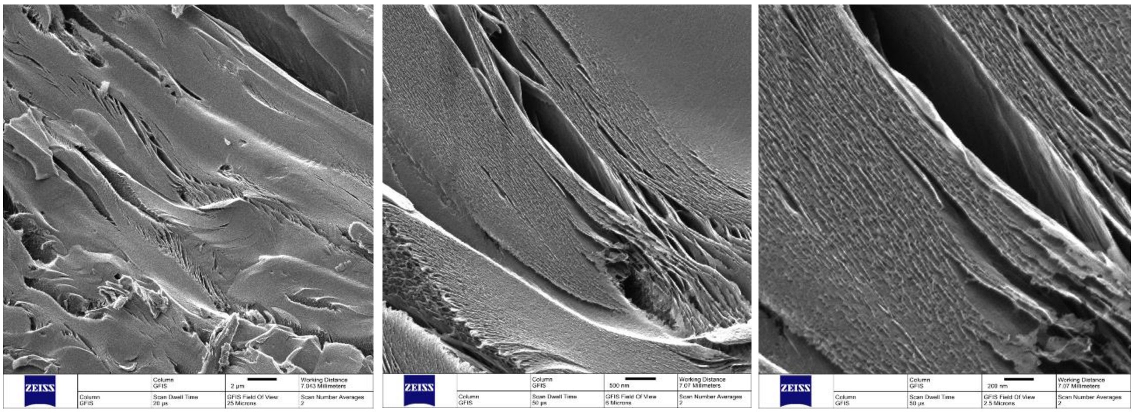


Figure 8. HIM images at successively high magnification of area damaged by TDS.

7. Pilot Anode Testing of TDS Shaft Calcined Coke

Pilot anode tests were conducted at Rain Carbon's pilot anode facility in Castrop-Rauxel with the low and high S cokes shown in Table 2. In the earlier paper [1], pilot anode results were shown from an external lab but this work was repeated due to mixing problems which led to low baked anode densities. Three sets of anodes were prepared as follows: 1) anodes with a baseline rotary kiln coke + 20% baked anode scrap: 2) anodes with 45% baseline rotary kiln coke + 35% high S coke + 20% baked scrap and 3) anodes with 45% baseline coke + 35% low S coke + 20% baked anode scrap. Key results are summarized in the charts in Figure 9.

The anodes prepared with the rotary kiln blend + 35% low S shaft CPC showed very similar properties to the anodes with the baseline rotary kiln coke. Normally, the baked anode density would be expected to be higher with shaft CPC in the blend but the low S coke was a very high VM green coke so the coke bulk density was lower than a typical shaft CPC. The anodes with 35% of the TDS high S coke required a significantly higher optimum pitch level (+1.5%) and showed a decrease in the baked anode density. The mechanical properties such as compressive strength, modulus of elasticity and flexural strength were also negatively impacted.

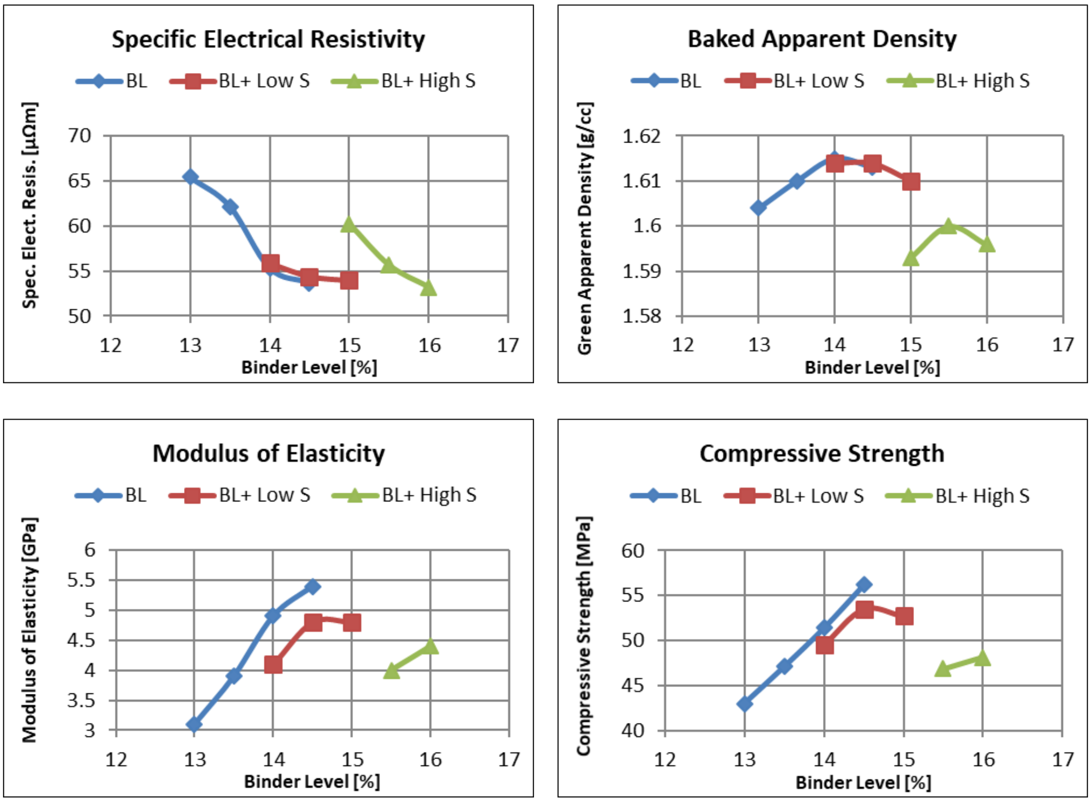


Figure 9. Pilot anode results with baseline rotary kiln blend (BL), baseline + 35% low S shaft CPC (BL + Low S) and baseline + 35% high S shaft CPC (BL + High S)

Many more pilot anode results are included in the earlier paper [1] and all show the same trends when using TDS coke in the anode blend. In general, as the level of TDS increases, the negative impact on properties increases even when using modest amounts of TDS coke in the blend (eg 25%). The results are even worse when TDS coke is concentrated in the ball mill fines fraction only. Despite the significantly higher real densities achieved in a shaft calciner after TDS, coke bulk densities and pilot anode properties are still negatively impacted in a significant way.

8. Discussion and Conclusions

The results from this study highlight the 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 reduction in real density and 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. Based on the more extensive pilot anode results reported in the earlier paper [1], it will not be possible to make an anode with 100% of a coke that has been desulfurized 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, this approach can bring value for the industry. Ultra-low S GPC (<1.0% S) prices have shown a rapid increase in 2017 due to additional demand from the graphite electrode industry as well as the aluminium industry. This will put further pressure on all GPC prices and continued use of greater volumes of high S cokes is inevitable.

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 scrubbing SO_2 from the low concentration, high flue gas volumes in a smelter.

TDS in a shaft calciner is not without its practical problems however and most shaft calciners will not pursue this given the significant negative impact on refractory life [1]. It would never be economic to rebuild a shaft calciner every 2-3 years due to the accelerated refractory wear that occurs with TDS when regular, high SiO_2 refractory bricks are used. At least one major shaft calciner producer in China built a new, high temperature calciner with alternative quality refractory bricks specifically to TDS coke to high levels (40-75%). The furnaces had to be abandoned however and rebuilt with regular refractory bricks. This was due to a combination of refractory, operating and product quality problems.

9. References

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10. Acknowledgements

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