

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 SO₂ during calcination is more efficient than removing SO₂ 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, CH₄ and hydrogen gas.

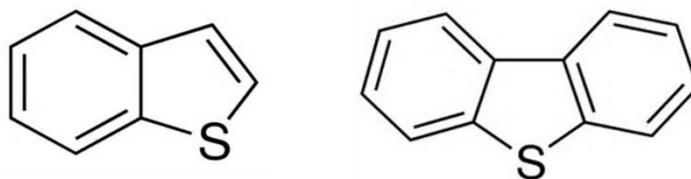


Figure 1. Benzothiophene and Dibenzothiophene

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%.

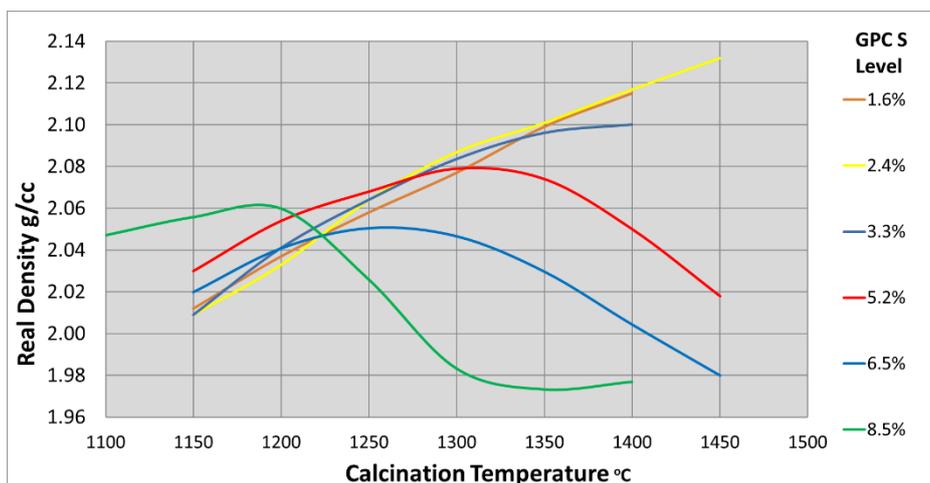


Figure 2. Real density vs temperature relationship for green cokes with different S levels

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

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 SO₂ emissions is increasing. From this perspective, it is more economic to remove S from coke and scrub SO₂ at the calciner than scrubbing SO₂ 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 SiO₂ 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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