Insights into Accumulation Behavior of Harmful Elements in Cohesive Zone with Reference to Its Influence on Coke

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The accumulation behavior of harmful elements (K, Na, Zn) in the upper area of the cohesive zone was reported for the first time. The alkalis-bearing aluminosilicate minerals and the kalsilite were found in the coke, while a number of zinc oxide crystals mainly existing as hexagonal wurtzite habit and zinc-bearing minerals were observed in the mixture-like phase of slag-iron. The findings further deepen the understanding of degradation behavior of coke in the cohesive zone.

KEY WORDS: coke; cohesive zone; alkalis; zinc.

1. Introduction

As a major component of the current steel production process, the blast furnace ironmaking process will continue to dominate in the foreseeable future. Consequently, an in-depth understanding about the mineral phase behavior and inner phenomena within blast furnace is essential for optimizing the ironmaking process, especially in the context of widespread use of inferior raw materials due to increasing cost pressures. In the cohesive zone at the lower part of the blast furnace, the ore layer occurs as a solid-liquid mixture, and the iron ore is partially melted and filled in the gap of the coke bed.1) Wherein, coke as a key solid material plays an important role in providing structural support for burden column and permeability for upward flowing gases as well as downward flowing liquid, affecting the distribution of gas flow and also the stability of blast furnace operation. Therefore, coke performance in the cohesive zone is a crucial factor determining the operational efficiency of blast furnace.

Nowadays, numerous studies have been carried out regarding the influences of harmful elements (K, Na, Zn) on coke degradation, which catalyzes the gasification reaction of coke and reduces the strength of coke.2–7) However, owing to the complex and harsh environment in the lower section of blast furnace, it’s usually impossible to extract samples from a working blast furnace for laboratory research. Although the application of a tuyere drilling technique facilitates the observation of the inner phenomena of blast furnace,8–10) it is still difficult to obtain representative samples above tuyere level. Fortunately, manual dissection during overhaul period, which allows us an opportunity to collect samples from blast furnaces, provides potentially useful information for understanding the accumulation behavior of harmful elements in the cohesive zone.

2. Samples and Methods

In this work, the samples taken from the upper section of the cohesive zone of a water-quenched blast furnace, which was located near the top region of the cohesive zone, were examined with SEM/EDS. The further information and operating data of the blast furnace can be found in the previous publications.11,12) Two representative samples, coke and mixture-like phase of slag-iron, were selected for investigation. The selected samples were cut into suitable pieces under dry conditions and then mounted in an epoxy slow-setting resin in round plastic containers with 25 mm diameter. The mounted samples were subsequently ground on three different grades of silicon carbide paper (180, 800, and 1 200 grit) under running distilled water, and then polished with a pad. After the grinding and polishing process, the sample surfaces to be detected were rinsed with high flowrate water, then washed thoroughly with alcohol and finally dried with hot wind. The ATM SAPHIR 550 automatic single-disc machine was adopted for grinding and polishing, while the self-lubricating polycrystalline diamond suspension with particle size of 2.5 μm was used during the polishing procedure. Finally, the dry mounted samples were coated with carbon for SEM/EDS studies. The FEI Quanta 250 Environmental scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectrometer (EDS) was used for chemical analysis and mapping, and a ZeissEVO-18 Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray spectrometer (EDS) was also used due to the former’s going out of service for maintenance.

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3. Results and Discussion

As shown in Fig. 1, a large amount of white mineral phases appeared inside the coke, which are widely distributed in the matrix, pores and pore walls of the coke. The EDS results indicate that these mineral phases are mainly aluminosilicates of alkali metals, and the abundance of potassium and sodium seems to be all high in the minerals. In addition, the kalsilite crystal was observed in the coke pore, which is in line with the previous findings. The presence of these alkali-bearing minerals further confirms the recirculation and enrichment of potassium and sodium in the upper section of the cohesive zone. Many studies have shown that the recirculating potassium in blast furnace enhances the solution loss reactivity of coke. Gupta et al. also found that the potassium content of tuyere cokes increases significantly compared to that of the feed coke and the recirculating potassium has strong catalytic effect on the apparent reaction rate of the tuyere cokes. In additional to the catalytic effect on gasification reaction of coke, the volume expansion of aluminosilicate minerals of potassium and sodium can also lead to cracks of coke, and is considered to be an important cause of coke degradation. Meanwhile, the alkali vapors interact with the graphite crystallites of coke to form intercalation compounds which can cause an expansion of the coke carbon matrix and further promote the degradation of coke. It’s well known that the temperature of the cohesive zone is around 1 473–1 673 K that conforms with the thermodynamic conditions of the formation of intercalation compounds. Even so, this possible degradation mechanism still needs to be approached cautiously because no intercalation compounds were found in the given coke.

Furthermore, the EDS mapping suggests that metallic iron, iron oxide and calcium oxide are also presented in the coke matrix, which are identified as catalytic minerals and significantly increase the gasification reactivity of coke. On the other hand, the iron oxide in coke is believed to enhance the coke carbon dissolution rates, while the CaO can react with S in molten iron to form CaS at the coke-iron interface or modify the liquidus temperature of coke ash, thus affecting the kinetics of coke carbon dissolution reaction. As can be seen in Fig. 1(c), in comparison with the feed coke, the present coke appeared lots of deep macro pores as well
as honeycomb caverns, and some pore walls became thinner or disappeared, which implies the coke in the cohesive zone suffers violent gasification solution loss reaction. Based on the preceding discussions, besides the inherent gas-solid solution loss reaction, the greatly reacted coke is expected to be correlated with the catalysis of catalytic minerals, especially the K and Na vapors as well as their minerals, which results in further degradation of coke in the cohesive zone.

The SEM micrographs and EDS maps of the mixture-like phase of slag-iron are illustrated in Fig. 2. From the EDS maps in Fig. 2(b), the gray-white phases are abundant in Zn and Fe, and some Si and Pb elements were also detected to be distributed in them. It is noteworthy that a number of zinc oxide crystals with visible \{0001\} and \{01\overline{1}0\} faces

![SEM micrographs and EDS maps of the mixture-like phase of slag-iron.](image)

**Fig. 2.** SEM micrographs (BSE mode) and EDS analyses of the mixture-like phase of slag-iron. (a) SEM micrographs. (b) EDS mapping taken from image B and EDS spot analyses taken from image D. (c) EDS mapping and EDS spot analyses taken from image C. See text for details. (Online version in color.)
and sharp crystal edges were clearly observed in the further magnified images (Figs. 2(a) C–D). As found in the tuyere cokes, the zinc oxide crystals in the current sample exist mainly as euhedral, hexagonal wurtzite habit (Fig. 2(a) C), while some occur as cubic zincblende habit. The wurtzite structures are reported to be the most stable under ambient conditions and thus most common, whereas zincblende forms are stabilized by growing ZnO on substrates with cubic lattice structures. It may also be noted that some undeveloped crystals without perfect regular shapes present as twins or various intergrowths. Both types of crystals usually appear inside the pores and on pore walls or pore throats, which may be attributed to the high surface area thus providing many nucleation sites for crystal growths, and the sufficient three-dimensional space as well as specific environment.

From the EDS spot analyses of Fig. 2(a) C, except for zinc oxide crystals, there are many Ca–Si–Zn–O phases and Si–Zn–Fe–O phases immersed in the phases of zinc oxides. The only ternary compound existing in the CaO–SiO2–ZnO system is Ca2ZnSi2O7 that has a congruent melting point of 1698 K. Furthermore, the EDS spectrum data taken from the area near the center of the Ca–Si–Zn–O phase indicates atomic ratio of Ca:Zn:Si is close to 2:1:2 that corresponds to Ca2ZnSi2O7 stoichiometry. As for the Si–Zn–Fe–O phase, it’s likely to be a crystalline phase of solid solution that consists of ZnO, SiO2 and Fe2O3. As shown in Fig. 2(b), the EDS spot analyses of Fig. 2(a) D suggests that the existence of insignificant iron was identified in zinc oxides, even though its spectrum intensity is relatively very weak. This is probably because some zinc oxides can associated with iron oxides to form solid solutions or complex aggregates. For example, the metallic iron also found adjacent to the Zn-rich phase.

One can see from Figs. 3(a) B–D that the relative well-shaped crystal adjacent to the hexagonal wurtzite is
probably hematite crystal or magnetite crystal. According to Fig. 3(b), the gray-black phase surrounded by Zn–Fe-rich phase (Fig. 3(a) A) consists of Si–Mg-rich mineral phase. The EDS mapping in Fig. 3(c) shows that calcium is associated with silicon, while sulfur seems to be associated with iron to form compounds that may be resulted from the interaction of liquid iron and ascending sulfur-containing gases. In some cases, the sulfur can also replace oxygen to unite with zinc to form zinc sulfide if the sulfur potential is strong enough because zinc has a low affinity for oxides and prefers to bond with sulfides, as shown in Fig. 4.

As is well known, zinc is charged into blast furnaces with feed materials, such as sinter in particular and injected pulverized coal. The detailed process of recirculating and accumulation of zinc in blast furnaces was also reported in previous literatures. An obvious effect of zinc is that it promotes coke solution loss reaction and decreases coke strength after reaction (CSR). Along with enhances the coke degradation and the generation and accumulation of coke fines. Furthermore, a recent study revealed the influence mechanism of zinc on the solution loss reaction of coke and also confirmed the serious damage of coke structure resulting from the zinc catalysis, thereby decreasing the coke strength. However, unlike the findings in the tuyere cokes, no zinc oxides or zinc-bearing minerals were observed in the current polished coke by careful inspection. Even so, the zinc was reported to be gasified at the high temperature zone in blast furnace and then can ascend with the gas flow. Therefore, since the catalysis is derived from zinc not the zinc-bearing minerals, the severe catalytic effect of zinc vapor on coke is still likely an important factor leading to coke degradation in the cohesive zone.

4. Conclusion

In summary, besides the alkalis-bearing aluminosilicate minerals, the kalsilite, calcium oxide, iron oxide and metallic iron were found in the coke obtained from the upper area of the cohesive zone. The coke was confirmed to be greatly reacted and a number of deep macro pores and honeycomb cavens were formed. The zinc oxide crystals occurring as especially euhedral, hexagonal wurtzite habit as well as cubic zinclhende habit were observed in the mixture-like phase of slag-iron. These zinc oxide crystals and zinc-bearing minerals imply the accumulation of recirculating zinc in the cohesive zone. In view of the very similar environment of the coke and the mixture-like phase of slag-iron, the catalysis of zinc vapor is probably a nonnegligible factor affecting the coke degradation. As a result, the accumulation behavior of harmful elements such as K, Na and Zn have critical influences on the degradation of coke in the cohesive zone. Nevertheless, further research is still required about the harmful elements and their mineral phases, especially the effects of zinc oxide crystals and zinc-bearing minerals on the coke behavior under the blast furnace environment.

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Fig. 4. Schematic diagram of sulphur substituting oxygen in zinc oxide. (Online version in color.)