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Geochemical behavior of hazardous volatile elements in coals with different geological origin during combustion

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ABSTRACT

The geochemical behaviors of hazardous elements in the combustion process of Chinese coals with different geological origins at different temperatures were studied. The analyzed coal samples were placed in a fixed bed reactor with a quartz tube and heated to six desired temperature points, from 400 °C to 900 °C with 100 °C for each interval. The mineral morphology and composition of coal and coal ash were determined by X-ray fluorescence (XRF), scanning electron microscope-X-ray Energy Dispersive Spectrom (SEM-EDS) and X-ray powder diffraction techniques (XRD). Sequential chemical extraction procedure was used to describe the modes of occurrence of selected hazardous elements in coal. The content of arsenic (As) in coal and coal ash was analyzed by inductively coupled plasma mass spectrometry (ICP-MS), and the content of selenium (Se) and mercury (Hg) in coal ash was analyzed by atomic emission spectrometry (AES) and atomic fluorescence spectrometry (AFS). The volatile characteristics of As, Se and Hg in coal were studied by thermogravimetry (TG). The results show that: 1) the mineral phases of Liuzhuang (LZ) and Huajiahu (HJH) coal samples are mainly composed of clay minerals and silicate minerals and the contents of As, Se and Hg were closely related to the organic matter and inorganic mineral in coal; 2) As mainly exists in organic matter and Se, Hg mainly exists in silicate minerals. The organic As in coal is closely related to the low-rank, low ash content and low As content of coal. The modes of occurrence of Se and Hg may be related to the low element content, low sulfide content in coal and stable sedimentary environment; 3) the relationship between volatilization rate (Vr) of As, Se and Hg elements and combustion temperature is the closest. The differences of Vr of As, Se and Hg elements in coal of different geological origin are mainly related to elements concentration and coal quality; 4) at different heating rates, the Vr curves of As, Se and Hg elements have the characteristics of "S" type, logarithmic type and linear type, respectively; The Initial stable temperature of Vr is different under the influence of element geochemical characteristics. The volatility of As reaches the maximum at 800 °C, and Se and Hg reach the maximum at 700 °C and 600 °C, respectively; 5) The heating rate and the difference of coal quality under different geological origin are important factors affecting the Vr of As, Se and Hg. The maximum weight loss temperature (T_P) can be used as an important index to reflect the influence of coal quality and heating rate on the Vr of hazardous elements (As, Se and Hg).

1. Introduction

According to the yearbook of the national bureau of statistics of China [1], by the end of 2016, coal accounts for 60% of China's primary energy structure. Wang et al. [2–4] reported that in the next 10 years, coal will still occupy the dominant position of primary energy, and its main use is power generation, followed by industrial boiler heating, domestic coal, coking coal, etc. Besides, the pollutants produced by coal combustion are an important source of air pollution. For example, coal ash particles produced by coal combustion can cause respiratory and cardiovascular diseases [5,6], pulmonary diseases [7] and hazardous elements produced by coal combustion can even cause pollution to soils in neighboring cities [8,9].

On the basis of Liu et al. [10], Ruhl et al. [11], Chen et al. [12] and Dai et al. [13], coal particles have complex physical and chemical reactions during coal combustion, resulting in hazardous elements in coal evaporated to the atmosphere or attached to the surface of fine particles (fly ash). These hazardous elements can be inhaled or adsorbed on crops and food, or absorbed by livestock or bioaccumulated in birds and fish. It is estimated that the total emission of As, Se and Hg from coal

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combustion is about 406.4 tons, 538.6 tons and 139.4 tons in China (2012), respectively [14].This has led to serious problems, such as water quality and soil pollution around coal mines [15], primary DNA lesions caused by ultrafine/nanoparticles [16,17], endemic arsenism, selenium poisoning and lung cancer [18], etc.

According to Clarke and Sloss [19], trace elements in coal can be divided into three types based on their enrichment behavior in fly ash, namely non-volatile elements (Mn, Ni, etc.), volatile elements (As, Pb, Mo and Cd) and most volatile elements (Se, Hg and Halogen). Among the above elements, US National Research Council classified As, Se and Hg as the most noteworthy elements in the utilization of coal [20], and U. S. Clean Air Act Amendments (CAAA) also listed 11 kinds of elements such as As, Se and Hg as the main hazardous air pollutants In 1990 [21]. Since the Chinese government pays high attention to the emission of pollutants from coal combustion products, it is significant to investigate the geochemical behavior and volatile characteristics of hazardous elements during coal combustion.

In recent years, the migration and transformation features of volatile hazardous elements during coal combustion have been widely concerned by more and more scholars. The performance is as follows: 1) studying on migration, transformation and enrichment of hazardous elements [21–23,25,27–33,41–46]; 2) simulating the migration and release laws of elements in different boiler combustion processes, such as fixed bed, circulating fluidized bed, titration furnace simulated combustion, etc [34–36,39,40,48]; 3) using thermodynamic software to simulate the chemical reaction kinetics of various elements in the combustion process [36,38,47]; 4) studying on migration, transformation and release law of elements in mixed combustion process with sludge, garbage, biomass, etc [36,39]; 5) combustion simulation experiment of adsorbing volatile elements by means of absorbents such as limestone and silicate, etc [24,26,37,47,49]. Considering that previous research objects were mostly bituminous coal or anthracite coal with high rank, the geochemical characteristics of hazardous elements in low-rank bituminous coal (such as the modes of occurrence of elements, migration and transformation characteristics during combustion) have not been more clearly understood. In this study, volatile hazardous elements (As, Se and Hg) were selected to conduct a more systematic study on their geochemical behaviors during combustion:

(1) Arsenic (As)

As has attracted considerable attention because of extensive and serious health problems caused by high As content in drinking water in Bangladesh, west Bengal, India, China, Argentina, Mexico and other places [25]. Elemental-arsenic (As) and As_2O_3 are considered as two possible forms of As in oxidizing flue gas environment. Liu et al. [26] concluded that almost all As compounds were hazardous and 0.7–52% As exists in gas phase during combustion. The abundance of As in continental crust was 1.7 μg/g according to Wedephol [27]. The average content of As in world coal was 9.0 μg/g [28] and its average content in Chinese coal was 3.79 μg/g [29]. On the basis of Swaine et al. [30] and BouŠka et al. [31], As was closely related to pyrite or other sulfides in coal, which may be related to more sulfides in coal and higher coal rank. However, Kolker et al. [32] and Say-Gee Sia [33] suggested that As in low-rank coal seems to be associated with organic matter, and low-rank coal usually had a larger proportion of organic-As. In respect of volatilization of As, Liu et al. [34] concluded that organic-As evaporated below 600 °C and As combined with sulfide evaporated at 800–900 °C. The volatilization behavior of As was greatly influenced by the modes of occurrence, temperature, coal rank and minerals, etc and temperature was the main control factor [26,35]. In respect of migration and adsorption mechanism of As during combustion, Zhou et al. [36], Zhang et al. [37] and Wang et al. [38] reported that As is closely related to the chemical composition of coal, the existence of iron, calcium, magnesium, aluminum, sodium and potassium was not conducive to the volatilization of As, and the existence of silicon in coal had the positive effect. It may be related to the adsorption mechanism of As. Furthermore, Liu et al. [26] and Zhang et al. [37] also showed that the correlation coefficients between Ca, Fe, Mg and As were as follows: Ca > Mg > Fe. However, Al is negatively correlated with As. Therefore, studying the geochemical behavior of As during combustion needs to payţ attention to the comprehensive influence of the content and modes of occurrence of As, coal quality and combustion conditions.

(2) Selenium (Se)

According to statistics, in 2007, the total emission of Se from power plants was 50.96 tons in Anhui, China [39]. Some chemical forms of Se, such as Na_2SeO_4 and Na_2SeO_3, are extremely hazardous. Although the content of Se in coal is low, a large number of coal power generation will lead to a large number of accumulated emission of Se [40,41]. According to Wedephol [27], the abundance of Se in continental crust was 0.12 μg/g. The average content of Se in world coal was 1.6 μg/g [28] and its average content in Chinese coal was 2.47 μg/g [29]. According to Finkelman et al. [42], Tewalt et al. [43], Hower et al. [44], Se in coal mainly existed in pyrite, followed by clay minerals and organic macerals. Besides, Finkelman et al. [45] indicated that the leaching behavior of Se in low-rank coal was very different, so it was difficult to draw a conclusion. The modes of occurrence of Se was also diverse, which was closely related to the sedimentary environment of coal [29,46]. In the process of coal combustion, Se volatilizes in the form of SeO_2, SeO and Se elements, and gaseous Se can be chemisorbed on the fly ash surface or exist in gaseous form [47]. Furthermore, by using on-line analysis system of trace elements in coal-fired flue gas, Shen et al. [48] made an in-situ determination of Se release in the process of fluidized bed combustion and gasification. The results showed that Se-containing compounds ($CaSeO_4$) in coal gradually decomposed and the content of SeO_2 in flue gas rapidly increased in the range of 350–600 °C. The increase of SeO content mainly occurred after 900 °C, while the content of se in flue gas was relatively small and changed smoothly. In respect of transport and adsorption mechanism of Se during combustion, Zhou et al. [49] indicated that the volatilization rate of Se increased with the increase of Fe, Ca, Al, Na and K content in ash, while the content of Si had significant influence on the release of Se, and the Se retention efficiency of Fe_2O_3, CaO and MgO reached the maximum at 600 °C, 600 °C and 700 °C respectively. Therefore, studying the geochemical behavior of Se during combustion need to pay attention to the comprehensive influence of coal quality, coal rank and combustion conditions.

(3) Mercury (Hg)

As early as 1997, the U.S. environmental protection agency (EPA) announced that Hg released from coal combustion might cause human health problems. Hg is a highly volatile hazardous trace element and coal combustion is the main source of Hg emission to the environment [50]. The emissions of Hg from coal-fired power plants accounted for about 80% of the total anthropogenic Hg emissions [51]. According to Wedephol [27], the abundance of Hg in continental crust was 0.04 μg/g. The average content of Hg in world coal was 0.1 μg/g [28] and its average content in Chinese coal was 0.20 μg/g [29]. Hg in coal mainly existed in sulfide, followed by clay minerals and organic macerals [52]. However, Finkelman et al. [45] indicated that the low concentration of Hg in coal may lead to high analysis uncertainty, and the modes of occurrence of Hg in low-rank coal was not as clear as bituminous coal. Therefore, the modes of occurrence of Hg was closely related to the geological origin of coal [30,46]. During combustion, Hg in coal can be converted into three substances: (i) particulate bound-Hg (Hg_p); (ii) gaseous elemental mercury (Hg^{0+}) and (iii) gaseous mercuric oxide (Hg^{2+}) [53]. Generally, mercury in coal began to volatilize at a temperature lower than 200 °C, which was almost unrelated to the appearance modes of Hg in coal. When the temperature was higher than