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INFLUENCE OF GPC PROPERTIES ON THE CPC QUALITY

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Abstract

A detailed study was carried out on green petroleum coke (GPC) from refineries in different locations in China and the corresponding calcined coke (CPC). The significant influence of GPC properties on the CPC quality was revealed. The content of ash and metal impurities such as Si, V, and Ni etc. increases during calcination, while the sulfur content is reduced. This shows that the sulfur in GPC from the different sources has a quite different reactivity due to the complex nature of sulfur and only a part of the sulfur reacts during calcination. The data revealed inhibition of CPC CO_2 activity by sulfur. Sodium and calcium enhance the coke CO_2 reactivity, while impurities such as vanadium and nickel promote air reactivity.

Introduction

GPC is the main raw material for anode manufacture and has to be calcined before use. Coke calcination is a heat treatment process with the objectives to remove water and volatiles, improve the coke structure, increase density and strength, increase the electric conductivity, and enhance the oxidation resistance.

In anode recipes without butts (as usual in some Chinese anode plants) CPC accounts to about 85% of the green anode weight and its properties impact directly the anode quality and anode behavior in the smelting process.

The CPC and anode quality depends on the GPC properties [1], [2] and the calcination technology. Jinan Aohai Carbon Corporation Limited has carried out three major overhauls of its GPC vertical shaft calciners since 2001 with the objectives of energy savings and emission reduction. Changes included a larger calciner structure, automatic GPC loading and CPC discharging systems, heat insulation and sealing of the calciner, online monitoring and control systems for temperature and pressure, surplus heat recovery for power generation, and sulfur removal by ammonia process etc [3]. The annual capacity of one shaft calciner has reached up to 100,000 tons of CPC, while the CPC output of its individual pots is higher than 160 kg per hour. The variability of the CPC quality has been significantly reduced. Meanwhile, Aohai Carbon conducted trials and studies on the GPC and CPC properties and their interactions.

The GPC samples originated from oil refineries allover China, including Xinjiang. The various properties of the GPC samples and the corresponding CPC were tested and analyzed. Correlations between the various coke properties were established.

The results show that the composition and other GPC properties significantly influence the CPC quality. The different behavior of the various impurities during calcination and their influence on the CPC reactivity are revealed.

Based on the results, it is possible to produce high quality CPC in large, efficient shaft calciners by using GPC blending technology [4], [5] for GPCs from different sources with a variety of properties.

Test procedures

1. GPC sampling

GPC samples for the study were taken by a normative sampling method from oil refineries in different Chinese provinces (Shandong, Henan, Hubei, Tianjin, Guangdong, Zhejiang, Shanghai, Hunan, Anhui, and Xinjiang etc). The samples are identified by numbers from 1 to 24.

The GPC samples contained different concentrations of sulfur and metal impurities reflecting the oil sources used in the various refineries.

2. Property tests

Various properties of the GPC samples and the corresponding CPC were determined, including:

- Ash, water, and volatiles contents;
- Impurity concentrations;
- Physical properties, such as real density, specific electrical conductivities, granule stability, and bulk density etc.
- CO_2 reactivity and air reactivity of CPC samples.

3. Test equipment and procedures

GPC laboratory calcinations were conducted in a RDC-164 GPC calciner produced by R&D Carbon (Fig. 1).

Figure 1 Laboratory coke calciner and CO_2 reactivity test apparatus made by R&D Carbon Limited

Different R&D Carbon test apparatuses were used for the determination of GPC and CPC properties, including CO_2

reactivity and air reactivity of the CPC samples. All tests were carried out based on the standard test procedures.

Test results and discussion

1. GPC properties

Figure 2 shows the volatiles and water contents of the GPC samples. The average volatile content of the 24 samples was 10.7% with a range of 9-13%, while the average water content was 9.0% with a range of 6-16%.

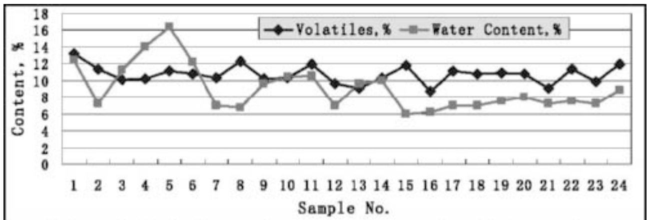

Figure 2 Volatiles and water content of the GPC samples

As shown in Figure 3 the average sulfur content in the GPC samples was 3.7%. Several samples (#1, #4, #8, #9, #17, #20, and #22) contained very little sulfur (about 1%). However, other samples (#3, #10, #11, #14, #15, #18, #19, and #23) contained over 5% of sulfur. Most probably, these cokes were produced from high-sulfur Middle Eastern crudes.

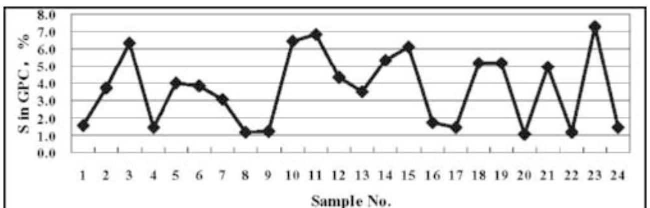

Figure 3 Sulfur content of the GPC samples

The concentrations of metal impurities that have a negative impact on the anode quality fluctuated considerably between the samples (Fig. 4). The average concentrations and range for the different impurities are listed in Table 1.

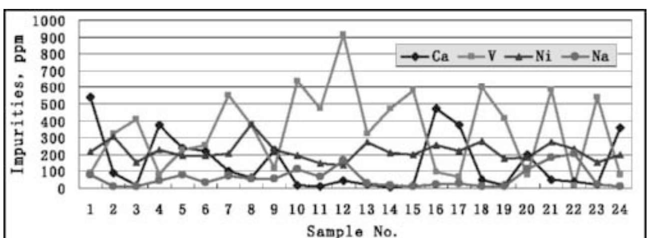

Figure 4 Concentrations of some metal impurities in the GPC samples

Table 1
Average concentrations and range for the different metal impurities in the GPC samples (ppm)

Impurity	Average	Range		
Ca	149	6	-	540
Na	61	10	-	209
Ni	218	137	-	308
V	347	18	-	916

2. Impurities in CPC and in the corresponding GPC

Figure 5 presents the ash contents of the CPCs and the corresponding GPCs. It can be seen that the ash content in CPC is higher as compared to GPC. However, this difference varied between the samples. For example, the ash content in CPC #18 is 45% higher than in the corresponding GPC possibly due to a high content of the volatiles lost during calcination, which concentrated the ash compounds.

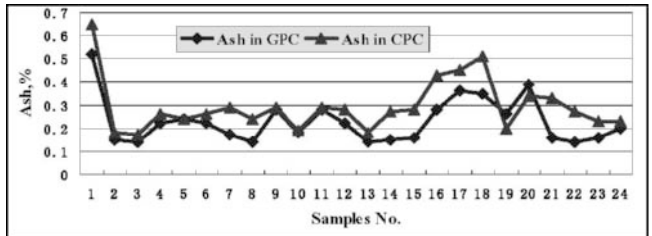

Figure 5 Ash contents of GPC and the corresponding CPC

The concentration of metal impurities increased during calcination. As an example, Fig. 6 shows the vanadium concentration in the cokes before and after calcination. Almost all the vanadium remained in the CPC.

The behavior of the other non-volatile elements was similar. This provides the know-how for blending of GPC's with different composition, allowing to produce CPC suitable for high quality anodes.

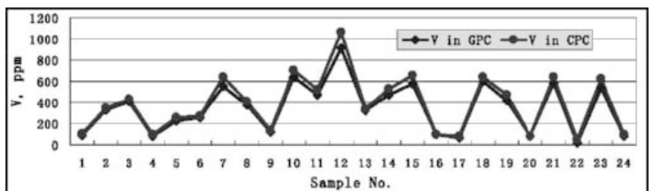

Figure 6 Vanadium concentration in GPC and the corresponding CPC

The behavior of sulfur during calcination is quite different than for the impurities discussed before. As shown in Fig.7, the sulfur content in CPC was lower as compared to the corresponding GPC. Apparently, during calcination a portion of the sulfur reacted and formed volatile products. In general, desulfurization increased with increasing GPC sulfur content. For some high-sulfur GPCs (*e.g.* cokes #10, #11, #15, #19, and #23), the sulfur content was reduced by more than 30%. This confirms that a significant portion of the GPC sulfur was transformed into volatiles and that partly desulfurization can be achieved by calcination.

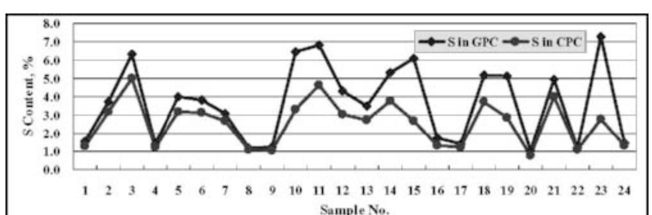

Figure 7 Sulfur concentration in GPC and the corresponding CPC

Most of the sulfur present in coke is present in organic environment, such as in thiophenes, side chains of aromatic structures, or in cycloparaffins. Some sulfur is chemically adsorbed on the coke surface and very small quantities might exist in inorganic environment such as sulfates or pyrites.

A portion of the GPC sulfur reacts during calcination and is mostly emitted as SO_2. Desulfurization depends on the initial sulfur content, the nature of the sulfur compounds, and the calcination temperature.

The higher the sulfur content the more sulfur is removed. An increase of the calcination temperature has the same effect since more GPC sulfur groups are decomposed at higher temperatures.

3. CPC CO_2 reactivity

Fig. 8 reveals the correlation between the sulfur content and the CO_2 reactivity of the 24 CPC samples. In general, CPC samples with high sulfur concentrations had low CO_2 reactivities.

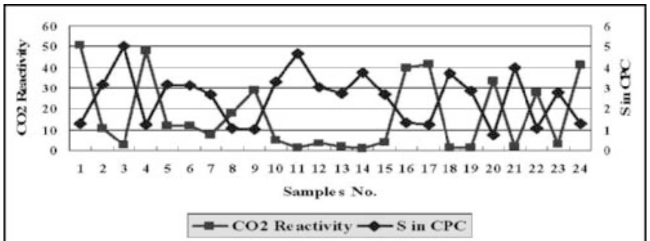

Fig. 8 Sulfur content and CO_2 reactivity of the CPC samples

8 CPC samples with low sulfur concentrations (1-1.3%) were selected for studying the correlation between the CO_2 reactivity and the combined Na & Ca concentration. The CO_2 reactivities of these cokes increased with the Na & Ca concentration (Fig. 9).

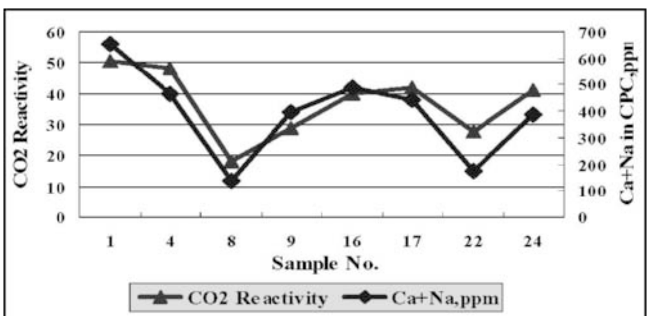

Fig.9 CO_2 reactivities and combined Na & Ca concentration for low-S CPC samples

8 CPC samples with sulfur concentrations ranging from of 2.6 to 3.3% were selected to study the correlation between the CO_2 reactivity and the combined Na & Ca concentration at a higher sulfur level. Fig. 10 confirms this clear correlation.

It is shown in Fig. 9 and Fig. 10 that the CPC CO_2 reactivity is closely related with the Na & Ca concentration. This is a major factor to reduce the CO_2 reactivity of CPC.

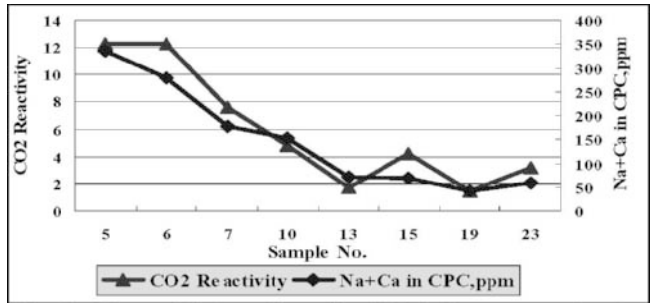

Fig.10 CO_2 reactivities and combined Na & Ca concentration for high-S CPC samples

10 CPC samples with medium combined Na & Ca concentrations (200-400ppm) were selected to study the correlation between the CO_2 reactivity and the sulfur concentration. Fig. 11 shows a clear inverse relationship, *i.e.* the high-sulfur CPCs had a low CO_2 reactivity and vise versa, which means that sulfur strongly inhibits the CPC CO_2 reactivity.

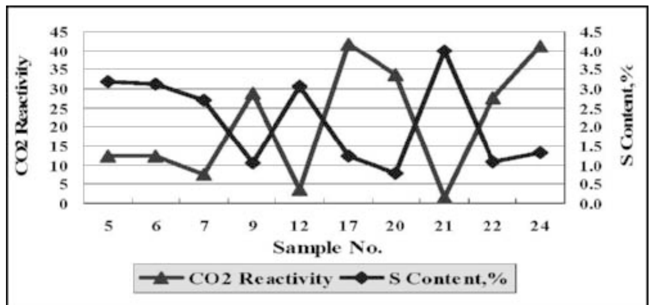

Fig.11 CO_2 reactivities and S concentration for CPC samples with medium Na + Ca concentration

8 CPC samples with combined V & Ni concentrations between 330 and 480ppm were selected to study the correlation between the CO_2 reactivity and the concentrations of sulfur and Na & Ca, respectively. As shown in Fig. 12 and Fig. 13, for these samples the CO_2 reactivity increases with the Na & Ca concentration and decreases with the sulfur concentration.

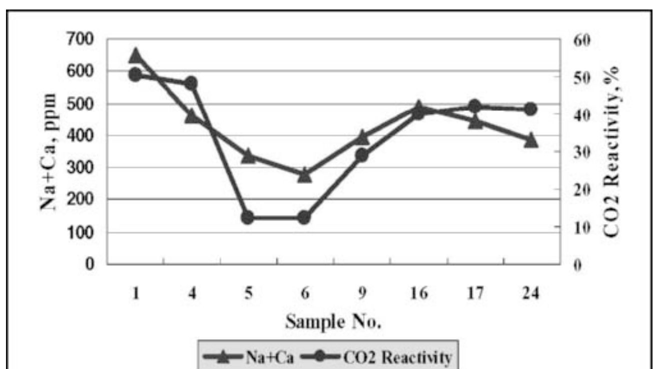

Fig.12 Correlations of CO_2 reactivity with total Na+Ca (ppm)

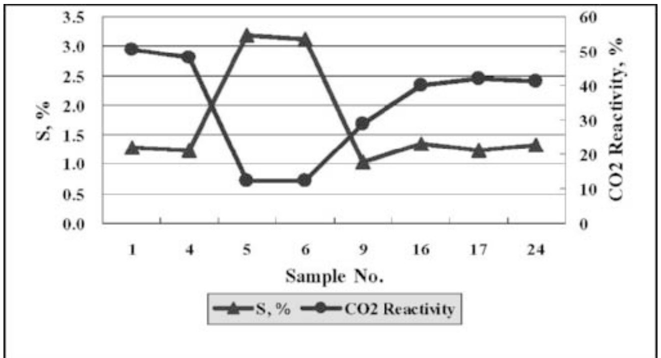

Fig.13 Correlations of CO_2 reactivity with S (%)

4. CPC air reactivity

Fig. 14 shows the correlation between the air reactivities of the 24 CPC samples and the combined V & Ni concentrations. It can be observed that V and Ni have a major impact on the air reactivity. The influence of V alone on the air reactivity is presented in Fig. 15. The better correlation between V alone with the air reactivity as compared to the combined V & Ni concentration suggests that V has a more significant impact than Ni.

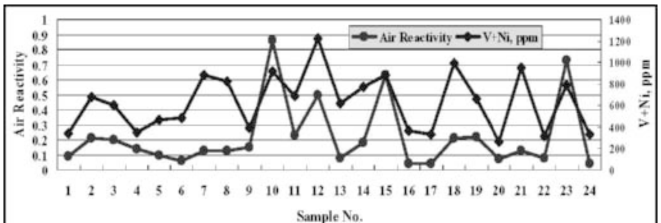

Fig.14 Air reactivities and combined V & Ni concentrations of the CPC samples

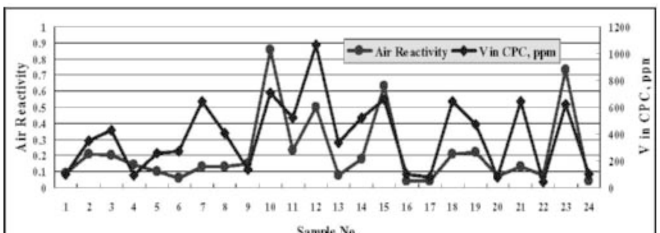

Fig.15 Air reactivities and combined V concentrations of the CPC samples

The correlation between the air reactivities of CPC samples and the combined V & Ni and sulfur concentrations, respectively, was studied for 10 CPC samples with a medium Na & Ca concentration (200-400ppm). It appears that the CPC air reactivity increased with the combined V & Ni concentration (Fig. 16), while sulfur was not able to provide a strong inhibition effect (Fig. 17).

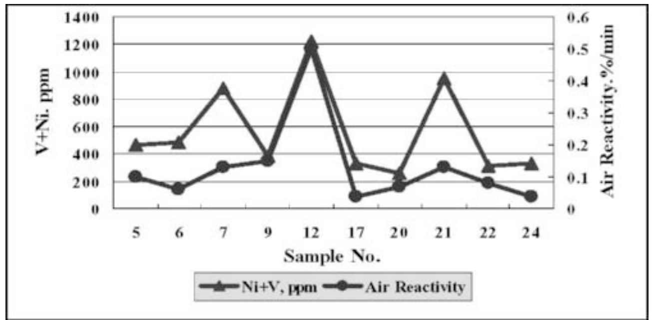

Fig.16 Air reactivities and combined V & Ni concentrations of CPC samples with a medium Na & Ca concentration (200-400ppm)

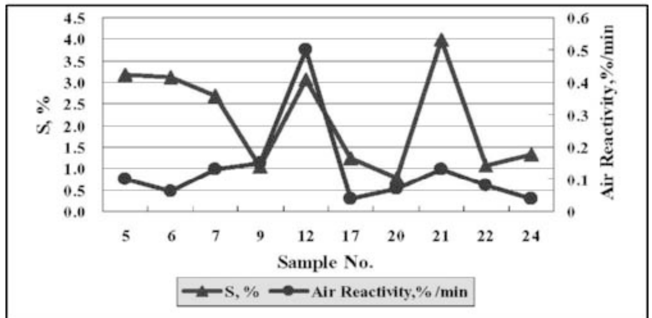

Fig.17 Air reactivities and S concentrations of CPC samples with a medium Na & Ca concentration (200-400ppm)

The correlation between the air reactivities and the combined V & Ni concentrations is presented in Fig. 18 for 7 high-sulfur CPC samples (3-4% sulfur). Fig. 19 shows the corresponding data for low-sulfur CPC samples (1-1.3%). The data show that the air reactivity is closely related to the combined V & Ni concentration, whereas the combined Na & Ca concentration has a smaller negative impact.

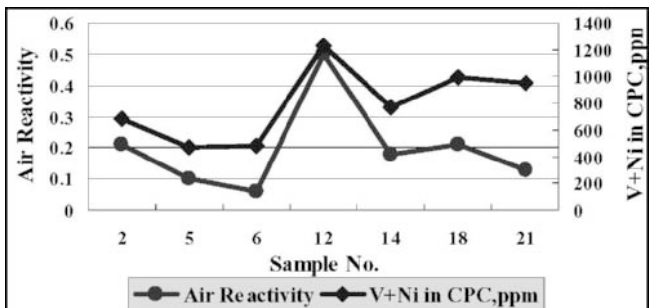

Fig.18 Air reactivities and combined V & Ni concentrations of CPC samples with a high S concentration (3-4%)

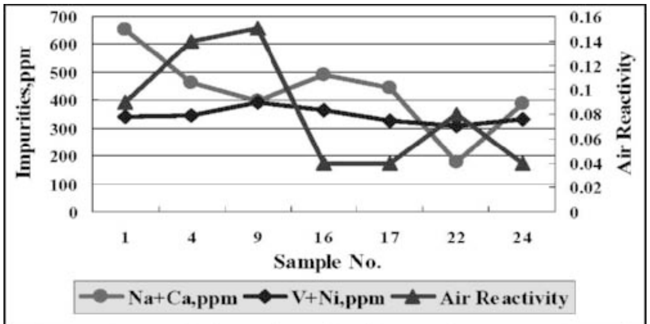

Fig.19 Air reactivities and combined V & Ni concentrations of CPC samples with a low S concentration (1-1.3%)

Conclusions

(1) A systematic study was carried out on various properties of GPCs and the corresponding CPCs. The GPC samples originated from refineries all over China and were produced from different crude oils.

(2) The concentrations of ash and metal impurities increase during calcination.

(3) The coke sulfur content decreases during calcination. A portion of the sulfur reacts and removed with the volatiles. The degree of sulfur loss varies between the samples.

(4) Na and Ca increase the CPC CO_2 reactivity, whereas sulfur significantly inhibits this reaction.

(5) Ni and V increase the CPC air reactivity.

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