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Occurrence and Fate of Some Trace Elements during Pyrolysis of Yima Coal, China

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Modes of occurrence and transformation behaviors of selected trace elements during coal pyrolysis were studied. By considering the environmental effect, chemical features, and thermal immovability, six heavy-metal elements (V, Cr, Mn, Co, Ni, and Cu) and six rare earth elements (Y, Eu, Tb, Dy, Yb, and Sc) were selected for this study. The coal samples were collected from the Yima coal district, China. The pyrolysis experiment was carried out in a simulated quartz bed reactor at three temperatures: 500, 700, and 900 °C, with a heating rate of 20 °C/min and under a nitrogen atmosphere. The element content in coal and chars was determined by inductively coupled plasma–mass spectrometry (ICP–MS). The elemental occurrence in raw coal was analyzed through a sequential extraction procedure and determined by inductively coupled plasma–atomic absorption spectroscopy (ICP–AAS). The trace elements in Yima coal are separated into five fractions: water soluble, ion exchangeable, carbonate, organic material, and residue (mainly silicates and sulfides bound). The results are as follows: (1) All of the elements studied mainly exist in the residue fraction. With regard to heavy-metal elements studied, the residue fraction takes about 50–80% and the organic fraction takes about 15–40%; other chemical forms occurred at a very low level. Only Mn and Ni showed a sizable distribution of water-soluble, ion-exchangeable, and carbonate fraction. (2) During coal pyrolysis, part of the element became released from the coal body and some other parts became enriched in chars. All of the elements showed a increasing release ratio with the temperature ascending; at the same pyrolysis temperature, the release ratio (Rr) of heavy-metal elements is higher than that of the rare earth elements (REEs). At the temperature of 900 °C, the volatilizable fraction of the coal body is nearly depleted, the pyrolysis almost came to an end, and the release intensity (Ri) was approaching zero. (3) All of the elements studied showed an enrichment in chars, and the enrichment ratio (Er) increases with the temperature ascending. (4) The modes of occurrence of the element is a key role affecting the transformation during pyrolysis. With regard to REEs, there is a negative correlation between the elements left in chars and the residue fraction in raw coal. This dedicates that the element content left in chars for REEs is a result of the element distribution in the residue fraction in raw coal.

1. Introduction

Some trace elements existing in coals are considered to be of great environmental concern.^{1,2} During the process of coal use, these elements may release into the atmosphere and result in severe pollutions to the environment, ecosystem, and human health.^{1–4} Some hazardous elements, for example, As, Hg, F, Cr, and Mn, were considered to be of special environmental interest. Part of them, such as Se and Hg, can easily release into the atmosphere and enter the human body or ecosystem by ingestion and bioaccumulation in tissues. Some others, such

as Cr and Mn, will enrich in the chars or ashes after pyrolysis or combustion. These potential pollutants may become active through rainfall leaching or weathering during the storage, transportation, and burial and then leaching into soil and groundwater, adversely affecting the plant nutrition and ecosystem. The problem with clean-coal technology is becoming urgent for the important berth of coal as a major energy resource with a huge amount of usage. Especially, in many advancing countries, coal often plays a dominant role in the energy configuration, which means that the hazardous trace elements released during coal utility can reach a sizable level.

Research has been focused on the trace elements for the widespread presence and the great concern for their toxicological and environmental effects on the ecosystem and human health.⁵ Many papers have shown that coal use, especially coal combustion and pyrolysis, takes a great part in the emission of hazardous elements to the environment by human activities.^{1–3,6} During these treatments under high temperatures, hazardous elements transform from the solid phase to the gas or liquid phase and become accessible and active. In some areas, direct and severe

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endemic disease has occurred because of improper use of coals with hazardous trace elements highly enriched.^{6,7} Therefore, it is important to realize the roles of trace elements (especially the hazardous elements) during coal mining, storage, transport, cleaning, combustion, pyrolysis, and other coal treatment.

During the process of coal use for energy production, such as coal combustion and pyrolysis, trace elements release rapidly, while the coal decomposes acutely under high temperatures. Hence, coal combustion and pyrolysis is considered as the main process of element emission in the whole process of coal treatment. Therefore, it is important to understand the toxicity and transformation behaviors of the trace element during coal use, especially during coal combustion and pyrolysis. Thus far, many papers have studied the trace element in coal combustion. However, different from coal combustion, pyrolysis is often operated in a close system at high temperature under inert, reductive surroundings.¹ Only a few papers have studied the behaviors of trace elements during coal pyrolysis.^{5,8–14} Guo et al. had reported the mobility and some dynamic features of the trace element during coal pyrolysis. The effects of some factors were also discussed.^{8–12} The previous study of the authors has reported the behaviors of 44 elements during coal pyrolysis of Yima coal, mainly from the aspect of chemical features.⁵ In this paper, 12 trace elements (V, Cr, Mn, Co, Ni, Cu, Y, Eu, Tb, Dy, Yb, and Sc) were chosen for discussion. The modes of occurrence of elements were analyzed by a sequential extraction procedure and were determined by inductively coupled plasma–atomic absorption spectroscopy (ICP–AAS). The purpose of this study is to obtain a further understanding of the transformation behaviors of some hazardous elements during coal pyrolysis under different temperatures and to seek the possible reasons that caused these performances. The influence of the elemental chemical forms is also discussed, which proves that the elemental chemical forms have a strong impact on the transformation of the element during coal pyrolysis, especially to the rare earth elements (REEs).

2. Experimental Section

2.1. Sampling. As an important industrial coal production area, the Yima coalfield is located in Henan province, China. Coal samples were collected from one underground mine of the Yima coalfield. To be representative for the coal seam studied, the samples

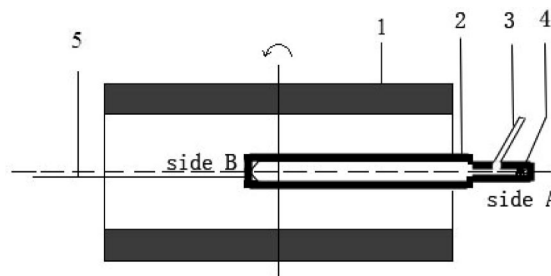


Figure 1. Schematic diagram of the experimental apparatus: (1) furnace, (2) reactor, (3) gas inlet and outlet, (4) samples of Yima coal, and (5) thermocouple.

were taken by cutting channels downward and then stored immediately in sealed plastic bags to prevent contamination and weathering. The bulk samples were air-dried, milled, and split until about a bulk of 0.5 kg was obtained. After that, the coal was pulverized to less than 200 mesh and dried in a desiccator for 12 h.

2.2. Pyrolysis and Sequential Extraction Test. **2.2.1. Pyrolysis Experiment.** The pyrolysis experiments were carried out in a simulated quartz bed reactor at the State Key Laboratory of Coal Conversion, Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences. Figure 1 is a schematic diagram of the experiment apparatus, which mainly consisted of an electrically heated tube furnace and a stainless-steel reactor (20 mm in diameter), with a quartz bed to contain the samples. Approximately 2.5 g of coal was placed in the quartz bed and pushed into the reactor at side A before the system was sealed and filled with a desired gas (nitrogen in this experiment) under a certain pressure. The gas flue is to sweep the vapor through the bed of coal to prevent the vapor from diffusing in the wrong direction and to sweep them into gas washing bottles. Then, the heating process began to operate until side B reached the desired pyrolysis temperature. At the desired temperature, the reactor was turned from a horizontal direction to a vertical direction with side A up, so that the samples fell down to side B in the reactor. Then, the pyrolysis began to happen, and the system was held for 7 min for fast pyrolysis. After that, the reactor was pulled out from the furnace and quenched in cold water. After the samples were cooled, the chars were collected for analysis and determination.

Three fixed temperatures (500, 700, and 900 °C) were used for pyrolysis under an initial N₂ pressure of 0.1 MPa, with the N₂ flow rate of 120 mL/min, a heating rate of 20 °C/min, and a holding time of 7 min.

2.2.2. Sequential Extraction Test. The sequential extraction test was performed to determine the modes of occurrence of elements. Basically, the methodology follows the previous studies.^{15–17} According to the stepwise extraction (see Figure 2), the element distribution in coal can be assigned to five groups: water soluble, ion exchangeable, carbonate, organic material, and residue (mainly silicates and sulfides bound).

2.2.3. Determination. The proximate and ultimate analyses were performed by the American Society for Testing and Materials (ASTM)¹⁸ standard procedures, at the Laboratory for Coal Chemical Analysis at the Anhui University of Science and Technology, Huainan City, Anhui province, China. Table 1 shows the result of proximate and ultimate analyses of the Yima coal. The trace element

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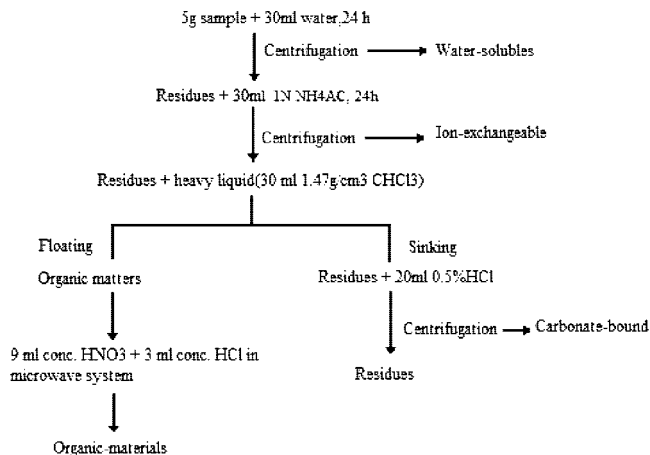


Figure 2. Schematic of the sequential extraction test.

Table 1. Proximate and Ultimate Analyses of Yima Coal (wt %)

proximate analysis			ultimate analysis, daf				
V_{daf}	A_{ad}	M_{ad}	C	H	N	S	O
41.8	19.9	1.80	80.2	4.3	0.8	2.4	12.3

content in coal and chars was determined by the inductively coupled plasma–mass spectrometry (ICP–MS) instrument (PE Elan 6000). The data are listed in Table 2. The elemental occurrence were determined by ICP–AAS. The data are listed in Table 3.

1. Results and Discussion

As the main index to evaluate the release and enrichment of the element during pyrolysis, release ratio (Rr), enrichment ratio (Er), and release intensity (Ri) are defined as

$$Rr = (1 - \text{char yield} \times \text{concentration in char} / \text{concentration in coal}) \times 100\%$$

$$Er = \text{concentration in char} / \text{concentration in coal}$$

$$Ri = d(Rr)/dT$$

Apparently,

$$Rr = (1 - \text{char yield} \times Er) \times 100\%$$

Release ratio (Rr) means the elements released during coal pyrolysis, while enrichment ratio (Er) means the multiple of element concentration in chars to that of raw coal. T represents the pyrolysis temperature, and Ri is the intensity of Rr and means the first derivative of Ri to temperatures. In this study, illustrative software (Origin) was used to construct the figure of Ri . To a fixed temperature ascending speed, Ri instructs the release speed of the element at different temperatures compared to the coal body decomposing. Transformation behavior of the total 12 elements was studied in the following section.

3.1. Chemical Distribution. The occurrences of trace elements in coal are important factors in anticipating the behavior of the trace elements during coal cleaning, combustion, as well as weathering and leaching of the coal and coal waste products.^{19–21} The chemical forms may vary significantly to different elements and greatly influence the transformations in coal treatment. Hence, it is very important to understand the

modes of occurrence of elements for realizing the role of trace elements during coal thermal treatment, especially to some hazardous elements with special environmental concerns. For example, some research has reported that the elements existing in water-soluble and organic material fractions may emit out easier than those in the silicate materials.^{22,23}

Figure 3 shows the histogram of modes of occurrence of the 12 elements. The x axis represents the element sequences. The y axis represents the elemental occurrences indicated by various symbols. Trace elements in coal are assigned into five forms: water soluble, ion exchangeable, carbonate, organic material, and residue (mainly silicates and sulfides bound). The following can be concluded in this figure: (1) With regard to most trace elements studied, they mainly exist in two major fractions in coal, residue and organic materials. Taking Cr as an example, in this study, about 26% of Cr exist in organic fractions and about 74% in residue. Guo et al. studied the Datong and Yima coals^{8,9} and pointed out that Cr mainly existed in residue (89%) and HCl soluble (11%) for Yima coal and residue (97%) for Datong coal. (2) With regard to the elements Mn, Cu, and Ni, the organic fraction takes a fair part of the element distribution, while other trace elements showed tiny organic fractions. This may suggest that Mn and Ni in Yima coal have a close affinity with organic materials. Water-soluble and ion-exchangeable fractions were also observed only in Mn and Ni. (3) The REEs showed significant stable forms of existence in coals. Nearly over 90% of REEs exist in the residue fraction in coal. This may be due to the immovability and mineralogical features of REEs.

With the coal structure decomposing during pyrolysis, the elements coexisting within different fractions may emit out. The chemical distribution is a very important index to predict, compare, and estimate the possible behaviors of trace elements during coal pyrolysis. The discussion of the chemical distribution and its impact to the release, enrichment behaviors was conducted in the following section.

3.2. Release Behavior. Figure 4 showed the release ratio of trace elements at various pyrolysis temperatures of Yima coal. The x axis represents the element sequences. The y axis represents the release ratios (Rr in Figure 4).

The following can be concluded from Figure 4: (1) The release ratio (Rr) increases with the temperatures ascending. To the same element, the result of $Rr(900^\circ\text{C}) > Rr(700^\circ\text{C}) > Rr(500^\circ\text{C})$ suggests that a higher pyrolysis temperature led to a more thorough decomposing of coal, while the elements coexisting in all kinds of fractions can emit out at a bigger amount. (2) The Rr of heavy-metal elements is higher than that of REEs; this may because the chemical and thermal features of REEs are more immovable, which can also be proven from their existence in Figure 3. With regard to the occurrences of REEs, nearly more than 90% of the element exist in residue fraction. This fact means a very stable feature to thermal treatment. With regard to the heavy-metal elements, the organic materials, water-soluble, ion-exchangeable, and carbonate-bound fractions were observed and the properties cannot be neglected, with some elements being quite considerable. For example, the organic fraction takes about 42% of element Mn. These fractions tend to decompose at a relative low temperature and result a high Rr of heavy-metal elements. (3) The distribution of Mn

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Table 2. Content of the 12 Elements in Raw Coal and Chars under Different Pyrolysis Temperatures (ppm)

elements	V	Cr	Mn	Co	Ni	Cu	Y	Eu	Tb	Dy	Sc	Yb
coal	144	91.5	171	23.8	7.9	43.5	42.2	2.03	1.26	8.13	28.2	4.43
chars												
500 °C	164	104	183	25.7	8.72	54.6	47.4	2.49	1.53	9.98	25.5	5.89
700 °C	176	115	191	29.2	9.66	64	56.9	2.88	1.83	12.1	31	7.1
900 °C	180	118	203	30.8	9.96	60.9	61	3.13	2.01	13.1	32.8	7.76

Table 3. Modes of Occurrence of the 12 Elements (%)^a

	wat	ion	org	car	res
V	0.17	0	16.23	0.50	83.22
Cr	0	0	26.57	0.05	73.79
Mn	4.69	7.88	42.60	5.48	39.35
Co	0.37	0.26	13.20	1.01	85.15
Ni	7.32	4.42	32.15	3.87	52.24
Cu	0.16	0.54	25.55	3.83	69.93
Y	0	0.48	2.44	2.17	94.94
Eu	0.09	0	10.15	2.00	88.28
Sc	0.01	0.03	7.87	0.64	91.45
Tb	2.59	0.79	0	3.26	93.51
Dy	0	0.05	0.40	2.69	97.20
Yb	0	0.32	2.74	1.44	95.54

^a wat, water soluble; ion, ion exchangeable; org, organic materials; car, carbonate; res, residues, mainly silicates and sulphides.

and Ni showed a big organic-bound existence, while Cu showed a significantly low R_r at low temperatures; therefore, Mn, Ni, Cu, and Sc were selected for further discussion.

Figure 5a shows the R_r of trace elements at various temperatures. An average R_r of heavy-metal elements, REEs, and the coal volatile yield are showed for comparison. The release intensity of Sc, Mn, Ni, and Cu and the volatilize intensity of the coal body were shown in Figure 5b. In Figure 5a, V_y, AveHem, and AveREE represents coal volatile yield, average release ratio of heavy-metal elements, and average release ratio of REEs, respectively.

In Figure 5b, CDI, AveHemI, and AveREEI represents the coal body decomposing intensity, average release intensity of heavy-metal elements, and average release intensity of REEs, respectively.

In Figure 5a, (1) besides Cu, the release ratio of REEs is the lowest, while the R_r of heavy-metal elements is higher in a big scale, especially Mn. The chemical distribution may explain the reason; because of the sizable distribution of Mn and Ni in organic-bound, carbonate-bound, water-soluble, and ion-exchangeable fractions, these fractions decomposed much more easier than the residue fractions. Therefore, the elements that coexist in these fractions may emit into the atmosphere and lead to a high release ratio. The high release intensity of Mn and Ni can be observed in Figure 5b as a confirmation. (2) With regard to nearly all of the trace elements, coal volatile yield (V_y) is higher than the release ratios of elements, suggesting a faster decomposition speed of coal bulk. At low temperatures, Sc showed a significant release behavior. Because the occurrence of Sc in Yima coal is mainly bound to residue (about 91%) and organic materials (about 8%), the very high release ratio may be a result of chemical features of Sc. Sc is quite vivid (as a potential reductant), and this might be the reason that caused the very high release ratio at low temperatures for Sc. (3) The element Cu showed a special behavior in this study. Contrary to the element Sc, Cu showed a significant low release ratio, even lower than the REEs. The chemical form distribution of Cu in Yima coal is ion-exchangeable (0.5%), organic-bound (25.5%), carbonate-bound (3.8%), and residue (70%). Because the existence of organic- and carbonate-bound fractions is to a big extent, the undersized R_r may suggest that the Cu content that proposed to emitted out at low temperatures may have been

absorbed by some minerals by the interactions, then become enriched in chars in other fractions, and hence, lead to a very low release ratio. During the whole pyrolysis procedure, the R_i of Cu changes little, suggesting that Cu emitted from the coal at a low and constant speed. A further study on the behavior of Cu is needed to obtain a better understanding.

In Figure 5b, the R_i of most trace elements decreases with the temperature ascending. Up to 900 °C, the R_i of all of the 11 trace elements is approaching zero (except Cu), dedicating that the volatilizable fraction of elements is nearly depleted at that temperature. It could be deduced that there may exists a maximum of R_r during the coal pyrolysis under common pyrolysis operations.

It is clear that the pyrolysis temperatures and the modes of occurrence of elements are both the index influencing the elemental transformation. Because of the stable chemical features and existence of REEs mean that the REEs content in raw coal is quite insensitive to the thermal treatment, hence, the modes of occurrence of REEs become the primary parameter controlling the transformation behaviors. Thus, there may exist a correlation between the residue fraction and maximum R_r. In this study, the R_r (900 °C) is taken as the maximum R_r. To be more representative, besides the elements discussed above (Y, Eu, Tb, Dy, and Yb), another three REEs was added (Nd, Sm, and Er). Figure 6 showed the pertinence of R_r (900 °C) of REEs to their residue fractions. The figure showed a clear negative correlation between the R_r (900 °C) and residue fraction. This may be because of the fact that REEs existing in the residue fraction are very steady and decomposed little after pyrolysis. The more residue fraction taken in raw coal, the lower release ratio occurred during pyrolysis. This result dedicates that, at high pyrolysis temperatures (more than 900 °C for Yima coal in this study), the R_r of REEs has a obvious negative correlation to the residue fraction, means, the maximum of R_r for REEs that can be predicted by the residue fraction in the raw coal before pyrolysis.

3.3. Enrichment Behaviors. Some trace elements actually have little environmental impact for their very low concentrations in coal, even to hazardous elements concerned to be of environmental interest. However, after coal use, these elements often became enriched in chars or ashes, and therefore, the concentration was raised and may reach a dangerous level. With regard to some elements, they can even reach a financial level (some REEs as an example). Many papers have studied the enrich behaviors of trace elements during coal combustion,^{1,24–26} but only a few papers have studied the trace element enrichment during coal pyrolysis.

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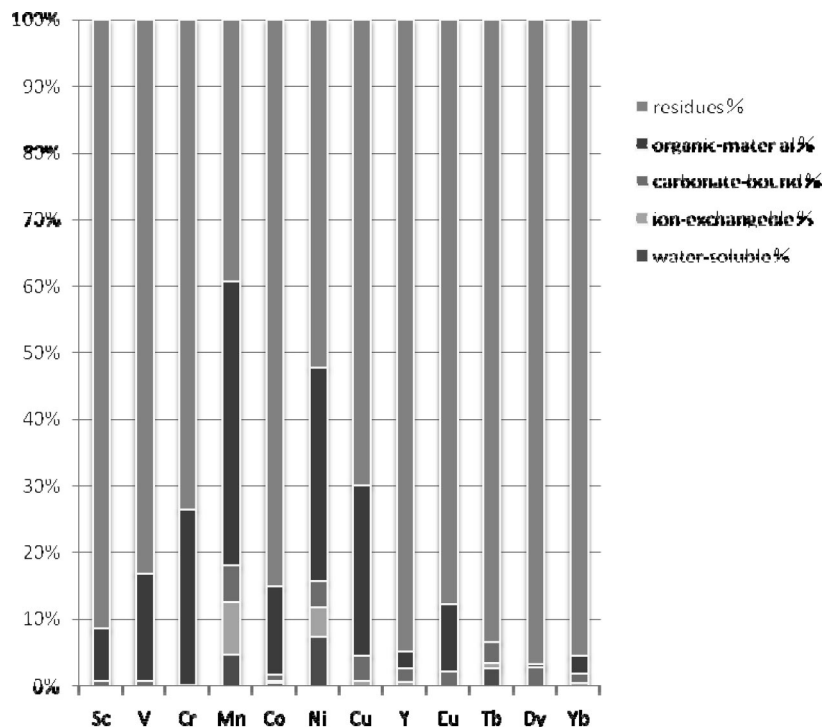


Figure 3. Modes of occurrence of trace elements in Yima coal. The x axis represents the element sequences, while the y axis represents the elemental occurrences indicated by various symbols.

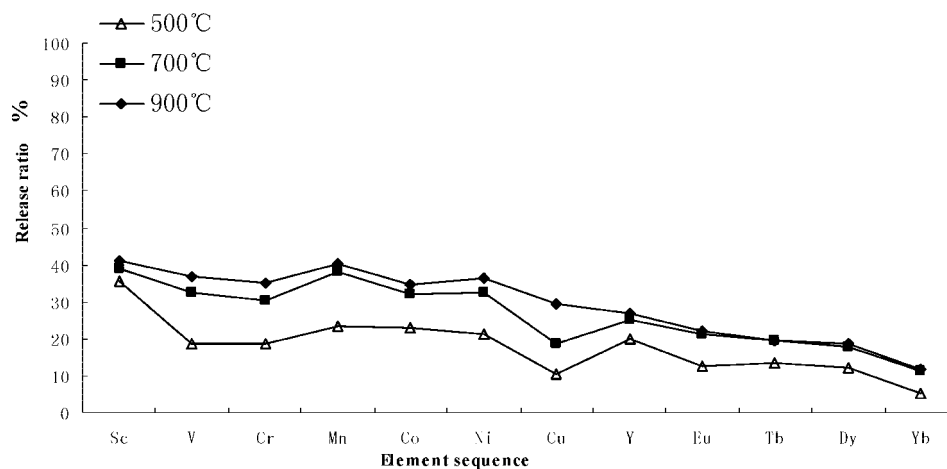


Figure 4. Release ratios of trace elements under different pyrolysis temperatures.

Different from the release ratio, the enrichment ratio (Er) showed the relative multiple of the element concentration in chars to the element concentration in raw coal. During coal pyrolysis, the elements emitted out with coal decomposing; both the elements and the coal are losing weight, but the speed may not be the same. Hence, the Er can not only represent the enrichment ability of elements after pyrolysis but can also be regarded as an index to estimate the release speed of elements compared to the coal body decomposing speed. If the coal decomposing is faster than the element releasing, the elemental concentration would increase in chars, leading to an enrichment with Er above 1. During pyrolysis, Er > 1 means that the speed of the coal body decomposing is faster than the elements releasing, Er < 1 means the coal mass reduction is slower, while Er = 1 means a perfect synchronization of the elements releasing with the coal body decomposing.

Figure 7 showed the enrichment ratio (Er) of elements Sc, Mn, Ni, and Cu at various temperatures for Yima coal. The AveHemE means the average enrichment ratio (Er) of heavy-metal elements, while AveREEsE represents the average Er of

REEs. To most trace elements, Er increases while the temperature is becoming higher. REEs showed a significant enrichment during coal pyrolysis. The average Er of REEs is about 1.6 at 900 °C, indicating that the REEs enriched in chars strongly. In comparison to REEs, the Er of heavy-metal elements is much lower at about 1.1–1.3. Er of elements Mn and Ni showed a lower level than the AveHem because of their sizable existence in the organic and carbonate materials, which release easily during coal pyrolysis. Sc showed a very low Er value, while Cu enriched in chars largely. From room temperature to about 300 °C, Er of Sc decreased with the temperature ascending. At about 300 °C, the Er of Sc reached the minimum. Because Er can be seen as the index to compare the speed of the element releasing and coal body decomposing, it can conclude that, at about 300 °C (also the enrichment ratio minimum of Sc), the disparity between the two speed reached a balance, suggesting that Sc released very rapidly at temperatures of about 300 °C. After that, Er of Sc began to increase. Contrary to Sc, Cu released at a low, constant speed, lower than the speed of coal body decomposing at low temperature, and overcame the CDI

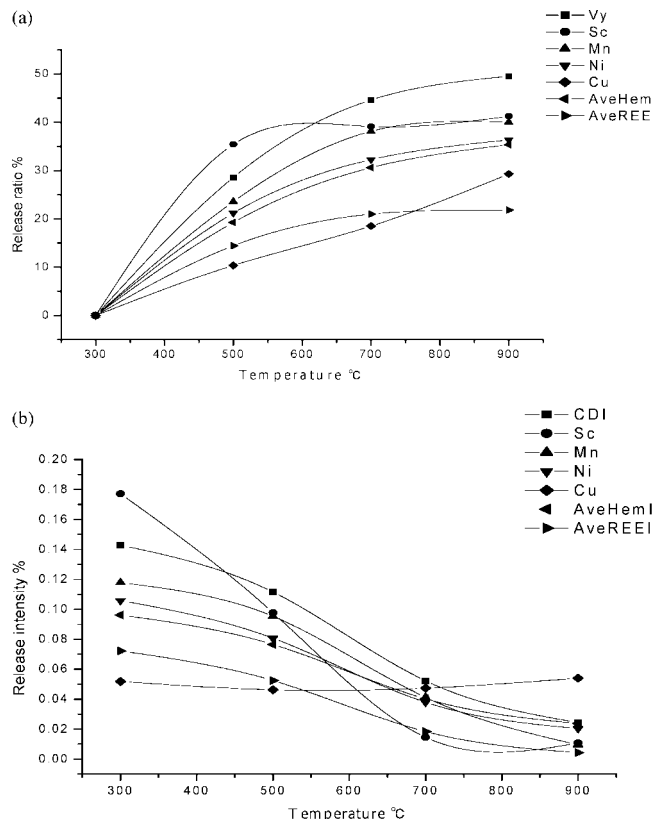


Figure 5. (a) Release ratio of elements, coal volatile yield (Vy), average release ratio of heavy-metal elements (AveHem), and average release ratio of REEs (AveREE). (b) Release intensity of elements and coal, the coal decomposing intensity (CDI), average release intensity of heavy-metal elements (AveHemI), and average release intensity of REEs (AveREEI).

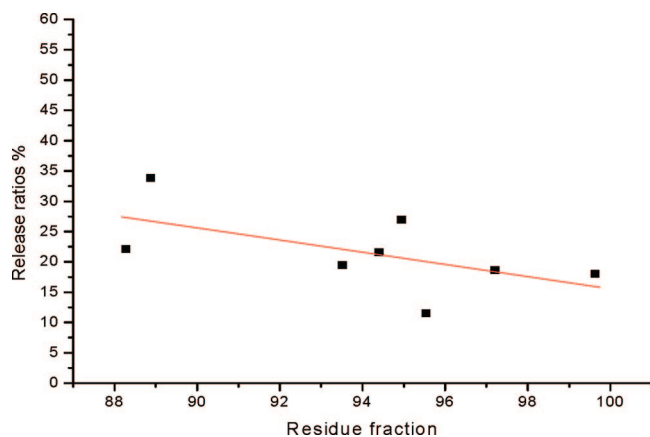


Figure 6. Pertinence of the release ratio (900 °C) for REEs (Y, Eu, Tb, Dy, Yb, Nd, Sm, and Er) to their residue fractions (mainly silicates and sulfides bound). $R^2 = 0.342$.

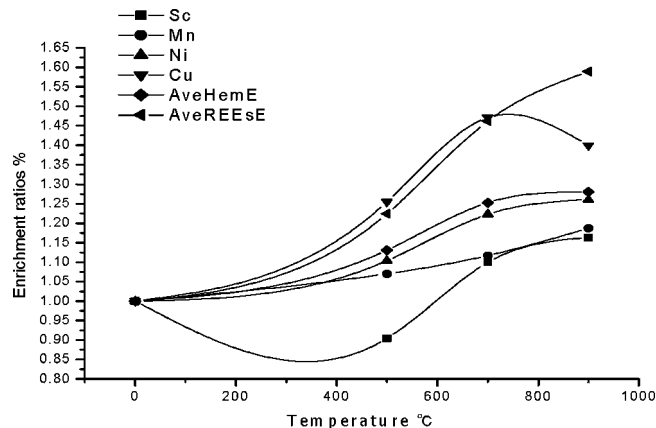


Figure 7. Enrichment ratios (Er) of trace elements. The AveHemE means the average Er of heavy-metal elements, while AveREEsE represents the average Er of REEs.

in the end of pyrolysis, making the Er of Cu increased first and then decreased at the pyrolysis end.

4. Conclusion

The release and enrichment of 12 trace elements were studied. The modes of occurrence of these elements were analyzed. According to the transformation behaviors discussed, the results can be concluded as follows: (1) Organic material and residue are the main fractions of the existence of the trace elements. Elements Mn and Ni showed a sizable distribution of organic and carbonate fractions. Water-soluble and ion-exchangeable fractions are also observed only in Mn and Ni. (2) Rr increases with the temperature ascending. The release ratio (Rr) of heavy-metal elements is higher than that of REEs under the same pyrolysis temperature; up to 900 °C, the volatilizable fraction of elements was nearly depleted and the Ri (release intensity) was approaching zero. (3) All of the elements selected in this study showed an enrichment behavior in chars, and with regard to most trace elements, Er (enrichment ratio) increases with the temperature ascending. Er can also be regarded as an index to appraise the elements releasing speed compared to the coal body decomposing speed. (4) The modes of occurrence of the element play a key role in affecting the transformation during pyrolysis. With regard to REEs, there is a negative correlation between the elements left in chars and the residue fraction in raw coal, indicating that, at high pyrolysis temperatures, the elements content left in chars may be a result of the property of the element existing in residue fractions.

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