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Behavior of trace elements and mineral transformations in the super-high organic sulfur Ganhe coal during gasification

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ABSTRACT

A coal containing high concentrations of hazardous trace elements F, V, Cr, Se, Mo, Cd, and U was selected for the gasification experiment based on the Lurgi fixed-bed pressurized gasifier. The feed coal was a super-high organic sulfur coal sampled from the Ganhe Mine, Yanshan Coalfield, Yunnan Province, China. Fluorine, Ga, Se, Cd, In, Tl, Pb, and Bi were volatilized during gasification, whereas V, Mo, and U were significantly enriched in the residue. The erosion of the gasifier internals resulted in the abnormal enrichment of Cr and Ni in the residue, with the maximum concentrations of Cr and Ni of 26,073 μg/g and 23,982 μg/g, respectively. Except for quartz, other minerals in the feed coals were transformed. The newly formed phases such as mullite, hercynite, magnetite, Fe aluminosilicate, and Al-Si-O-glass containing Fe-Ca-Mg-V-K-Ti were identified in the gasification residue. Pyrite was transformed to elemental iron in some cases. Pyrrhotite with a magnetite rim, representing the high temperature transformation product of pyrite, was observed in the gasification residue by scanning electron microscopy.

1. Introduction

Gasification of coal is considered to be superior to conventional pulverized-coal combustion for the reduction of hazardous trace element emissions, and was recognized as one of the most promising technologies for the clean use of coal [1,2]. However, faced with pressure from environmental pollution, the behavior of hazardous trace elements during coal gasification is still an important concern. The minerals in coal are the carriers of most trace elements [3–6], for example, Cu, Zn, Ni, Mo, As, Se, Co, Cd, Sb, Hg, and Pb are commonly associated with the pyrite and other sulfide minerals [3,5,7–10]. The transformation of minerals during coal gasification has also attracted much attention [11–13].

The trace elements in coal can occur as individual minerals or associated with minerals and organic matter [14–17]. Thermodynamic equilibrium calculations and gasification tests were used to predict and simulate the partitioning and speciation behavior of trace elements during coal gasification [18–23]. Speciation predictions indicated that Hg, AsH_3, H_2Se, gaseous Pb, PbSe, Cd, CdS and PbS/Pb/PbCl could potentially exist in the gas phase [20,23]. For highly volatile trace elements, such as Hg, As, and Se, good agreement between the prediction and test results was obtained [10,18–20]. Generally, Hg is the most volatile element in the thermal process [20] and adsorption on carbon/char probably contributes to its presence and that of other volatile trace elements in the ash [20,24].

Mineral matter in coal occurs as minerals and as inorganic elements associated with minerals, the organic matter and pore water [25,26]. In the coal gasification process, minerals have a possible catalysis effect on the reactivity of hard coal [1]. Sekine et al. [27] indicated that the gasification rate was constantly determined by the ash morphology rather than the carbonaceous structural change. As the temperature and pressure are elevated during gasification, a large portion of the minerals/non-mineral inorganic elements in the coal tends to partially melt and form liquid phases [11]. If these liquid phases cool slowly, crystallization will occur, whereas rapid cooling will result in the formation of glassy materials [28]. Using a variety of technologies, the minerals in the gasification residue have been extensively studied and identified [2]. High temperature crystalline phases such as mullite, anorthite, cristobalite, quartz, diopside, and abundant glass (amorphous) are often found in the coal gasification residue [2,11–13]. Glass, composed mainly of Ca, Mg, and Na aluminosilicates with some Fe, is the dominant phase in the reduction and combustion zones [29]. Pyrite

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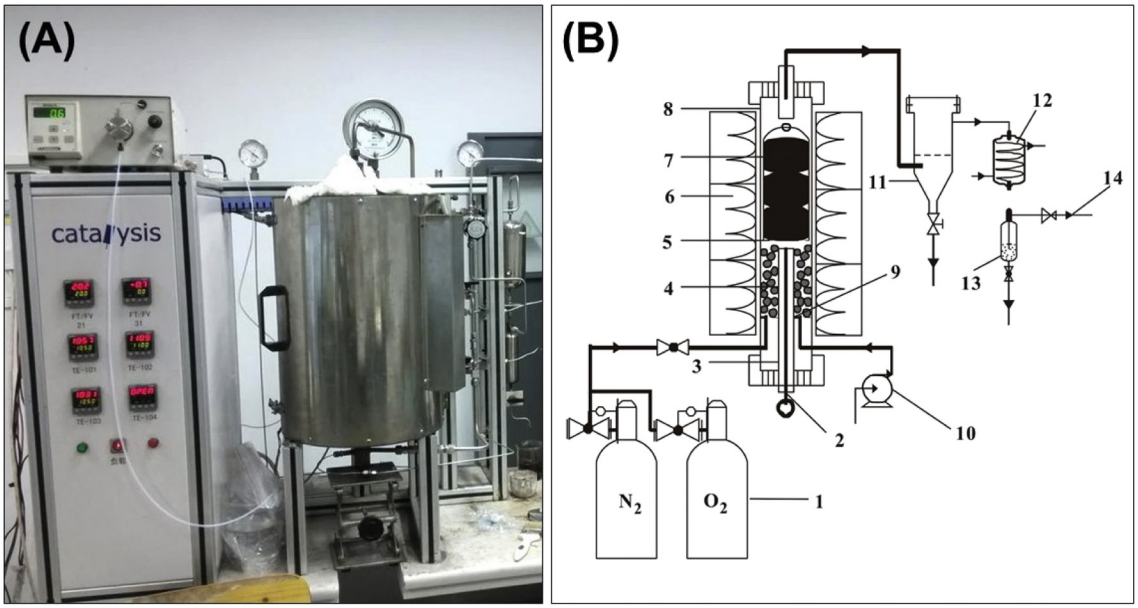

Fig. 1. Lab-scale fixed-bed pressurized gasifier. (A), the gasification apparatus. (B), schematic diagram (modified after Liu et al. [30]), 1, gas container; 2, thermocouple; 3, thermowell; 4, Al_2O_3 porcelain ball; 5, sample support; 6, heating furnace; 7, lump coal; 8, reactor; 9, sieve plate; 10, high pressure pump; 11, cyclone separator; 12, condensor; 13, liquid collector; 14, gas outlet.

decomposition leads to the formation of iron-rich glass, and anorthite crystallizes from calcic glass [13].

The reactions between various materials in the coal gasifier are rather complicated. To some extent, the behavior of trace elements and minerals during coal gasification can be better understood by laboratory-scale experiment. This study aims to 1) study the volatility of hazardous trace elements in super-high organic sulfur (SHOS) coal during the gasification process and 2) to undertake a preliminary investigation of the mineral transformation during SHOS coal gasification.

2. Materials and methods

2.1. Samples and gasification experiment

The six feed coals (numbered FC-1 to FC-6) selected for the gasification experiments were sampled from the Permian Ganhe coal, Yanshan Coalfield, Yunnan Province. The coal is a super-high organic sulfur coal.

The gasification experiment was performed using a lab-scale Lurgi fixed-bed pressurized gasifier (Fig. 1). The reaction tube (50 mm in diameter and 600 mm in length) of the gasifier is made of an 800H nickel – iron – chromium alloy [30]. The operation of the gasification experiment was conducted following the method outlined by Liu et al. [30]. The coal was broken into particles with a size of about 10 mm before feeding it into the heating furnace. Coal samples of about 50 g were fed into the furnace, and Al_2O_3 porcelain balls were placed underneath and on the coal samples. Nitrogen was selected as the protective gas during the heating process. The gasification temperature and pressure selected for this gasification experiment were 1100 °C and 3 MPa, respectively. The gasification agents were oxygen and water vapor. The whole gasification process lasted for about 3 h. The coal gasification residue was collected when the furnace cooled to ambient temperature. Corresponding to the feed coal samples, the residues were numbered from GR-1 to GR-6.

2.2. Analytical methods

Proximate and ultimate analyses were performed on the feed coal samples following the ASTM standards D3173-11 [31], D3174-11 [32], and D3175-11 [33]. The forms of sulfur were determined following the ASTM standard D3177-02 (Reapproved 2007) [34]. Carbon, hydrogen, and nitrogen were analyzed according to the ASTM standard D5373-08 [35]. The contents of major element oxides in the coal and gasification residue were determined by X-ray fluorescence spectrometry (XRF). An Axios mAX X-ray fluorescence spectrometer was used to determine the major element contents, with the voltage and current of 50 kV and 50 mA, respectively. Loss on ignition (LOI) was performed following the ASTM test method D7348-13 [36]. The unburned carbon (UBC) content was estimated as the LOI value. Content of Hg was analyzed using DMA-80 Mercury Analyzer, as outlined by Dai et al. [37]. Other trace element concentrations in coal and the gasification residue were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), based on the methods outlined by Dai et al. [38].

The feed coal and the gasification residue were ground to pass 200 mesh and then analyzed by X-ray diffraction (XRD) to determine the mineral species. A Panalytical X'Pert PRO powder diffractometer with Cu-Kα radiation was selected for XRD investigation, using an accelerating voltage and current of 40 kV and 40 mA, respectively. The XRD pattern for the feed coal was recorded over a 2θ interval of 2.5–70°, with a step size of 0.02°. The XRD pattern for the residue was recorded over a 2θ interval of 5.0–70°, with a step size of 0.13°.

In order to evaluate more fully the petrological characteristics of the coal gasification residue, samples of crushed residue (< 20 mesh) were mounted in epoxy resin and prepared as polished sections for conventional optical microscope analysis and electron microscope study. The scanning electron microscope with associated energy-dispersive X-ray spectrometer (SEM-EDX) was used to study the minerals and to determine the elemental distribution in the residue samples, using 15 kV accelerating voltage. The polished sections were carbon coated before SEM analysis.

3. Results and discussion

3.1. Basic properties of the samples

Proximate and ultimate analyses and the forms of sulfur for the feed coal samples are presented in Table 1. The feed coal used for gasification is a low volatile bituminous coal, according to the ASTM Standard