



Effect of carbon dioxide on the high temperature transformation of siderite under low oxygen conditions



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HIGHLIGHTS

- In 7% O₂/93% N₂ and 7% O₂/93% CO₂, pure siderite only produces magnetite.
- Under the above conditions, excluded siderite produces wustite and magnetite.
- Replacing N₂ with CO₂ leads to more magnetite produced from excluded siderite.
- In the same atmosphere, coal addition causes more extensive particle melting.
- For excluded siderite, replacing N₂ with CO₂ suppresses particle melting.

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ABSTRACT

The knowledge of siderite transformation is critical to the understanding of ash deposition behavior in oxy-fuel combustion. This work aims to explore the effect of CO₂ on the transformation of siderite in different modes under low O₂ conditions, which are common in real boilers. Two samples, i.e. pure siderite and excluded siderite simulated by the addition of siderite into a demineralized coal sample, were combusted at 1350 °C in a drop tube furnace. Two conditions, i.e. O₂/N₂ = 7/93 and O₂/CO₂ = 7/93 were tested for elucidating the effect of CO₂. The combustion products were analyzed by scanning electron microscopy and X-ray diffraction. The results show that, for pure siderite, the products generated in both conditions have similar morphology and mineralogy, suggesting negligible effects of CO₂. They are dominated by irregular particles with sharp edges, and only magnetite is detected. However, for excluded siderite, the products generated in both conditions are distinctly different in morphology and mineralogy, which indicates significant effects of CO₂ on the transformation of excluded siderite. The product generated in O₂/CO₂ = 7/93 is dominated by irregular particles with rounded edges, while that generated in O₂/N₂ = 7/93 is dominated by spherical particles. Wustite and magnetite are detected in both products, but the production of magnetite is much higher in O₂/CO₂ = 7/93 than that in O₂/N₂ = 7/93, which is attributed to the presence of a high concentration of CO₂. Compared with pure siderite, excluded siderite experiences more reducing conditions and higher temperatures due to coal combustion, which results in the survival of wustite and more extensive melting.

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1. Introduction

Siderite (FeCO₃) is an important iron-containing mineral in coal, which has significant impacts on ash slagging during coal combustion [1,2]. Therefore, the knowledge of the transformation behavior of siderite at high temperature is quite critical to the understanding of its slagging behavior in pulverized coal boilers [2].

Upon heating, siderite will first decompose into wustite (FeO) and CO₂. The decomposition temperature is about 450 °C [3,4],

but it may change when the atmosphere and other factors vary [5,6]. The subsequent oxidation of the produced wustite is a complicated process and is dependent on a number of parameters such as the association of siderite with carbon matrix and the combustion atmosphere [4–6]. Under reducing conditions, wustite may survive through the combustion [7], or be further reduced into iron [8].

The transformation behavior of siderite in air combustion has been studied by Wall's group [7,9–11]. Siderite in different modes (e.g. pure mineral, siderite sample separated from coal) was tested under oxidizing or reducing conditions. The results show that excluded siderite is transformed into magnetite (Fe₃O₄) and/or hematite (Fe₂O₃) under oxidizing conditions, but wustite is

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produced under reducing conditions. In the case of included siderite, its transformation behavior is similar to that of excluded siderite if there are no interactions with other minerals. But in real coal, included siderite is usually associated with other minerals like aluminosilicates. As a result, interactions between them will take place, leading to the formation of Fe-glass phases.

In oxy-fuel combustion [12,13], the transformation of siderite has not been investigated. Compared with air combustion, oxy-fuel combustion is particularly featured by a much higher concentration of CO_2 in the boiler. Such difference not only has significant effects on coal combustion, but also may affect the transformation of minerals such as siderite. The effect of CO_2 on the transformation behavior of siderite in different atmospheres with the absence of oxygen was studied by the thermo gravimetric analysis (TGA) method [6]. It was found that increasing CO_2 not only increased the decomposition temperature of siderite, but also could enhance the oxidization of wustite into magnetite. Compared with the TGA conditions, oxy-fuel combustion is characterized by the different temperature–time history and the presence of oxygen. The effect of CO_2 on siderite transformation under these conditions is still unknown.

Of particular interest in this work is the effect of CO_2 on the high-temperature transformation of siderite under low O_2 conditions, which are common in coal boilers especially when low- NO_x technology is adopted or the fuel is only carried by a portion of the recycled flue gas. Siderite samples were tested in a drop tube furnace at a high temperature of 1350 °C, which is similar to that encountered in real coal combustion. Two siderite samples were investigated. One is pure mineral siderite. The other is the excluded siderite sample that is simulated by mixing pure siderite with a demineralized coal sample.

2. Experimental

2.1. Sample preparation

The pure siderite sample tested was prepared from a rock sample, which was crushed, grounded and sieved into 63–90 μm . The composition data (as oxides) of the siderite sample is shown in Table 1, which was obtained by X-ray fluorescence (XRF). It is dominated by Fe_2O_3 , but also contains some impurities such as Na_2O , MgO , Al_2O_3 and SiO_2 . As shown in Fig. 1, only siderite was detected by X-ray diffraction (XRD). The siderite particles, as characterized by scanning electron microscopy (SEM), are generally in irregular shape and possess sharp angles (Fig. 2).

The excluded siderite sample was prepared by mixing pure siderite with a demineralized coal sample from a Chinese sub-bituminous coal (mass ratio: siderite/coal = 5/95). The demineralization process is similar to that used by Willett et al. [14]. 500 g coal sample was sequentially leached by 4 L of 1 mol/L ammonium acetate ($\text{CH}_3\text{COONH}_4$), 3 mol/L hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48%), and 2 mol/L nitric acid (HNO_3) in a 5 L plastic cylinder. For each step, the mixture of the coal sample and the liquid was stirred for 18 h. The mixture was then allowed to stand for half an hour to separate into layers. Afterward, the liquid on the top was poured out and the sediment was obtained. When these steps were finished, the coal sediment was constantly washed by deionized water until the liquid became neutral. Through these processes, most of the minerals in coal were removed. The ash content of the demineralized coal sample is only

0.18%. Finally, the coal sample was sieved into <200 μm and was stored in sealed container for subsequent tests. The proximate and ultimate analysis data of the demineralized coal sample are shown in Table 2.

2.2. Combustion experiments and analysis

A drop tube furnace (DTF) was used to investigate the transformation behavior of siderite. The reactor is an alumina tube, which is 2000 mm in length and 58 mm in diameter. The furnace is electrically heated by silicon carbide rods. The furnace temperature was set at 1350 °C for all cases. The sample feeding rate was kept at about 0.3 g/min. Both the excluded siderite (STCL) and pure siderite (ST) samples were combusted in $\text{O}_2/\text{N}_2 = 7/93$ and $\text{O}_2/\text{CO}_2 = 7/93$, respectively. When excluded siderite was combusted, the oxygen–fuel stoichiometric ratio was about 0.78. When pure siderite was burned, the same flow rate was adopted.

At the sampling point, N_2 was injected into the flue gas as a quenching gas in a water-cooled jacket, and then the mixed gas was extracted by a vacuum pump. Combustion products were collected by a glass fiber filter. The facility and collected system were introduced elsewhere [15]. SEM was used to observe the particle morphology of the samples, while the composition was determined by XRD.

3. Results

3.1. Morphology and mineralogy of residues from pure siderite

The morphology of the residues from high temperature heating of pure siderite in $\text{O}_2/\text{N}_2 = 7/93$ and $\text{O}_2/\text{CO}_2 = 7/93$ is shown in Fig. 3(a) and (b), respectively. Compared with the raw sample (Fig. 2), most of the residue particles retain irregular shapes and sharp edges, indicating insignificant melting during heating. Nevertheless, with careful examination, some differences can still be noticed. On one hand, a few large spherical particles with smooth surfaces are observed in both residue samples (Fig. 3(a) and (b)), suggesting full melting of a small number of particles occurs at the reaction temperature investigated. On the other hand, the large particles in Fig. 3 are generally covered with individual fines and their agglomerates. In addition, isolated agglomerates with different sizes are also present in both residue samples. These are not observed in the raw sample (Fig. 2), and are considered a result of particle sintering during reaction.

When the residue sample obtained in $\text{O}_2/\text{N}_2 = 7/93$ (Fig. 3 (a)) is compared with that in $\text{O}_2/\text{CO}_2 = 7/93$ (Fig. 3(b)), no distinct difference in particle morphology is noticed. This suggests that substituting CO_2 for N_2 has insignificant effects on particle morphology when pure siderite was heated at a very low oxygen concentration of 7%.

Fig. 4 presents XRD patterns of both residue samples from heating of pure siderite. It is clear that magnetite is the only iron-containing species identified in these samples. The result demonstrates that, under the conditions investigated, pure siderite is dominantly oxidized into magnetite and the replacement of CO_2 does not affect the final products. Since the melting point of magnetite (about 1590 °C) is much higher than the experimental temperature of 1350 °C, significant melting of the particle is unexpected. This is consistent with the observation of particle morphology shown in Fig. 3, which shows that the residue samples are dominated by irregular particles and CO_2 has insignificant effects on the particle morphology.

3.2. Morphology and mineralogy of residues from excluded siderite

The morphology of the residues from combustion of excluded siderite in $\text{O}_2/\text{N}_2 = 7/93$ and $\text{O}_2/\text{CO}_2 = 7/93$ is examined in

Table 1
The composition (as oxides) of siderite by XRF (wt.%).

| Fe_2O_3 | Na_2O | MgO | Al_2O_3 | SiO_2 | P_2O_5 | SO_3 | K_2O | CaO |
|-------------------------|-----------------------|--------------|-------------------------|----------------|------------------------|---------------|----------------------|--------------|
| 81.39 | 6.29 | 4.05 | 2.38 | 2.28 | 0.33 | 2.63 | 0.06 | 0.58 |

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