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Research Paper

Influence of hydrothermal dewatering on trace element transfer in Yimin coal

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HIGHLIGHTS

- Typical lignite Yimin coal can be upgraded through HTD.
- HTD has influence on minerals and XRD analysis in Yimin coal.
- HTD influence on Hg, As and Se was discovered.
- SCEP experiments show occurrence fractions of Hg, As and Se of raw and upgraded coals.
- Mechanism of HTD influence on Hg, As and Se was discussed.

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ABSTRACT

In this study Yimin lignite coal from Inner Mongolia was taken for investigating the influence of hydrothermal dewatering (HTD) on trace elements (Hg, As, Se) under different conditions. First, the coal samples were treated through HTD process at a temperature range of 200–300 °C, then proximate analysis was performed to check changes in the coal. Meanwhile, inductively coupled plasma-mass spectrometry and atomic fluorescence spectrometry were used to detect the concentrations of trace elements. Furthermore, minerals in samples were analyzed by powder X-ray diffraction (XRD). Sequential chemical extraction procedure (SCEP) was also performed to determine the occurrence modes of trace elements. The results showed that HTD treatment is effective in removing moisture and upgrading coal rank, and the operating temperature should be in good control at a certain range due to the loss of volatile mass. Minerals in this type of coal mainly include quartz and kaolinite, and HTD may have an effect on removing minor minerals muscovite and siderite. HTD can remove all three elements mentioned above. The highest removal rate detected is about 15% for As, 45% for Hg and 43% for Se. The experimental result shows that occurrence mode of Hg and As exist mainly in pyritic fraction while Se mainly in pyritic fraction and organic fraction. During HTD, all fractions of Hg and Se decrease obviously. However, for As, the decreasing amount in carbonate and pyritic fractions is much smaller than that in organic and silica bond fractions. It can be inferred that pyrite in coal may not decompose but only lose the bonds with trace elements. Pyrolysis behavior of coal and the strong solubility of sub-critical water should be responsible for the removal of trace elements.

1. Introduction

Coal is the primary source of energy in China. According to China National Bureau of Statistics, larger than 75% of the total power supply is from coal-fired power stations in recent decades. The status quo will not change much in the coming years [1]. Thus high efficiency and clean utilization of coal is important in building an environment-friendly and low-carbon society. Low rank coals (LRCs), generally with low calorific value such as lignite, brown coal and sub-bituminous, show greater importance due to its rich reservation and low price. It is reported that the reserves of lignite in China are about 190.3 billion tons, 41.18% of its total coal reserve [2]. However, LRCs are not widely utilized due to its low energy density, high moisture content and high spontaneous combustion tendency [3]. Thus their upgrading is considered of much commercial necessity and social significance.

Hydrothermal dewatering (HTD) is a typical non-evaporative dewatering process. The major advantage of this process is that

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water is removed as liquid so that the latent heat of vaporization is saved [4]. In HTD process the LRCs undergo physical and chemical changes at high temperature and pressure (higher than saturation vapor pressure to keep the water as liquid) in subcritical water. After HTD process, moisture content in LRCs significantly decreases and thus calorific value increases [4–8], with coal quality improved. Besides, water–soluble inorganic element such as sodium species is partly removed [5]. It was reported that some trace elements could be extracted under the subcritical water condition [9,10]. As HTD process condition is similar to subcritical water condition, trace elements may also be removed through HTD process. However, since most of the previous researches aim to remove trace elements rather than coal dewatering, the temperatures adopted were relatively too high (higher than 350 °C) compared with conventional HTD. In this study, HTD is primarily a dewatering process, in which trace elements removal efficiency is also appraised. As previous work lacked low-temperature verification of trace elements removal, this study aims at this section.

In general, trace elements in coal refer to the elements at ppm or ppb level, such as As, Cd, Cr, Hg, Se, Pb, B, Cu, Mn and Ni, most of which are detrimental to human health and environment safety due to the air and water pollution. Despite the low concentration of trace elements in coal, the emission of trace elements is still a great menace to the environment problem considering the amount of its consumption [8]. Considering that the elements mercury, arsenic and selenium (Hg, As and Se) are the most volatile and difficult to capture [11] before combustion flue gas entering into the air, those three elements were emphatically investigated in this paper.

In this study, a Chinese lignite was treated through HTD process over a range of temperatures (200–300 °C). The changes in coal composition and trace elements (Hg, As and Se) concentrations were detected, the occurrence modes of the trace elements were also investigated, and finally the influence of HTD process on trace elements was discussed.

2. Materials and methods

2.1. Coal sample preparation

Coal sample used in this study was Yimin (YM) lignite from Inner Mongolia, the largest lignite reserve and producing province of China. The coalfield is located in Yimin basin, which is in the southwest (70 km away) of Hailar city. Detailed geological information of Yimin coalfield can be found in [12]. The YM lignite is an attractive resource with an estimated proved reserve of 12.6 billion tons. At the current production of 30 million tons per year, it can last for hundreds of years. However, as typical lignite, its moisture content is high (about 25% on air dry basis) and its calorific value is low. The detailed coal analysis is shown in Table 1.

Before processed in the HTD reactor, the raw coal samples were ground into particles smaller than 2 mm, then both raw coals and upgraded coals were milled in a ring mill for 30 s and sieved through the 74 μm Hole Sizer.

2.2. HTD process description

The HTD system was made up of a 2L volume stainless steel autoclave and the heating system, as shown in Fig. 1, with maximum working pressure 25 MPa and the maximum temperature 350 °C. When the experiments began, a mixture of raw coal samples and deionized water (dry coal to water at the ratio 1:3 in quantity) was added into the autoclave first, then the sealed autoclave was injected N_2 and the pressure in the autoclave was set to be 4 MPa for 2 h to ensure the absence of leaks. After N_2 was released, the autoclave was heated to the certain temperature (200 °C, 250 °C and 300 °C) at the constant ramping rate of 3 °C/min, and kept at the final temperature for 1 h. The stirring worked at 100 rpm since the heating started and stopped until the whole system had cooled down. The products prepared at 200, 250 and 300 °C are marked YM-200, YM-250 and YM-300 respectively.

After HTD process, the upgraded coal sample and water mixture was taken out of the autoclave and separated through filtration. Both solid and liquid products were collected. Solid products, namely the upgraded coals, were dried at 40 °C in an oven and then weighted. Liquid products, which may contain certain concentration of trace elements, were made up to 500 mL with deionized water and kept in a sealed container for trace elements determination.

2.3. Coal analysis and trace elements measurement

Proximate analysis was carried out following the international standards ISO11722, ISO1171 and ISO562, with moisture, ash and volatile matter in coal as the measurement indexes. The calorific value was obtained with the adiabatic bomb calorimetric method following ISO1928. The C, H, N and S contents of the coal samples were measured with an LECO-CHNS 932 Elemental Analyzer, whereas the O content was calculated based on the difference.

Minerals in raw and upgraded coal samples were analyzed by powder X-ray diffraction (XRD). A Rigaku D/MAX 2550/PC diffractometer with Cu Kα radiation and a scintillation detector was used to collect the XRD patterns. Each pattern was step-scanned from 5° to 80° and one step size was 0.02° (2θ). The Reference Internal Standard Method and software Jade 6.0 were used to obtain a semi-quantitative estimation of the minerals in coal samples.

Elements As and Se were determined using a ThermoFisher inductively coupled plasma-mass spectrometry (ICP-MS) equipped with collision/reaction cell technology (CCT) to avoid disturbance of polyatomic ions [13]. Before the determination by ICP/MS, coal samples were digested in a Microwave Reactor with HNO_3 and HCl as the solvent. Mercury was determined by cold Atomic Fluorescence Spectrometry (AFS) following ISO15237.

2.4. Occurrence modes experiment

Sequential Chemical Extraction Procedure (SCEP) is a widely-accepted method for element occurrence modes research

Table 1
Coal analysis of raw coals and upgrading coals.

Condition	Proximate analysis (ad, %)				Calorific value (J/g)	Ultimate analysis (daf, %)					Ao/c
	Moisture	Ash	Volatile	Fixed carbon		C	H	O	N	S	
Raw coal	24.35	9.58	29.42	36.65	18834	74.22	4.32	19.7	1.03	0.73	0.27
YM-200	11.57	11.64	33.17	43.62	22109	76.33	4.61	17.33	1.16	0.57	0.23
YM-250	9.97	11.91	31.76	46.36	22895	77.49	4.58	16.24	1.14	0.55	0.21
YM-300	7.37	12.59	30.80	49.24	23585	78.43	4.55	15.31	1.25	0.46	0.20

Notes: ad is air dried basis, daf is dry ash free basis, Ao/c is oxygen to carbon atomic ratio.