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The migration of heavy metal elements during pyrolysis of oil shale in Mongolia

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ABSTRACT

The migration of trace elements during the pyrolysis of Mongolian oil shale is studied at the macroscopic (the porosity change) and microscopic (the occurrence state) levels. Four groups of oil shale (904, 1054, 10513 and 10807) in the Dalai Bulang mining area of Mongolia were studied. Oil shale samples were heated in a tube furnace in argon atmosphere. Final temperatures of pyrolysis varied from 300 °C to 900 °C resulting in different char. The content of eight kinds of heavy metal elements in the oil shale and the pyrolysis semi-coke were determined by inductively coupled plasma mass spectometry (ICP-MS), through which the distribution and the migration of these elements were analyzed. The specific surface area and pore distribution of different semi-coke were detected by specific surface area analyzer. The influence of surface area and pore distribution on heavy metal element migration was investigated. The sequential chemical extraction (SEC) was carried out on the original oil shale samples. Trace elements in different occurrence models were also detected by ICP-MS. Then the relationship between occurrence models and trace element migration during pyrolysis was also analyzed. The results show that: 1) The concentrations of heavy metal elements in four kinds of oil shale groups are similar, and the occurrence models of the same kind of heavy metal elements in four samples are also similar. 2) The migration amount of Zn and Cu is small at the temperature below 500 °C, while both of the elements escaped rapidly at the temperature above 700 °C. Because Zn and Cu are mainly present in the carbonate which decomposed rapidly at the temperature above 600 °C. 3) The mobility of most of the elements in the sample shows a downward trend during 500–600 °C and 800–900 °C. During these temperature ranges the specific surface area of the semi-coke was increased, because the elements was reabsorbed by the semi-coke.

1. Instruction

Oil shale is an organic-rich and fine-grained sedimentary rock [1]. Currently, oil shale is widely used in oil refining and combustion, which is an important link in the world energy structure. Oil shale is rich in trace elements, the content of which is generally higher than that of coal. The content of oil shale is roughly distributed in the range of 1–50 ppm [2], showing a downward trend toward both ends. Due to the enrichment of trace elements, long-term development and utilization of oil shale lead to harmful effects on the environment and even on human body. Therefore, the migration of eight kinds of harmful metal elements (V, Mn, Ni, Cu, Zn, Ga, Ge and Pb) during oil shale pyrolysis was studied, which is significant to solving the pollution problem.

Recently, the research on the migration of harmful elements in fossil fuels mainly focuses on the influence of temperature on the utilization of coal [3]. In general, pyrolysis is an initial stage of coal conversion process. Therefore, in order to control the volatilization of toxic trace elements the mechanism of the trace elements transformation in coal pyrolysis process have been studied [4]. During the pyrolysis of coal, the fuel characteristics, the forms of the elements and the pyrolysis conditions (pyrolysis final temperature, heating rate and pyrolysis atmosphere) all have effects on the volatility of the elements. The final temperature of pyrolysis played a very important role in the volatilization of trace elements. With the pyrolysis temperature increased, the volatilization of trace elements tended to increase. Wang Yunhe et al. [5] studied the distribution and migration of five trace elements, Hg, As, Cd, Pb and Cr, in coal during pyrolysis at 600 °C, 700 °C and 800 °C. The results showed that the volatile Pb and Cr were the weakest ones. The pyrolysis conditions and ash contents had an impact on the contents of heavy metal elements in pyrolysis products, which indicated that the final pyrolysis temperature had the greatest effect on the distribution of heavy metal elements in pyrolysis solid products; Zajusz-Zubek et al. [6] studied the pyrolysis of coal in muffle furnaces at 400 °C, 600 °C, 850 °C and 1 000 °C. The results showed that Cd, Hg and Pb have the strongest volatility, in the sequence of Se, Ni, Mn, As and Be, the volatility of the element became weaker. The results of Guo

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et al. [7] showed that the volatility of trace elements, As, Pb, Cr, Cd and Mn, increased with the increase of pyrolysis temperature. As, Pb and Cd had strong volatile, but their volatilization temperatures were different: the volatilization of As occurred mainly in the 300–700 °C; Cd mainly volatilized above 500 °C, and Pb mainly volatilized above 800 °C. As a result, during coal pyrolysis, the migration of trace elements in coal increases with pyrolysis temperature increases, and the volatilization of elements will not reach 100% before 1000 °C.

There are few studies on the migration of trace elements during the pyrolysis of Mongolian oil shale and the research methods are simple. But in the present study, four groups of oil shale in Mongolia were used as samples, and the influence factors of trace element migration during pyrolysis at the macro level (porosity change) and the micro level (occurrence state) was described. The samples and their semi-coke were measured by ICP-MS. The contents of eight major heavy metal elements (V, Mn, Ni, Cu, Zn, Ga, Ge and Pb) were examined. The specific surface area analyzer was used to measure the specific surface area of the original sample and the semi-coke at different final temperatures. The migration rules of these elements were analyzed, and the relationship between specific surface area and migration was also explored. SCE was used to separate elements of different occurrences, and the content of trace elements in different forms was determined by ICP-MS. The relationship between the occurrence and migration of these trace elements was also analyzed.

2. Experimental

Four oil shale samples from the Dalapulage mine in Mongolia and their semi-coke at different final temperatures were selected. All the experimental procedures were conducted at the Oil Shale Engineering Center of Northeast Electrical Power University.

2.1. Proximate analysis

The proximate analysis of oil shale refers to the national standard "Proximate analysis of coal" (GB/T212-2001); The results are shown in Table 1.

2.2. Semi-coke preparation

1 g of the sample merged to 200 mesh was put into a tube furnace. The final temperatures were in the sequence of 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C.(Samples were heated up to 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C, respectively, at the rate of 10 °C/min). The heating rate was 10 °C/min. The sample was stayed in the tube furnace for 20 min after heating. And the carrier gas used in the experiment is argon gas.

2.3. Determination of trace elements

First of all, oil shale and their semi-coke were digested. Then ICP-MS (Nexlon-350X) was used to determine the content of the trace elements.

2.4. Sequential chemical extraction

Sequential chemical extraction (SEC) method is one of the best quantitative research methods for the occurrence of elements. This method is developed from a method used to extract trace elements in soil. Recently, sequential chemical extraction has been widely used to investigate the mode of occurrence of trace elements. In this study, we developed a 6-step SEC method (Table 2) to analyze the Mongolian oil shale samples. During the experiment, samples were processed in parallel and blank samples were incorporated at all levels. Reagents used in this experiment were premium grade pure or analytical pure; water was secondary distilled water; glass and plastic utensils were soaked overnight in 1:1 HNO_3 solution before being rinsed with secondary distilled water.

2.5. Determination of specific surface area

The experiment is carried out on Ge-mini 2380 automatic surface area and aperture analyzer. 0.3 g of the sample was with nitrogen for 60 min and then was put into the specific surface area analyzer for analyzing.

3. Results and discussion

3.1. Semi-coke yield

As shown in Table 3, with the increase of the final temperature, the yield of semi-coke decreases gradually. This phenomenon shows that the inorganic minerals are gradually enriched during pyrolysis.

3.2. Migration of trace elements

3.2.1. Content and distribution characteristics of trace elements

Fig. 1 shows the content of the trace elements in oil shale samples and their corresponding concentration Clarke (K is the concentration of elements Clarke = elemental content/elemental crustal abundance) [8]. The crustal abundance represents the average content of chemical elements in the crust and it is the basis for the geochemical research [9–10]. Therefore, the geochemical characteristics of trace elements in oil shale can be judged by the crustal abundance of this element. If the content of some trace elements in oil shale is higher than the crustal abundance, indicating that this trace element is rich in oil shale. As can be seen from Fig. 1, the trend of trace elements in the oil shale in Mongolia is consistent with that of the crustal abundance. The higher abundance elements in the crust are also higher in the oil shale samples. Because the distribution of trace elements measured in oil shale is mainly affected by elemental geochemical cycles [11–12].

3.2.2. The occurrence of trace elements

The occurrence of trace elements has a significant effect on the migration of trace elements during pyrolysis [13]. Fig. 2 shows the occurrence of several heavy metal elements in oil shale samples from Mongolia. From 1 to 8, they correspond to eight elements of V, Mn, Ni, Cu, Zn, Ga, Ge and Pb. The occurrence of the same kind of element in different oil shale samples has a lot of similarities with coal [14]. These elements are mostly pro-sulfur elements, so in the sulfide the content of these elements is higher. At the same time, the content of elements in the exchangeable state is very low. However, there are some differences about the occurrence models between different elements. For example,

Table 1
Proximate analysis of oil shale samples.

Sample	External water (%)	Internal water (%)	Total water (%)	Semi-coal content (%)	Water content (%)	Volatile	Mad (%)	Aad (%)	Vad (%)	FCad (%)	Oil content (%)
YK-90-4	0.88	0.77	1.65	83.33	3.60	4.40	0.78	70.56	27.21	1.45	8.67
YK-105-4	1.12	0.7	1.82	84.62	3.20	2.65	0.71	69.79	27.30	2.20	9.52
YK-105-13	0.18	0.77	0.95	90.95	2.80	1.89	0.77	66.01	31.79	1.43	4.36
YK-108-07	0.78	0.78	1.56	89.99	4.20	1.79	0.79	83.58	15.11	0.52	4.02