CCSEM Analysis of Ash from Oxyfuel Combustion of Zhundong Coal

Tai Zhang, Zhaohui Liu, Xiaohong Huang, Qing Sun, Chao Liu, and Chuguang Zheng

Abstract

The present work was addressed toward the ash characteristic of Zhundong coal using computer-controlled scanning electron microscopy (CCSEM), and discussed the effect of gas phase conditions on the distributions of particle size, minerals, and elements. In this study, Zhundong coal was burned with air and three kinds of oxyfuel conditions in the high-temperature drop-tube furnace. The ash characteristics were measured by CCSEM, which can determine the size, composition, and abundance of minerals in coal and ash on a particle-by-particle basis. The CCSEM results indicated that the mass of fine particles in oxyfuel conditions was less than that in air condition, increased with the O_2 concentration and the mass of coarse ash particles in oxyfuel conditions was more than that in air condition, decreased with the O_2 concentration. It also can be found that higher particle temperature enhances the co-melting of mineral. Under oxyfuel conditions, the high CO_2 concentration not only affects the transformations of coal minerals, but also shortens the decomposition process and extends the oxidation process slightly, which leads to increase in carbonate mineral. The increase in particle temperature can not only enhance the vaporization of refactory oxide, but also enhance interaction of the finely dispersed combined with inherent mineral particles. Avoiding the enrichment of Ca and S in fine particles is a good idea to reduce the ash deposit potential.

Keywords

CCSEM analysis • Oxyfuel combustion • Zhundong coal

1 Introduction

Oxyfuel coal combustion is envisaged as a promising technology for near-future CO_2 reduction from conventional fuel power plants. Ash-related problems, as slagging, fouling, and corrosion, are still a matter of concern and are recognized as a major source of uncertainty in the technology [1, 2]. To study the ash-related problems under oxyfuel condition, the ash quality, the effects of gas composition on particle formation, the ash particle formation mechanisms, and the particle transport mechanisms need to be carefully considered [3].

Alkali metals were considered to be the main cause of fouling, slagging, and corrosion on the surface of the boiler heater. Many studies on the alkali metals in the pyrolysis and combustion of coal and biomass have been reported previously [4–7]. Wang et al. [6] found that there was higher degree of adherence to surfaces because of the higher level of Na in the deposit composition during the co-firing of coal with agricultural residues. Wang et al. [7] studied the release and transformation of sodium during pyrolysis of Zhundong coal. They found that high concentration of CO_2 would inhibit the release of sodium and its conversion into insoluble form, compared to that under pyrolysis of N_2 condition.

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Yu et al. [8] studied ash and deposition formation during oxyfuel combustion on 100 KW oxyfuel combustion facility. They suggested that the higher ash deposition rate under 32 % O_2/68 % CO_2 oxyfuel condition was determined by the lower gas flow rate, higher combustion temperature, and chemical changes of the flue gas. Fryda et al. [9, 10] found that the chemical compositions of fly ash and ash deposits were not significantly different between air condition and oxyfuel condition, but higher deposition rate and deposition propensity in oxyfuel condition. Sheng et al. [11] observed more iron melted into the glass silicates and less was oxidized using the X-ray diffractometer approach, because of the lower char temperature and the high CO concentration within the char particles.

CCSEM (computer-controlled scanning electron microscopy) is a useful technology on the basic of the mineral particles that can characterize the minerals of ash particles in term of size, shape, abundance, and associations. Miller and Schobert [12] found that more than 50 % of minerals in Beulah-Zap lignite ash is analyzed as “unclassified particles,” that cannot be classified into any specific category for minerals in raw coal. Matsuoka et al. [13] and Huffman and Shah et al. [14, 15] used CCSEM to classify the molten and crystalline quartz in air samples collected during power plant maintenance activities. Wen and Xu et al. [16] investigated the melting potential of various inorganic ash components by CCSEM.

In this study, high-sodium Zhundong coal was burned at 1450 °C under air condition and three kinds of oxyfuel conditions to generate ash samples. The ash samples were measured by CCSEM to investigate the physical and chemical changes of ashes as well as the ash deposit potential under different gas phase conditions.

2 Experimental Methods

2.1 Ash Sample Collection

A high-sodium Zhundong coal was sieved to the size fractions of 38–74 μm. The analyses of coal are listed in Table 1. The pulverized coal was burned at 1450 °C in a high-temperature drop-tube furnace (HDTF). Synthetic flue gases (20 % O_2/N_2, 20 % O_2/CO_2, 30 % O_2/CO_2, and 50 % O_2/CO_2) were used to simulate air and three kinds of oxyfuel conditions. The gas flow rate was maintained at 5L/min, and coal feed rate was set at 10 g/h. A water-cooled sampling probe was inserted into the bottom of HDTF to collect the ash samples, using a glass fiber filter with a pore size of 0.3 μm, which was placed at the outlet of the sampling probe.

Composition of coal ash (wt%)								
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
44.75	19.33	5.47	1.52	11.24	3.44	1.52	4.79	7.55

2.2 Sample Pretreatment and Analysis for CCSEM

The coal was mixed with carnauba wax in a mold, and then it was melted at 120 °C. Due to the fine size of ash particles, the ash samples are easily to agglomerate. So we add some graphites as dispersant, and mix the samples with resin other than carnauba wax to avoid it. Then add hardener to the mixture and place it in a temperature of 55 °C to solidify. Before analyzed by CCSEM, the samples were carefully grinded, polished, and carbon-coated for test. SEM (FEI Quanta 250) and EDAX GENESIS spectrometer combined with a controlling software program automatically characterized minerals in terms of size, shape, abundance, and associations. With the magnification of 1000×, 3500–5000 mineral particles were analyzed and classified into many undefined mineral groups automatically. The relative element contents of undefined mineral groups can be defined with EDS manually. According to the contents of elements normalized without oxygen, those undefined mineral groups were classified into 33 mineral categories, which were developed by Huggings et al. [17] and widely used by others [13, 16].

3 Results and Discussion

3.1 Size Distribution of Bulk Ash Particles

The results of ash particle size need to be corrected, because a random section of a particle of a given shape has only an upper bound and the size of particles is very likely to be

Table 1 Properties of coal

Proximate analysis (ad %)				Ultimate analysis (daf %)				
M	A	V	FC	C	H	N	S	O[a]
5.04	8.55	49.39	37.04	79.66	4.32	0.69	0.66	14.67

[a]By difference

smaller than the real size of solid. The correction equation for the transformation of actual size and sectioned area is given by King [18]

$$g(A) = \int_0^\infty p(A|D)f(D)\mathrm{d}D \quad (1)$$

In the Eq (1), *g(A)* was considered to be the probability density of measured sectioned area; *f(D)* was the probability density of actual size; *p(A|D)*was the probability of measuring a section from a particle of size. In our study, most of the particles are spherical in shape. *p(A|D)* can be simplified as follows [18]

$$p(A|D) = 1 - \left[1 - \frac{4A}{\pi D^2}\right]^{\frac{1}{2}} \quad (2)$$

And

$$p(A|D) = 0.0 \quad (A = 0)$$
$$p(A|D) = 1.0 \quad (A > A_{max})$$

Figure 1 shows corrected size distribution of bulk ash particles under air-firing and oxyfuel combustion. It can be seen that at the same O_2 concentration (20 %), oxyfuel combustion produced less fine particles (<10 μm) and more coarse particles (>10 μm) than air combustion, due to the lower particle temperature achieved during oxyfuel combustion, which reduced the ash vaporization and the particle fragmentation [19, 20]. With increase in O_2 concentration, there were more fine particles (<10 μm) and less coarse particles (>10 μm) in oxyfuel combustion, because the higher particle temperature increases O_2 concentration in oxyfuel combustion and enhances the refactory vaporization and the particle fragmentation [11, 19, 20].

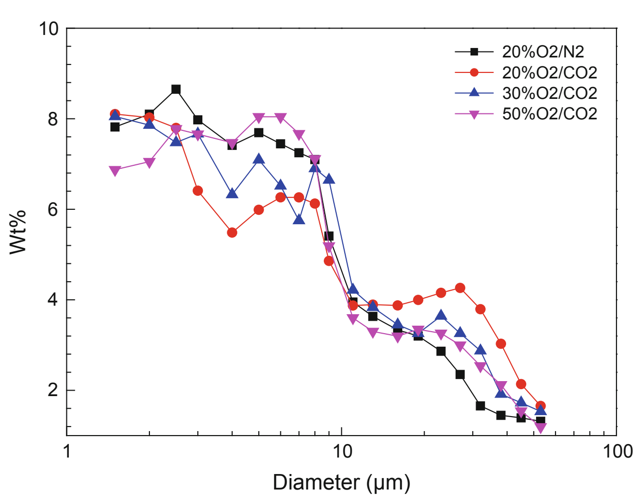


Fig. 1 Corrected size distribution of bulk ash particles under air-firing and oxyfuel combustion

3.2 Mineral Composition in the Bulk Ashes

Figure 2 shows the weight fraction of various mineral associations for Zhundong coal ashes under air-firing and oxyfuel combustion, based on the melting point of mineral. The minerals analyzed by CCSEM were divided into three types: high-melting-point minerals, co-melting minerals, and low-melting-point minerals. It can be seen that the weight fractions of low-melting-point minerals and high-melting-point minerals were decreased during oxyfuel combustion compared with air condition at the same O_2 concentration. The higher O_2 concentration enhanced the co-melting of mineral under oxyfuel combustion, because the higher particle temperature increasing with the O_2 concentration can promote the finely alkali and alkaline earth species to combine with the inherent mineral particles. The high CO_2 concentration not only affects the transformations of coal minerals, but also shortens the decomposition process and extends the oxidation process slightly, so it can be found that the carbonate minerals increased with increase in CO_2 concentration.

3.3 Ash-Deposition-Related Element Distribution

To study the ash deposit potential, the ash-deposition-related elements, namely Fe, Ca, Na, and S, were correlated from the CCSEM data. Among these three conditions, oxyfuel condition with 50 % O_2 centralization has the highest particle temperature and oxyfuel condition with 20 % O_2 centralization has the lowest particle temperature.

In Fig. 3, Fe transformed from fine particles to coarse particles, and other three kinds of elements were opposite to the transformation of Fe with increase in particle temperature. Although the vaporization of refactory oxide was enhanced by increase in particle temperature, the interaction of the finely dispersed combined with inherent mineral particles was also enhanced by the higher particle temperature. The bulge appeared in 10–30 μm from Fig. 3 (b-d) was just really clear on it.

Figure 3b, d shows that both Ca and S were enriched in fine particles together. The fine sulfate particles can deposit on the windwide of tube and capture other viscous particles. The sulfate deposition is hard to be removed by soot blowing. So avoiding the enrichment of Ca and S in fine particles is a good idea to reduce the ash deposit potential.

4 Conclusions

In this study, high-sodium Zhundong coal was burned out in a HDTF under air condition and three kinds of oxyfuel conditions to generate ash samples. The effect of gas phase

Fig. 2 Weight fraction of various mineral associations for Zhundong coal ashes under air-firing and oxyfuel combustion

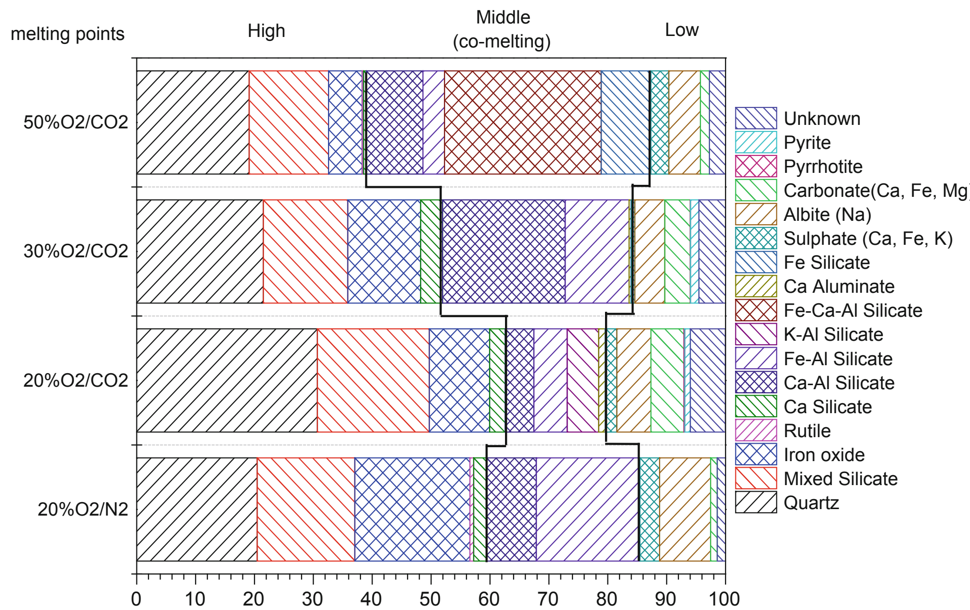
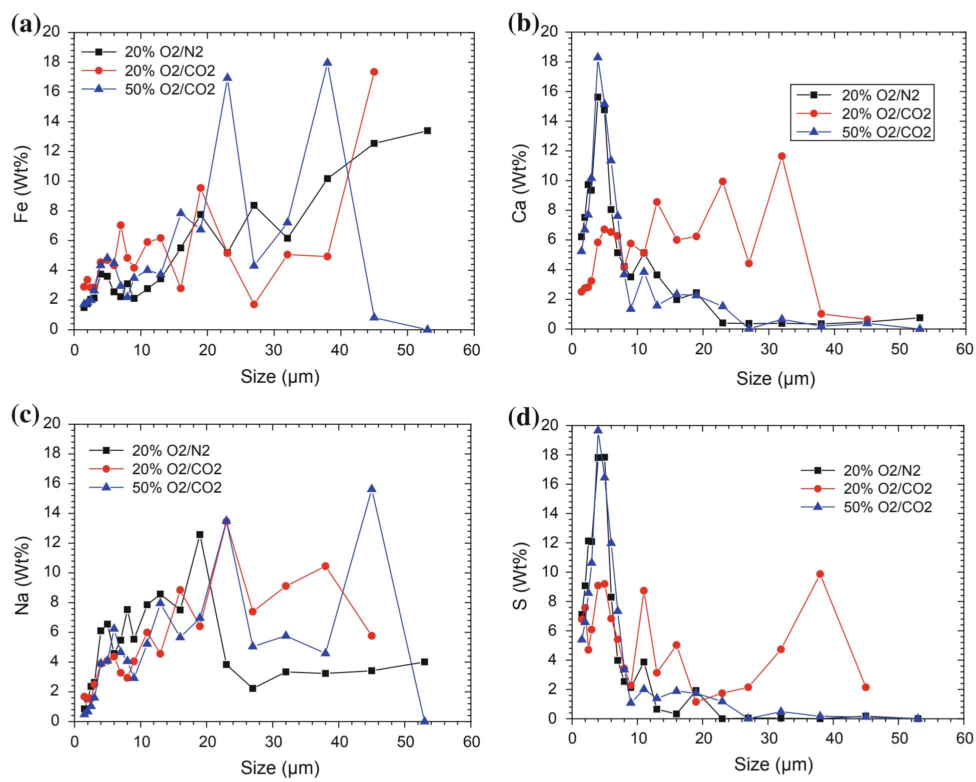


Fig. 3 Element distribution of ash from different conditions **a** Fe, **b** Ca, **c** Na, **d** S



conditions on the physical and chemical changes of ashes as well as the ash deposit potential was investigated. The following results are obtained:

(1) Oxyfel combustion produced less fine particles (<10 μm) and more coarse particles (>10 μm) than air combustion at the same O_2 concentration (20 %), and there are more fine particles (<10 μm) and less coarse particles (>10 μm) in oxyfuel combustion with increase in O_2 concentration.

(2) Higher O_2 concentration enhances the co-melting of mineral, and the carbonate mineral was increased with CO_2 concentration. The high CO_2 concentration not only affects the transformations of coal minerals, but

also shortens the decomposition process and extends the oxidation process slightly.

(3) The increase in particle temperature can not only enhance the vaporization of refractory oxide, but also enhance interaction of the finely dispersed combined with inherent mineral particles. Avoiding the enrichment of Ca and S in fine particles is a good idea to reduce the ash deposit potential.

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