



# Transformation of heavy metals in lignite during supercritical water gasification



Guifang Chen, Xinfeng Yang, Shouyan Chen, Yong Dong, Lin Cui, Yong Zhang, Peng Wang, Xiqiang Zhao, Chunyuan Ma<sup>\*</sup>

National Engineering Laboratory of Coal-fired Pollutants Emission Reduction, Shandong Provincial Key Lab of Energy Carbon Reduction and Resource Utilization, Shandong University, Jinan 250061, Shandong Province, PR China

## HIGHLIGHTS

- The transformations of heavy metals during lignite SCWG were investigated.
- The risks of heavy metals in lignite and residues after SCWG were evaluated.
- The effects of experimental conditions on corrosion during SCWG were studied.

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## ABSTRACT

Transformation characteristics of heavy metals during lignite supercritical water gasification (SCWG) were studied. A sequential extraction procedure (modified Tessier method) was used to selectively extract different fractions of Pb, Cd, Cr, Mn, Cu, Ni, and Zn. Heavy metals transformed into more stable fractions after SCWG. For Pb, Cd, Mn, Cu, and Zn, SCWG reduced the bioavailability and the risks posed by heavy metals in lignite. Under the experimental conditions, the conversion rates for Pb and Cd were 16.0%–25.2% and 16.3%–23.4%, respectively, whereas those for Mn, Cu, and Zn were much lower. Solid products enriched with Pb, Cd, Mn, Cu, and Zn were obtained after SCWG; the contents of these metals varied slightly in the liquid products under different experimental conditions. Excess Cr and Ni that did not originate from lignite were found in the residues, owing to reactor corrosion during lignite SCWG. Higher temperatures alleviated corrosion, whereas higher pressures and equivalence ratios (ER) had the opposite effect. None of the heavy metals were detected in the gas phase under the experimental conditions used in the present study. The correlation between the distributions of heavy metals and the experimental conditions were also studied. The transformation pathways of Pb, Cd, Mn, Cu, and Zn during SCWG were deduced according to the experimental results.

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## 1. Introduction

Lignite is abundant in China and several other countries but difficult to use because of its low calorific value and high moisture content. However, lignite has high reactivity and low viscosity, and contains a large amount of volatile components, which facilitate gasification. Thus, lignite is a good raw material for gasification, which is considered to be a technology with a high potential for lignite utilization [1]. Integrated gasification combined cycle (IGCC) is considered to be a key energy production technology for the 21st century, and hence, it is attracting increas-

ing attention [2–4]. However, the high moisture content of lignite results in substantial heat loss during gasification [5]. Thus, lignite must be dried in advance, which is an energy-intensive process. Supercritical water gasification (SCWG) of lignite avoids the drying process because it is carried out in water, which saves a great deal of energy. Many studies have demonstrated that gases with high hydrogen yields can be obtained during lignite SCWG and complete gasification can be achieved at lower temperatures than required for conventional gasification [6–15]. Hence, SCWG can allow the utilization of lignite.

Previous studies have concentrated on improving the H<sub>2</sub> yield of gaseous products [6–12,14], while the pollutant emissions of lignite in SCWG have been ignored. Several pollutants are produced during coal utilization, including particles, sulfur and nitrogen oxides, heavy metals, and alkali metals, which must be considered

<sup>\*</sup> Corresponding author.

E-mail address: [chym@sdu.edu.cn](mailto:chym@sdu.edu.cn) (C. Ma).

when implementing new technologies. We previously investigated the transformation characteristics of sulfur and alkali metals in lignite during SCWG [16,17]; the results offered a framework for the evaluation and control of sulfur and alkali metal emissions. Heavy metals have received more attention owing to their toxic effects on the environment and humans. Thus, it is essential to investigate the transformation characteristics of heavy metals during lignite SCWG.

Distribution and volatility behavior of heavy metals in products obtained by conventional coal gasification were investigated, as was the control of heavy metals [18–23]. However, the hazard of heavy metals to the environment is not only related to concentration, but also connected with fractions. Zhou et al. analyzed fractions of Mn, Mo, and Pb in coal and ash produced by conventional gasification, showing that exchangeable and carbonate associated fractions decreased in the gasification ash [24]. Lv et al. investigated the decomposition temperatures of different fractions of Pb, Cr, Co, Ni, and V during coal pyrolysis [19]. Pyrolysis and liquefaction promoted the transformation of the mobile fraction into a more stable fraction [25], and the liquefaction process significantly suppressed the mobility/leachability of heavy metals [26]. This proved that pyrolysis, gasification and liquefaction reduced the hazard of heavy metals to the environment [24–26].

Unfortunately, the SCWG reaction environment is different from that of conventional gasification, pyrolysis, and liquefaction, and the transformation characteristics of heavy metals in lignite SCWG have been ignored so far. The transformation and fractions of heavy metals in fly ash, polychlorinated biphenyls (PCBs), and sewage sludge during supercritical water (SCW) treatment have been investigated. Bo et al. [27] and Jin et al. [28] demonstrated that heavy metals in medical waste fly ash after SCW treatment transformed to more stable fractions. Heavy metals in municipal solid waste (MSW) leachate were converted to oxides or inorganic salts in Zou et al. [29]. Several studies have demonstrated that the risks of heavy metals in sewage sludge were reduced after SCW or subcritical water treatment [30–32]. These results prove that SCW treatment reduces the risks of heavy metals in fly ash, PCBs, and sewage sludge. However, their properties are different from those of lignite, which has not been explained. Moreover, there is no detailed discussion on heavy metal distributions in solid, liquid, and gaseous products. Therefore, the transformation of heavy metals in lignite SCWG has not been addressed, and the environmental hazard caused by heavy metals in lignite SCWG is unclear. Thus, it is essential that the transformation characteristics and environmental effects of heavy metals be investigated before further application of lignite SCWG. In the present study, the distributions and transformations of Pb, Cd, Cr, Mn, Cu, Ni, and Zn in lignite during the SCWG process were investigated and the risks to the environment were evaluated.

## 2. Material and methods

### 2.1. Materials

The lignite employed was obtained from Inner Mongolia. The lignite was broken and ground to obtain particles smaller than 0.2 mm. The results of the lignite analysis are shown in Table 1. Distilled water, hydrogen peroxide (reagent grade), and nitrogen (99.99% pure) were used in the experiments.

### 2.2. Apparatus and experimental methods

The internal volume of the batch reactor was 100 mL, and the design temperature and pressure were 600 °C and 30 MPa, respectively. The experimental apparatus is presented in Fig. 1. The experimental process has been described in detail previously [16]. After the reaction, the gaseous and liquid products were separated using a gas–liquid separator. The gaseous fractions were absorbed by two-stage 5% aqueous HNO<sub>3</sub>, and the liquid fractions were collected via outlets at the bottom of the gas–liquid separator. The solid residue was cooled to room temperature in the reactor and then collected for analysis.

### 2.3. Analytical methods

The lignite, residue, and liquid samples were pretreated by microwave digestion, as described in detail previously [17]. The gaseous fractions were absorbed by two-stage 5% aqueous HNO<sub>3</sub> and analyzed without pretreatment.

A sequential extraction procedure (modified Tessier method) was used to selectively extract various fractions of Pb, Cd, Cr, Mn, Cu, Ni, and Zn (Table 2) [24,30,33]. F1 is the exchangeable fraction, which is easily released to the environment. F2 is the fraction bound to carbonate, which can be released under acidic conditions. F3 is the fraction bound to iron and manganese oxides; and it is relatively stable but liable to be released at low redox potentials. F4 is the fraction bound to organics and sulfides, which is only released in strong oxidation environments. F5 is the residue fraction, which is stable and considered safe to the environment.

The concentrations of Cr, Mn, Cu, Ni, and Zn in the solid, liquid, and gas phases were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, OPTIMA 7000DV, PerkinElmer). Pb and Cd were analyzed by atomic absorption spectrophotometry (AAS, GGX-9, Haiguang).

## 3. Results and discussion

### 3.1. Risk assessment of heavy metals in lignite and solid products

Heavy metals damage the environment not only because of their concentrations, but also because of the metal fractions present in lignite and solid products. In the present study, Pb, Cd, Cr, Mn, Cu, Ni, and Zn were fractionated into five fractions using a modified Tessier method.

As fractions F1 and F2 are easier to release, an index was defined in Eq. (1) to illustrate the risks of heavy metals to the environment [30].

$$P_{BIO} = \frac{C_{F1} + C_{F2}}{\sum C_{Fi}} \quad (1)$$

where  $P_{BIO}$  is the risk index,  $C_{F1}$  and  $C_{F2}$  are the concentrations of F1 and F2, respectively, and  $\sum C_{Fi}$  is the total concentration of all fractions. The  $P_{BIO}$  values of lignite and the solid products are listed in Table 3 according to the concentrations of the various fractions. Clearly, the risks posed by Pb, Cd, Mn, Cu, Ni, and Zn present in the solid products were substantially lower than those present in lignite; Cr was not present in fractions F1 and F2, both in lignite and residues. During SCWG, fractions F1, F2, F3, and F4 could decompose to release heavy metals, which reacted with oxides,

**Table 1**  
Analysis of lignite.

Industrial analysis wt%				Ultimate analysis wt%					Heavy metals analysis (mg/kg)					
M <sub>ad</sub>	A <sub>ad</sub>	V <sub>ad</sub>	FC <sub>ad</sub>	C <sub>ad</sub>	H <sub>ad</sub>	N <sub>ad</sub>	S <sub>ad</sub>	Pb	Cd	Cr	Mn	Cu	Ni	Zn
11.25	18.98	48.44	21.33	49.51	4.42	0.84	0.58	11.5	0.135	29.2	194	27.3	38.1	49.9

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